A Computational Approach to Structure and Reactivity of Boron Containing Reactive Intermediates

Dissertation

vorgelegt von

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Tübingen

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A Computational Approach to Structure and Reactivity of Boron Containing Reactive Intermediates

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Abbreviations and Symbols

Å	Ångström
Ar	Aryl
CAAC	Cyclic (alkyl)(amino)carbene
CC	Coupled cluster
COD	1,5-Cyclooctadiene
Cp	Cyclopentadienyl
Cp*	Petntamethylcyclopentadienyl
Cy	Cyclohexyl
d	Distance
DBCOT	Dibenzo[*a,e*]cyclooctatetraene
DF	Density fitting
DFT	Density functional theory
Dipp	2,6-Diisopropylphenyl
Dur	2,3,5,6-Tetramethylphenyl
EDG	Electron donating group
EOM	Equation-of-motion
eV	Electronvolt
EWG	Electron withdrawing group
FMO	Frontier molecular orbital
HOMO	Highest occupied molecular orbital
IR	Infrared
IRC	Intrinsic reaction coordinate
L	Ligand
LUMO	Lowest unoccupied molecular orbital
M	Metal
Me	Methyl
Mes	Mesityl
MP2	Second-order Møller-Plesset perturbation theory
NHC	N-heterocyclic carbene
NTO	Natural transition orbital
Ph	Phenyl
R	Organic substituent
RI	Resolution of the identity
SAPT	Symmetry-adapted perturbation theory
SCS	Spin-component scaled
Tbt	2,4,6-Tris[bis-(trimethylsilyl)methyl]phenyl
***t*Bu**	*Tert*-butyl
TD	Time dependent
THF	Tetrahydrofuran
Tp	2,6-Di(2,4,6-triisopropylphenyl)phenyl
TS	Transition state
UV/Vis	Ultraviolet/visible
X	Halogen
ZPVE	Zero-point vibrational energy

Abstract

Computational chemistry methods were employed to study small boron containing reactive intermediates, such as borylenes, which are the analogs of carbenes and nitrenes, and borirenes and boriranes that are isoelectronic to cyclopropenyl and cyclopropyl cations, respectively.

Density functional theory (DFT) was used to study the electronic and molecular structure of various substituted borylenes BR (R = H, F, Cl, CH_3, CF_3, *t*Bu, NH_2, Ph and $SiMe_3$). Geometries of singlet and triplet borylenes were optimized at the B3LYP/def2-TZVP level of theory. The influence of substitution on the frontier molecular orbitals (FMO) energies, HOMO-LUMO energy gaps, and singlet-triplet energy splittings was also examined. In addition, two lowest singlet-singlet electronic transitions were computed using equation-of-motion coupled cluster singles and doubles (EOM-CCSD) and time-dependent density functional theory (TD-DFT; B3LYP, CAM-B3LYP, and ωB97X functionals were used), both methods in combination with the aug-cc-pVTZ basis set.

The reactivity of singlet borylenes towards unsaturated and saturated hydrocarbons was investigated. The geometries of the studied species were optimized at the MP2/cc-pVTZ level of theory. Energies were further recomputed at the CCSD(T)/aug-cc-pVTZ level of theory. To study the mechanisms of the addition and insertion reactions, ethyne, ethene, and methane were chosen as model hydrocarbons. The philicity of borylenes was also studied in terms of geometrical parameters of the transition states calculated for the addition reactions.

The aforementioned addition and insertion reactions involve weakly bound van der Waals complexes formed between hydrocarbons and borylenes that correspond to shallow minima on the potential energy surfaces. Spin-component scaled second-order Møller-Plesset perturbation theory (SCS-MP2) in conjunction with the def2-QZVP basis set was used to optimize the geometries of all complexes. Energies were refined with the CCSD(T) method employing the def2-QZVP and aug-cc-pVTZ basis sets. Symmetry-adapted perturbation theory (SAPT) analysis was performed to study the nature of the interaction in borylene-hydrocarbon van der Waals complexes.

The reactions of three-membered boron heterocycles (borirane and borirene) towards unsaturated hydrocarbons (ethyne and ethene) were investigated. Dimerization reactions of borirenes and boriranes were also studied. All geometries were optimized at the M062X/6-311+G(d,p) level of theory. Energies were recomputed at the CCSD(T)/def2-TZVP level of theory.

Zusammenfassung

In dieser Arbeit wurden kleine, borhaltige reaktive Zwischenstufen mit Hilfe quantenchemischer Methoden untersucht. Betrachtet wurden Borylene, die Bor-Analoga von Carbenen und Nitrenen, aber auch Borirene und Borirane, die wiederum isoelektronisch zu den Cyclopropenyl- bzw. Cyclopropylkationen sind. Dichtefunktionaltheorie (DFT) wurde angewandt um die elektronische und geometrische Struktur unterschiedlich substituierter Borylene BR (R = H, F, Cl, CH_3, CF_3, *tBu*, NH_2, Ph und $SiMe_3$) zu untersuchen. Die Molekülgeometrien der entsprechenden Singulett- und Triplett-Borylene wurden auf dem B3LYP/def2-TZVP Theorieniveau optimiert. Zudem wurde der Einfluss verschiedener Substituenten auf die Grenzorbitalenergien, die HOMO-LUMO-Energieabstände und die Singulett-Triplett-Energieaufspaltungen untersucht. Zusätzlich wurden die zwei energetisch tief liegendsten, elektronischen Singulett-Singulettübergänge sowohl mit der EOM-CCSD-Methode (equation-of-motion coupled cluster theory singles, doubles) als auch mit zeitabhängiger DFT (TD-DFT, time-dependent density functional theory; B3LYP, CAM-B3LYP und ωB97X) und dem aug-cc-pVTZ Basissatz berechnet.

Die Reaktivität der Singulettborylene wurde gegenüber gesättigten und ungesättigten Kohlenwasserstoffen erforscht. Dabei wurde die geometrische Struktur der jeweiligen betrachteten Spezies auf dem MP2/cc-pVTZ Theorieniveau optimiert und anschließend die Energie mittels CCSD(T)/aug-cc-pVTZ verfeinert [CCSD(T), coupled-cluster, singles, doubles, and perturbative triples]. Exemplarisch wurden Ethin, Ethen und Methan als Kohlenwasserstoffe gewählt, um die Mechanismen der Additions- und Insertionsreaktionen zu betrachten. Für die Additionsreaktionen wurde außerdem die Philie (Elektro- oder Nukleophilie) der Borylene im Übergangzustand anhand geometrischer Parameter untersucht.

Die gerade erwähnten Additions- und Insertionsreaktionen verlaufen zunächst über schwach gebundene van-der-Waals-Komplexe zwischen den verschiedenen Kohlenwasserstoffen und Borylenen, die flachen Minima auf der Potentialenergieoberfläche entsprichen. Die Geometrien aller Komplexe wurden mittels SCS-MP2 in Verbindung mit dem def2-QZVP Basissatz optimiert und die Energien mit der CCSD(T)-Methode unter Verwendung des def2-QZVP und aug-cc-pVTZ Basissatzes verfeinert. Eine Analyse der intermolekularen Wechselwirkung wurde mittels symmetrieadaptierter Störungstheorie (SAPT: Symmetry-Adapted Perturbation Theory) durchgeführt, um mehr über die Natur der Wechselwirkung in den van-der-Waals-Komplexen zwischen Borylenen und Kohlenwasserstoffen zu erfahren.

Des weiteren wurden Reaktionen zwischen dreigliedringen Borheterocyclen (Boriane und Borirene) und ungesättigten Kohlenwasserstoffen (Ethin und Ethen) betrachtet, wie auch die Dimerisierung von Borirenen und Boriranen. Alle Geometrien wurden mittels Dichtefunktionaltheorie [M06-2X/6-311+G(d,p)] optimiert und die Energien auf dem Theorieniveau CCSD(T)/aug-cc-pVTZ verfeinert.

List of Publications

Publications Included in the Thesis

Publication I

Reactivity of Borylenes toward Ethyne, Ethene, and Methane
Małgorzata Krasowska, Holger F. Bettinger *J. Am. Chem. Soc.* **2012**, 134, 17094-17103.

Publication II

Computational Study of Van der Waals complexes between Borylenes and Hydrocarbons
Małgorzata Krasowska, Holger F. Bettinger *Chem. Eur. J.* **2014**, 20, 12858-12863.

Publication III

Ring Enlargement of Three-Membered Boron Heterocycles upon Reaction with Organic π Systems: Implications for the Trapping of Borylenes
Małgorzata Krasowska, Holger F. Bettinger *Chem. Eur. J.* **2016**, 22, 10661-10670.

Publication IV

Electronically Excited States of Borylenes
Małgorzata Krasowska, Marc Edelmann, Holger F. Bettinger, *J. Phys. Chem. A* **2016**, 120, 6332-6341.

Other Publications

The Conformational Analysis of 2-Hydroxyaryl Schiff Thiosemicarbazones
Małgorzata Krasowska, Andrzej Kochel, Aleksander Filarowski, *CrystEngComm* **2010**, 12, 1955.

Mechanisms for the Formation of Acenes from α-Diketones by Bisdecarbonylation
Holger F. Bettinger, Rajib Mondal, Małgorzata Krasowska, and Douglas C. Neckers *J. Org. Chem.* **2013**, 78, 1851–1857.

Personal Contributions

Publication I

Reactivity of Borylenes toward Ethyne, Ethene, and Methane
Małgorzata Krasowska, Holger F. Bettinger *J. Am. Chem. Soc.* **2012**, 134, 17094-17103.

Scientific ideas 30%
Data generation 100%
Analysis and interpretation 60%
Paper writing 80%

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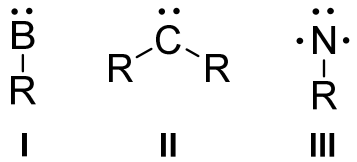
Scientific ideas 30%
Data generation 50%
Analysis and interpretation 70%
Paper writing 80%

*Part of the results presented in publication IV was obtained during the bachelor thesis of M. Edelmann.

1 Introduction

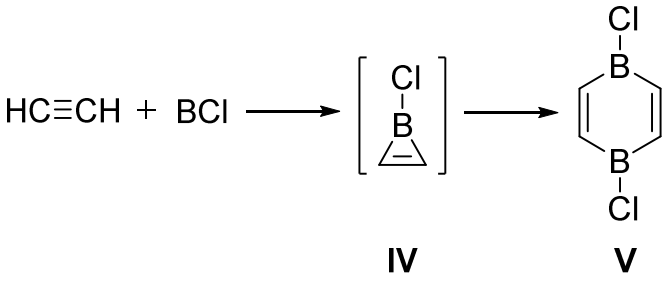
1.1 Borylenes as Reactive Intermediates

Borylenes **I**, monovalent boron species, which can be also called boranediyls or borenes are analogs of carbenes **II**[1-3] and nitrenes **III**[4-6] (see Scheme 1). The unique structure of borylenes makes them highly reactive and therefore extremely rare and elusive. Due to the empty p orbitals on boron atom borylenes are considered Lewis acids that are able to accept lone pairs of electrons.



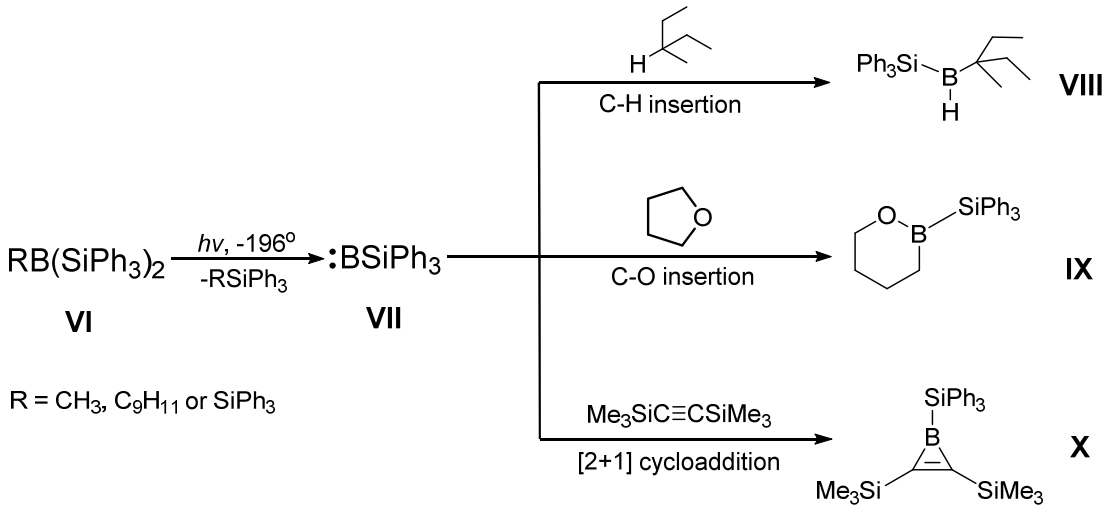
Scheme 1. Simplified structures of borylene **I**, carbene **II**, and nitrene **III**.

One of the most significant experiments in borylene chemistry was the high temperature generation of haloborylenes. In the late 1960s, Timms reported the first generation of subvalent boron monohalides by passing boron trihalide (BCl_3 or BF_3) over solid boron under high temperature and low pressure conditions.[7, 8] The thus generated haloborylenes were co-condensed with alkynes and alkenes at low temperature. This co-condensation of borylenes with unsaturated hydrocarbons resulted in formation of 1,4-diboracyclohexa-2,5-dienes **V** (Scheme 2) and 1,4-diboracyclohexanes. Although not detected directly, boriranes and borirenes, such as **IV**, were suggested as possible transient intermediates in this reaction. Diatomic borylenes BX (where X = H, F, Cl, Br, and I) generated in the gas phase were all investigated by means of microwave spectroscopy.[9-15]



Scheme 2. Reaction of chloroborylene with acetylene studied by Timms.[8]

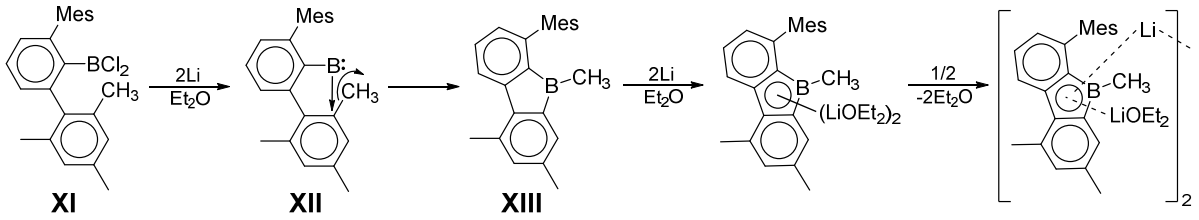
In 1984 Pachaly and West[16] generated triphenylsilylborylene, Ph_3SiB, **VII** by photolysis of organobis(triphenylsilyl)boranes, $RB(SiPh_3)_2$, or tris(triphenylsilyl)borane, $(SiPh_3)_3B$ (**VI**) in hydrocarbon (3-methylpentane) glass matrix at -196°C using UV light (λ = 254 nm) (see Scheme 3). Although the borylenes were not observed directly in these experiments, the intermediacy of silylborylene was deduced from the reaction products isolated after warming the matrix to room temperature. Without the trapping agent, the product of borylene insertion into the C-H bond of 3-methylpentane was isolated (**VIII**). Adding tetrahydrofuran (THF) to the glass matrix resulted in the formation of the cyclic C-O insertion product **IX**. In the presence of bis(trimethylsilyl)ethyne the corresponding borirene **X** was obtained as the product of borylene cycloaddition.[16]



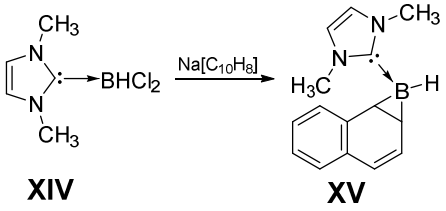
Scheme 3. Generation of (triphenyl)silylborylene and its reactions by Pachaly and West.[16]

Another experiment in which a borylene was concluded to be an intermediate was the metal reduction of bulky arylboron dihalides $2,6\text{-}Mes_2C_6H_3BX_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) (**XI**) and $2,6\text{-}Trip_2C_6H_3BBr_2$ (Trip = $2,4,6\text{-}i\text{-}Pr_3C_6H_2$) leading to the formation of 9-borafluorenyls (Scheme 4). During this reaction, the generated arylborylene **XII** underwent intramolecular insertion into a C-C σ-bond involving the *o*-Me group to produce borafluorenyl **XIII**.[17] More recently, dehalogenation of dichloroborane **XIV** that was stabilized by a N-heterocyclic carbene (NHC) with sodium naphthalenide $Na[C_{10}H_8]$ resulted in the formation of an enantiomeric mixture of the corresponding boriranes **XV** (Scheme 5). NHC-stabilized parent borylene was invoked as an intermediate that undergoes [2+1] cycloaddition with naphthalene.[18] However, Curran and coworkers proposed an alternative radical mechanism for the formation of trapping products.[19] A NHC-stabilized borylene was also proposed as a

transient intermediate that undergoes intramolecular C-H insertion in the photochemically induced isomerisation of C,C-chelate dimesitylboron ($BMes_2$).[20]

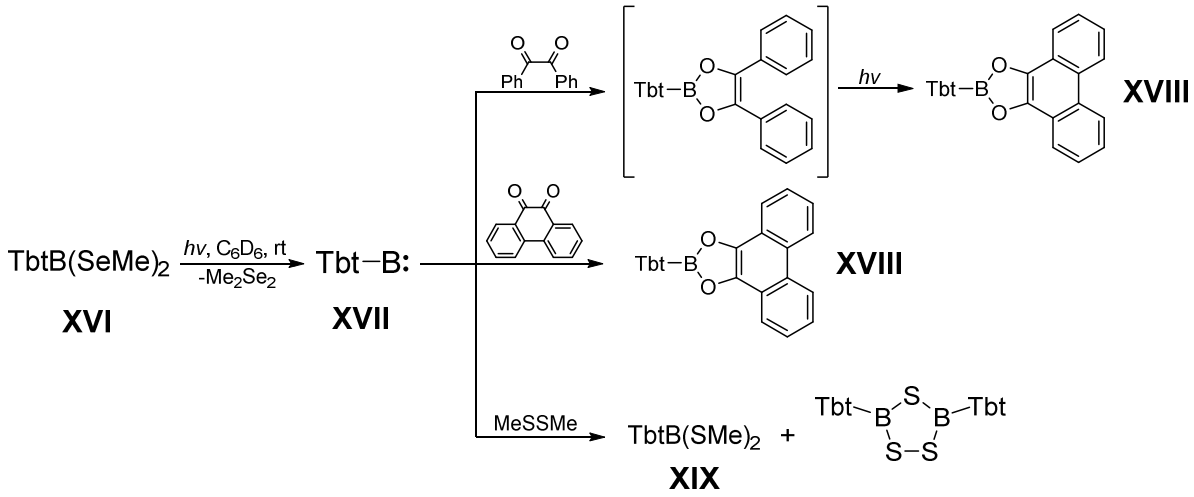


Scheme 4. Arylborylene as transient intermediate in the reduction of arylboron dihalides.[17]



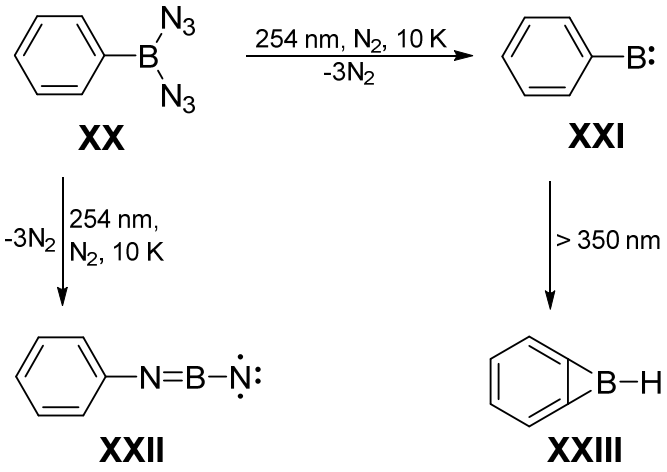
Scheme 5. Dehalogenation of NHC-stabilized dichloroborane by sodium naphtalenide.

In the experiments performed by Ito et al.[21] another arylborylene, TbtB (Tbt = 2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl) **XVII**, was inferred to be a transient intermediate in the photolysis of bis(methylseleno)borane, $TbtB(SeMe)_2$ (**XVI**). The photoreaction was carried out in the presence of benzil or phenanthrenequinone as trapping reagents (Scheme 6). In both cases, the formed product was 9,10-dihydroxyphenanthrene **XVIII**, a cycloadduct of borylene and benzil. When $TbtB(SeMe)_2$ was irradiated in the presence of dimethyl disulfide one of the obtained products, bis(methylthio)borane **XIX**, was ascribed to be a product of borylene insertion into the S-S bond.



Scheme 6. Photolysis of bis(methylseleno)borane $TbtB(SeMe)_2$ and subsequent trapping reactions of transient borylene with benzil and phenanthrenequinone (top) and dimethyl disulfide MeSSMe (bottom).

In the aforementioned experiments, the involvement of borylenes was inferred on the basis of the products formed during the trapping reactions. Direct spectroscopic observations of organoborylenes are limited and involve the infrared spectroscopy detection of ethynylborylene and phenylborylene. The former was observed with the help of IR spectroscopy along with other organoboron species formed after co-deposition of pulsed laser evaporated boron atoms and ethyne in an argon matrix at 15 K.[22] The latter organoborylene, phenylborylene **XXI**, was obtained, along with (B-nitreno-N-phenyl)iminoborane **XXII**, during the UV photodecomposition of diazidophenylborane $PhB(N_3)_2$ **XX** in solid nitrogen and neon matrices at 10 K (Scheme 7).[23] Further irradiation of phenylborylene with longer wavelength (λ = 350-450 nm) light resulted in the intramolecular insertion into the *ortho*-C-H bond of the phenyl ring and formation of benzoborirene **XXIII**. Inorganic aminoborylene (BNH_2) was detected as one of the products formed during the co-condensation of pulsed laser ablated boron atoms with ammonia in solid argon at 10 K.[24] All borylenes described in this section were identified by comparison of the matrix isolation infrared spectra with the computed vibrational spectra.[22-24]



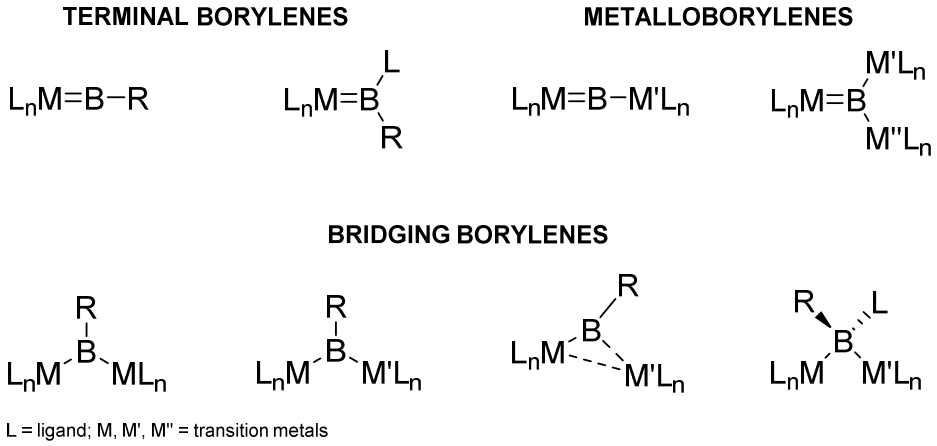
Scheme 7. Generation of phenylborylene and its intramolecular insertion into the *ortho*-C-H bond of the phenyl ring to form benzoborirene.

1.2 Stabilization of Borylenes

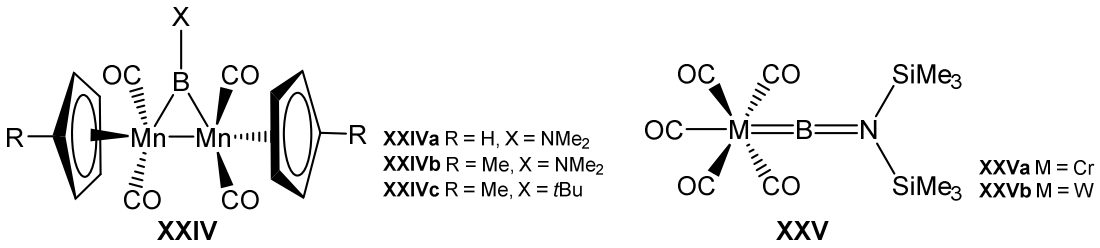
1.2.1 Stabilization by Metal Centers

Free borylenes could not be isolated, although borylenes stabilized in the coordination sphere of transition metals were generated and isolated. The chemistry of transition metal complexes of borylenes is well established and summarized in several review articles.[25-36] Borylene ligands of transition metal complexes can be categorized into three main types according to

the coordination number of boron (see Scheme 8).[31, 35] These are terminal borylenes (mono- and bisborylene), bridging borylenes (homo-, hetero-, and semibridging), and metalloborylenes with boron atom situated in between two or three metal centers. Moreover, Lewis base adducts of either terminal and bridging borylene ligands are known. The first transition metal borylene complexes were synthesized in 1995 by Braunschweig and coworkers (Scheme 9).[37] These are highly stable dinuclear manganese complexes **XXIVa-c** with bridging borylene ligands, which were isolated in the form of red crystals. Three years later the first terminal borylene complexes of chromium **XXVa** and tungsten **XXVb** were synthesized and structurally characterized (Scheme 9).[38]



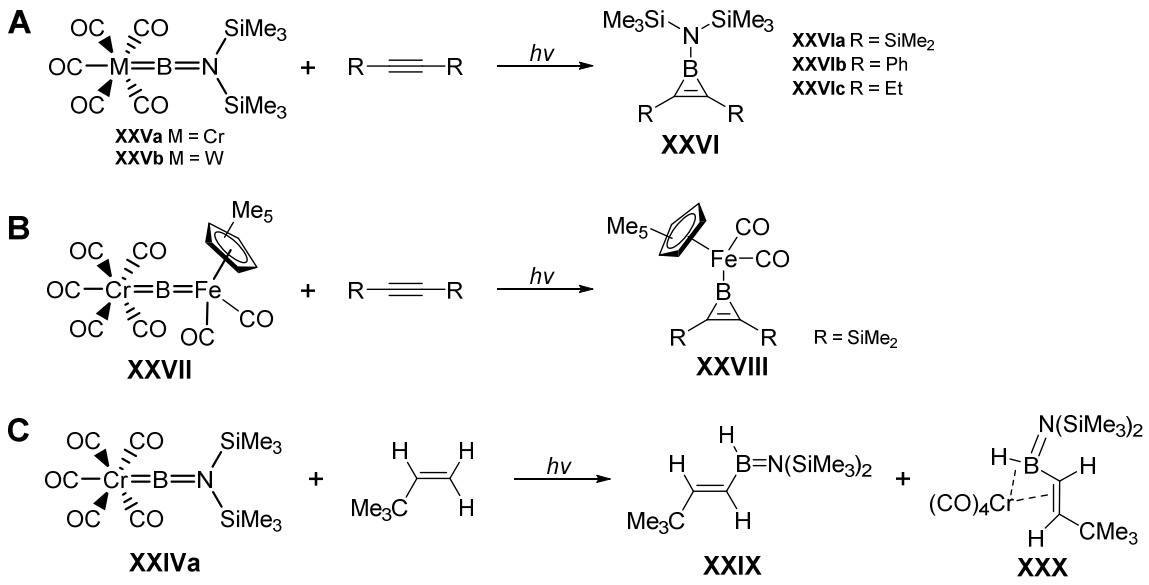
Scheme 8. General classification of borylene ligands.[31, 35]



Scheme 9. First transition metal complexes with bridging (left) and terminal (right) borylene ligands.

Transition metal complexes of borylenes can serve as convenient sources of the borylene unit.[32] Upon irradiation of these complexes the borylene ligand is readily transferred onto different molecules, like other transition metal complexes or even organic molecules (see Scheme 10). For instance, room temperature photolysis of terminal borylene chromium and tungsten complexes **XXV** of the general formula $(OC)_5M{=}BN(SiMe_3)$ in the presence of alkyne results in the formation of borirenes **XXVIa-c**, the products of borylene

cycloaddition to the CC triple bond (Scheme 10A).[39] Also metalloborylene complexes are known to be good sources of borylene ligands. The photolysis of $(OC)_5Cr{=}BFe(CO)_2(\eta^5\text{-}C_5Me_5)$ (**XXVII**) in the presence of 1,2-bis(trimethylsilyl)ethyne yields ferroborirene **XXVIII** (Scheme 10B).[40] On the other hand, irradiation of the mixture of $(OC)_5Cr{=}BN(SiMe_3)_2$ and 3,3-dimethyl-1-butene does not result in the expected cycloaddition product but rather in the product of borylene insertion into a terminal $C(sp^2)$-H bond of the butane derivative **XXIX** and the chromium complex **XXX** (Scheme 10C).[41] In addition to borirenes, photochemical borylene transfer from the terminal iron bis(borylene) complex onto substituted acetylenes provides an access to iron complexes of 1,4-diboracyclohexadiene and 1,4-dibora-1,3-butadiene.[42]

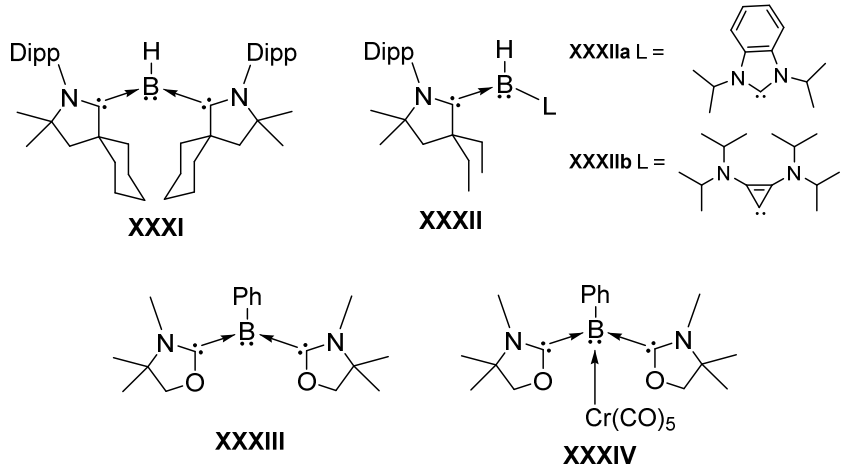


Scheme 10. Photochemically induced borylene transfer from metal centers and the obtained reaction products.

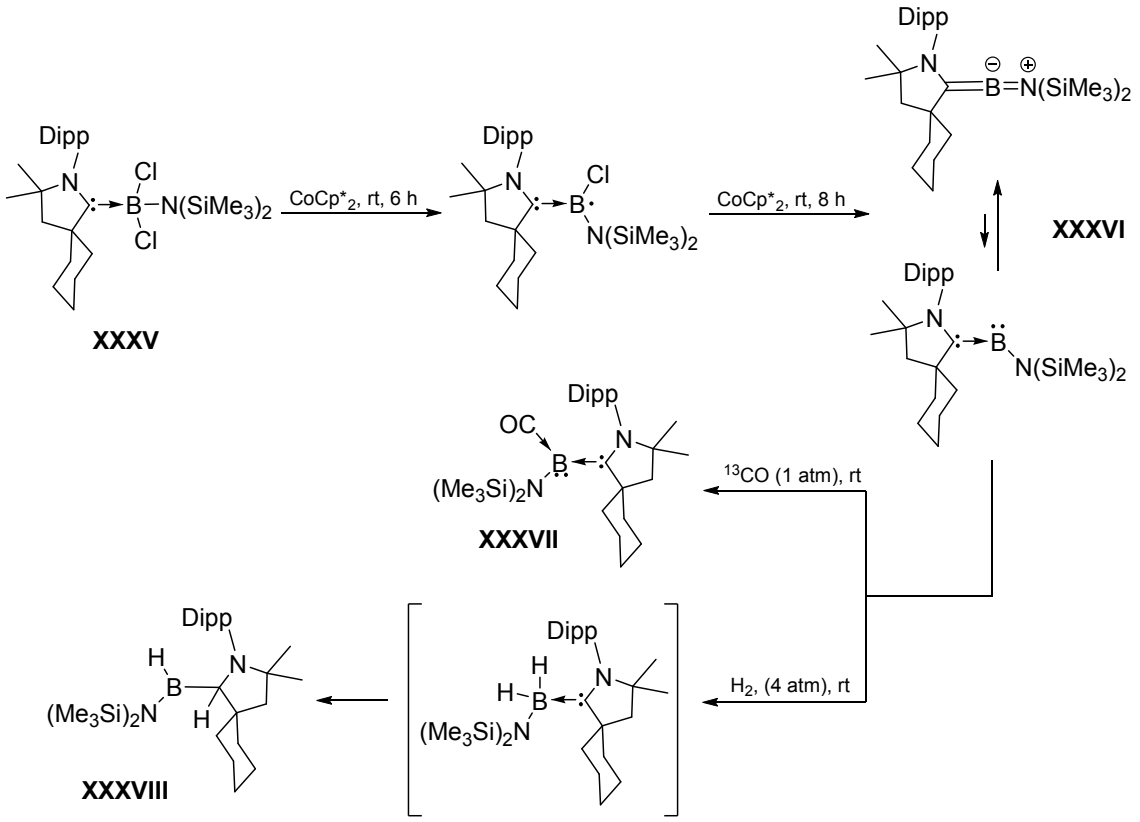
1.2.2 Stabilization by Lewis Bases

Borylenes can be also stabilized by nucleophilic carbenes (Scheme 11). In 2011 Kinjo et al. published the first synthesis and isolation of parent borylene, BH, stabilized by two cyclic (alkyl)(amino)carbenes (CAAC) bearing the bulky 2,6-diisopropylphenyl (Dipp) group on the nitrogen atom and cyclohexyl group on the carbon atom to protect the boron center (**XXXI**).[43] The bonding between boron atom and two CAAC ligands is best described by a donation of σ lone electron pairs of carbenes into the empty p orbitals of boron and a backdonation from the lone electron pair of the boron orbital into the p(π) orbitals of carbenes.[43] The $HB(CAAC)_2$ molecule was obtained by reduction of the CAAC-BBr_3 adduct

by potassium graphite KC_8. On the other hand, the reduction of N-heterocyclic carbene–tribromoborane adduct NHC-BBr_3 by KC_8 results in the formation of an air-sensitive carbene stabilized neutral diborane with a B=B double bond as reported by Robinson et al.[44, 45] Further investigations concerning synthetic approaches to Lewis base stabilized borylenes involve efficient preparation of two bis(carbene)borylenes **XXXIIa** and **XXXIIb** of the general formula (L)(CAAC)BH] (L is either benzimidazolylidene or cyclopropenylidene), achieved by two-electron reduction of bis(carbene) boronium salts (triflates) with KC_8.[46] In these compounds the boron lone pair of electrons is mainly delocalized on the CAAC due to the weaker electron accepting properties of L ligands compared to CAAC as confirmed by crystallographic characterization (shorter B-C(CAAC) bond) and DFT computations.[46] In 2014 Kinjo and coworkers synthesized and characterized a bis(oxazol-2-ylidene)-phenylborylene adduct **XXXIII** by KC_8 reduction of a boronium salt.[47] To asses electron donating properties towards Lewis acids, the phenylborylene adduct was reacted with the chromium complex [(thf)$Cr(CO)_5$]. The reaction afforded the terminal borylene-chromium complex **XXXIV**.[47] Also in 2014, Bertrand et al. were able to synthesize CAAC-aminoborylene adduct **XXXVI** (Scheme 12).[48] The reaction proceeded through the stepwise reduction of the CAAC-bis(trimethylsilyl)aminodichloroborane adduct **XXXV** with cobaltocene $Co(Cp^*)_2$ and yielded the corresponding nearly linear CAAC-supported singlet aminoborylene that is reminiscent of the singlet carbene, [bis(diisopropylamino)phosphino]-trimethylsilylcarbene, stabilized by push-pull substituents and possessing allenic, though flexible, structure.[49, 50] The CAAC-aminoborylene adduct displays electrophilic character of boron and is able to irreversibly bind carbon monoxide CO molecule (**XXXVII)** and to split molecular hydrogen (**XXXVIII**).

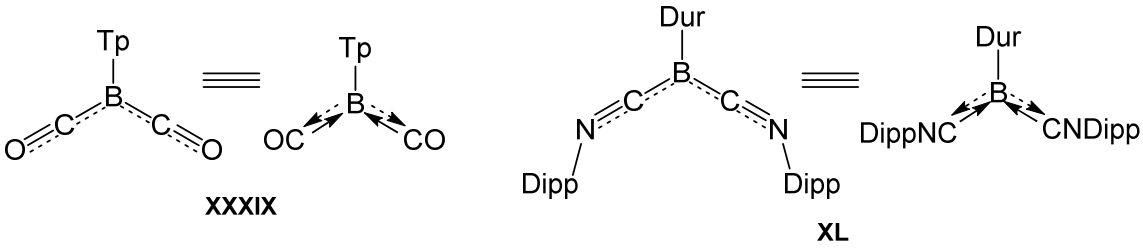


Scheme 11. Borylenes stabilized by cyclic carbenes.



Scheme 12. Synthesis and reactivity of CAAC–stabilized aminoborylene.[48]

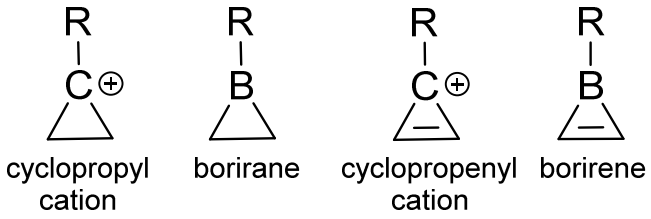
Quite recently, the neutral borylene dicarbonyl complex $TpB(CO)_2$[51] [Tp = 2,6-di(2,4,6-triisopropylphenyl)phenyl] **XXXIX** and borylene bis(isonitrile) $DurB(CNDipp)_2$[51, 52] (Dur = 2,3,5,6-tetramethylphenyl) **XL** were synthesized by Braunschweig and coworkers (Scheme 13). $TpB(CO)_2$ was prepared by the treatment of the molybdenum terminal borylene complex $[(OC)_5Mo(BTp)]$ with carbon monoxide CO, while $DurB(CNDipp)_2$ was obtained in the reaction of the iron terminal borylene complex $[(OC)_3(Me_3P)Fe(BDur)]$ with 2,6-diisopropylphenylisocyanide (DippNC). The computational analysis of the HOMO of the borylene complexes revealed π backdonation from the p(B) filled orbital into the empty π* orbitals of the ligands.[51]



Scheme 13. Borylene complexes with carbon monoxide and isonitrile.[51]

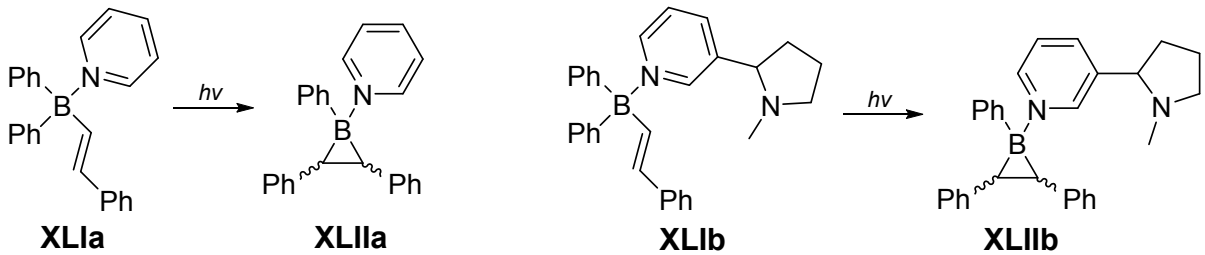
1.3 Boriranes and Borirenes

Three-membered monoboron heterocycles called boriranes and borirenes, are rather rare compounds and are isoelectronic to the cyclopropyl and cyclopropenyl cations, respectively (Scheme 14).[53, 54] Both borirane and borirene are highly strained molecules that have one empty p orbital on boron atom that is capable of accepting an electron pair. Boriranes are saturated alicyclic compounds, while borirenes are aromatic.[53-56] A number of experimental[16, 18, 39, 57-75] and theoretical[55, 76-83] studies have been carried out to reveal the properties of borirenes.

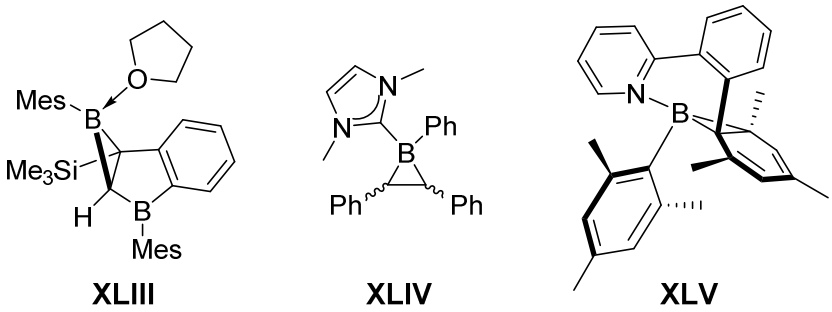


Scheme 14. Comparison of borirane to cyclopropyl cation and borirene to cyclopropenyl cation.

The chemistry of boriranes has hardly been investigated. The majority of the known boriranes were synthesized with Lewis base (e.g. pyridine, THF, NHC) coordinated to the boron atom through a dative bond.[18, 57-59] The pyridine-stabilized 1,2,3-triphenylboriranes **XLIIa,b** were obtained by photochemical cyclization of pyridine-borane complexes **XLIa,b** (Scheme 15).[57] On the other hand, the THF-stabilized borirane **XLIII** (Scheme 16) was generated in the reaction of tetracarbahexaborane(6) with tetrahydrofuran.[58] More recently, two NHC-stabilized boriranes **XLIV** were synthesized by Braunschweig and coworkers[59] in the reaction of trans-stilbene dianion ($Na_2[C_{14}H_{12}]$) with NHC-stabilized dichloro-phenylborane, NHC-B(Ph)Cl_2. Intramolecularly stabilized derivatives of boranorcaradienes **XLV** that can be obtained via the photoisomerization of the corresponding borane were also extensively studied by Wang et al.[20, 84-89]

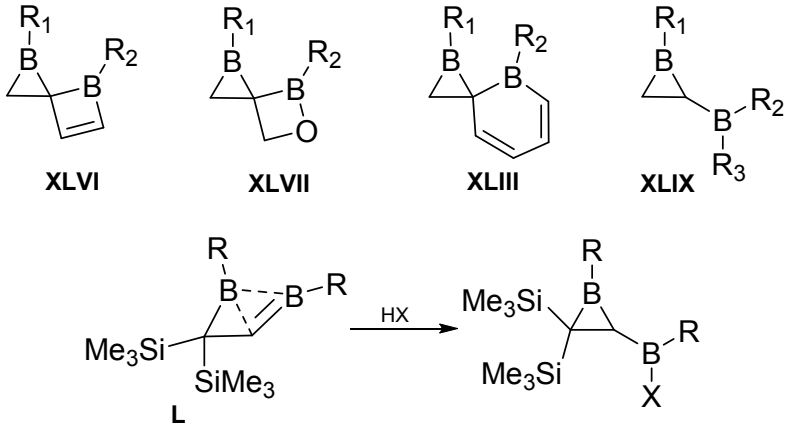


Scheme 15. Photoisomerization of pyridine-borane adducts and formation of boriranes.



Scheme 16. Examples of Lewis base-stabilized boriranes.

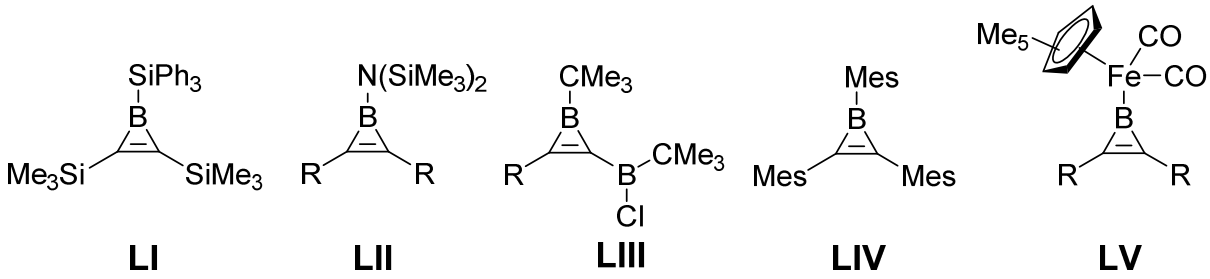
So far only few uncoordinated boriranes were synthesized. These are 1,4-diboraspiro-[2.3]hex-5-ene (**XLVI**),[60-62] 5-oxa-1,4-diboraspiro[2.3]hexane (**XLVII**),[60] 1.4-diboraspiro-[2.5]octa-5,7-diene (**XLVIII**),[62] and 2-borylborirane (**XLIX**)[63, 64] (Scheme 17). Boriranes **XLVI** and **XLVII** were first produced by Klusik and Berndt in 1983 by cycloaddition of acetylene and acetone, respectively, to methyleneborane.[60] Further addition of ethyne to 1,4-diboraspiro[2.3]hex-5-ene yielded 1.4-diboraspiro[2.5]octa-5,7-diene.[62] 2-Borylborirane was obtained by the addition of HCl to the C=B double bond of boranediylborirane **L** (Scheme 17).[63]



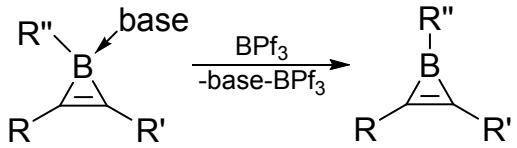
Scheme 17. Uncoordinated boriranes and synthesis of 2-borylborirane from boranediylborirane.

Heteroaromatic borirenes are more stable than boriranes and many uncoordinated[16, 39, 65-70] (Scheme 18) as well as Lewis base coordinated[71] borirenes were prepared. In metalloborirenes **LV**, that can be obtained by photochemical borylene transfer from a metalloborylene complex, the metal center is connected directly to the boron atom.[40, 90] The reactivity of the boron center in *B*-mesitylborirene **LIV** and *B*-trimethylsilylaminoborirene **LII** towards Lewis bases (pyridine, dimethylaminopyridine, N-heterocyclic carbene,

trimethyl- and tricyclohexylphosphine) was studied.[71] Neither *B*-mesitylborirene nor *B*-trimethylsilylaminoborirene reacted with phosphines. Addition of N-heterocyclic carbenes to both types of borirenes resulted in the formation of NHC-coordinated borirenes. Additionally, *B*-mesitylborirene reacted also with pyridines. The base can be removed by addition of tris(pentafluorophenyl)borane BPf_3. During this reaction uncoordinated borirenes are regenerated and the corresponding base adduct of BPf_3 is formed (Scheme 19).



Scheme 18. Examples of known borirenes and metalloborirenes.



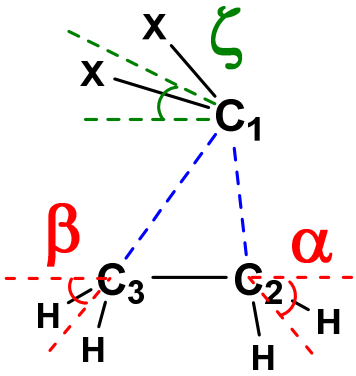
Scheme 19. Dequaternization of base-stabilized borirene.

1.4 Carbenic Philicity

The concept of the carbenic philicity is well established.[91-94] A number of experimental and theoretical measures are available to explain the differences in reactivity of various substituted carbenes. Most of the philicity scales are based on the addition reaction of carbenes to alkenes, for instance the empirical selectivity index m_{CXY} introduced by Moss.[91] One of the theoretical scales for the carbenic philicity is based on the energies of frontier molecular orbitals (FMO) of carbenes. Electrophilic carbenes possess low-lying HOMO and LUMO orbitals, while the HOMO and LUMO of nucleophilic carbenes are high-lying.[92] Depending on the substituents, carbenes can be classified into electrophilic (CF_2, CCl_2), ambiphilic (MeOCCl, MeOCPh), and nucleophilic [MeOCMe, $C(OMe)_2$, NHC].

Another theoretical measure of the philicity developed by Houk and Moss[95] is based on the geometrical parameters of the transition states in the cycloaddition reactions of carbenes with olefins. The tilt angle, ζ, is an important geometrical parameter describing the carbenic philicity (Scheme 20). The tilt angle of the ideal nucleophile would be 90° and in

case of the ideal electrophile it would equal 0°. The angles α and β that measure the distortion of the hydrogen atoms of ethene from planarity in the transition state, is also an important parameter for estimation of the carbenic philicity. The more nucleophilic character of the carbene is, the larger are angles α and β. The ratio of C1-C2/C1-C3 distances in the transition state can be used to determine the philicity. This ratio is closer to 1 in case of electrophilic and is decreasing in nucleophilic carbenes.



Scheme 20. Transition state parameters as measures of carbenic philicity according to Houk et al. [95]

2 Objectives and Expected Output of the Thesis

Computational chemistry, which plays an important role in physical organic chemistry, is essential in predicting possible reactions and explaining their mechanisms. It is also a convenient tool for the interpretation of experimentally obtained data. Moreover, computer chemistry offers unique insight into the properties of molecules when experimental results are unavailable.

Borylenes, BR, monovalent boron compounds, are exceptional but very elusive reactive intermediates. Contrary to carbenes, whose chemistry is well established, the knowledge available from experiments concerning the reactivity, electronic and geometrical structure, as well as excited states of borylenes is still limited.

The presented thesis provides information on the barrier heights, exothermicities and mechanisms of borylene reactions that could not be obtained from earlier experimental investigations. Details on the influence of substitution on the electronic structure, orbital energies, singlet-triplet energy separation, structures of transition states, and reactivity patterns are given. Knowledge of the low-lying electronically excited states and vertical singlet-singlet excitation energies of various larger borylenes e.g. phenylborylene, is highly valuable in detecting borylenes in prospective UV/Vis matrix isolation or time-resolved spectroscopy experiments.

The thesis presents also the novel low-energy reaction pathways for the reaction between three-membered boron heterocycles, boriranes and borirenes, and unsaturated hydrocarbons such as ethyne or ethene. The interaction between the empty orbitals of boron and the π bond results in a ring enlargement reaction that proceeds through an unusual pentacoordinate intermediate which resembles the olefin and acetylene complexes of transition metals or borylene stabilized by two hydrocarbon molecules. These intermediates are not expected to be detectable under the experimental conditions as the barriers for their disappearance are very low. But related 1,5-cyclooctadiene-borylene complexes have significantly higher barriers for reactions and it is predicted that they should be observable. The results obtained concerning the reactivity of boriranes and borirenes towards unsaturated hydrocarbons are important in terms of interpreting Timms' experiments discussed in Chapter **1.1**. Owing to the extremely low barriers, ring expansion reactions should be at least competitive to the formation of 1,4-diboracyclohexanes and 1,4-diboracyclohexadienes.

The present work contributes substantially to an underdeveloped area of boron chemistry and provides valuable information in terms of prospective experiments.

3 Methodology

The results presented in the following sections were obtained by means of state of the art computational chemistry methods. In particular density functional theory (DFT) and perturbation theory of second order (MP2) were used for geometry optimizations. These methods are well established, widely used, and generally give reasonably good results for molecular structures. Details on these methods and can be found in numerous review papers[96-100] and textbooks[101-104] on computational chemistry.

The energetics of chemical reactions and barrier heights, however, are more challenging to compute accurately. Therefore, coupled cluster theory with singles, doubles, and a perturbative estimate of triple excitations [CCSD(T)][105-107] was employed to improve energetics of the reactions that were studied. The CCSD(T) method is considered the "gold standard" in present day quantum chemistry and it is expected to provide energy data within chemical accuracy if the underlying single-determinant approximation provides a qualitatively correct description of the system. For details of the method the reader is referred to a number of comprehensive reviews. CCSD(T) scales N^7 with the number N of the basis functions, which makes this method computationally quite challenging. Recent technical improvements allow application of the resolution of the identity[108] (RI) approximation that speeds up CCSD(T) computations and allows application of large basis sets to medium sized molecules.[109] As large basis sets are required for obtaining reasonably accurate results with the highly correlated CCSD(T) method, here triple-zeta or quadruple-zeta basis sets[109] were employed.

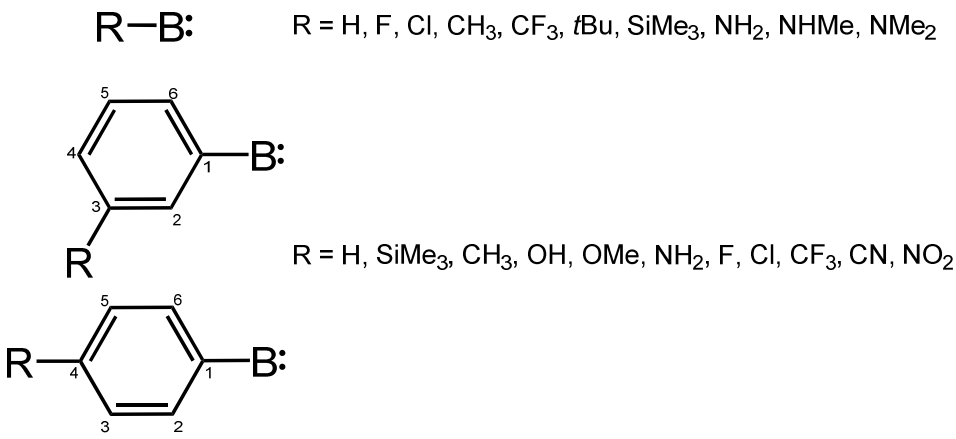
In chapters **4.1** and **4.2** ground state singlet and lowest triplet state geometries of substituted borylenes were optimized using the hybrid B3LYP density functional[110-112] in conjunction with the def2-TZVP[113, 114] basis set. Singlet-singlet vertical excitation energies presented in chapter **4.2** were computed employing equation-of-motion coupled cluster theory with single and double excitations (EOM-CCSD),[115-118] and time-dependent density functional theory (TD-DFT). [119-123] Both methods utilized the aug-cc-pVTZ[124-126] basis set. The functionals used in TD calculations were B3LYP, range-separated[127] hybrid CAM-B3LYP,[128] and ωB97X.[129] Excited state computations were performed using the geometries optimized at the B3LYP/def2-TZVP level of theory. Natural transition orbital (NTO)[130] analysis was carried out using the TD-ωB97X results to determine the main orbital contributions of the electronic excitation. Second-order Møller-Plesset perturbation theory (MP2)[131] was employed to optimize the geometries using the cc-pVTZ[126] basis set in

chapter **4.3.** Energies were further refined with coupled-cluster theory using single, double, and a perturbative estimate of triple excitations, CCSD(T),[105] in combination with the cc-pVTZ and aug-cc-pVTZ[124-126] basis sets. Geometries of van der Waals complexes discussed in chapter **4.4** were optimized using the spin-component scaled (SCS)[132, 133] second-order Møller-Plesset perturbation theory (MP2) combined with Ahlrichs' polarized quadruple-ζ def2-QZVP[113] basis set. Standard MP2 tends to overestimate the binding energies of stacked π-π complexes. Bachorz et al.[134] have shown that binding energies of π complexes can be corrected by using the SCS-MP2. However, binding energies of the systems with hydrogen bonding are underestimated.[134, 135] In 2004 Grimme et al.[136] proved the advantages of SCS-MP2 over standard MP2 for the computation of molecular geometries of simple molecules and weakly bounded systems. Energies were refined with coupled-cluster theory[105] of single, double, and a perturbative estimate of triple excitations [CCSD(T)] in combination with the def2-QZVP (def2-TZVP in case of phenylborylene complexes) and the aug-cc-pVTZ basis sets using SCS-MP2 geometries. Symmetry-adapted perturbation theory[137, 138] of third order with density fitting [(DF-SAPT2+3)][139, 140] in conjunction with the aug-cc-pVTZ was used to study the interaction energies of the van der Waals complexes. SAPT analysis was carried out using the SCS-MP2 geometries. The resolution of the identity approximation[108] was applied in SCS-MP2 and CCSD(T) calculations using suitable fitting basis sets.[141] All geometries in chapters **4.5** and **4.6** were optimized using the hybrid exchange-correlation density functional M06-2X[142] in combination with 6-311+G**[143-146] basis set. Energies were further refined with coupled-cluster theory using single, double, and a perturbative estimate of triple excitations, CCSD(T) using polarized triple-ζ def2-TZVP basis set. Additionally, frozen core approximation was applied in all MP2, CCSD(T), SAPT, and EOM-CCSD computations. The nature of the stationary points (minimum or saddle-point) was confirmed by subsequent analytical (numerical in case of SCS-MP2) computations of second derivatives and harmonic vibrational frequencies. Zero-point vibrational energy (ZPVE) corrections were added to the energies in chapters **4.1**, **4.3**, **4.5**, and **4.6**. All computations were performed for isolated molecules. All DFT, conventional MP2, EOM-CCSD, NTO, and standard CCSD(T) calculations were performed with the Gaussian 09[147] program. RI-SCS-MP2 and RI-CCSD(T) computations were performed using the Turbomole 6.5 program.[148] SAPT analysis was performed using the PSI4 program.[149] Figures of molecular structures and orbitals were prepared using the CYLView,[150] Chemcraft,[151] and Molekel[152] programs.

4 Results and Discussion

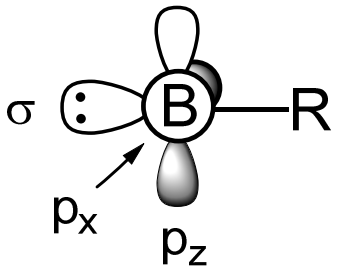
4.1 Electronic Structure and Geometries of Borylenes

In order to investigate the substituent effects on the electronic structure and geometry of borylenes, a wide variety of substituents R (where R = CH_3, *t*Bu, Ph, $SiMe_3$, NH_2, F, Cl, or CF_3) varying in the electron donating or electron withdrawing properties were chosen. Furthermore, the effect of substitution by electron donating and electron withdrawing groups (R = CH_3, OH, OMe, NH_2, $SiMe_3$, F, Cl, CF_3, CN, NO_2) in meta and para positions (relative to boron atom) in arylborylenes were studied (Scheme 21).



Scheme 21. Structures of studied molecules.

Borylenes, alike carbenes, possess one lone pair of electrons on the non-bonding n_σ orbital (Scheme 22). This sp type orbital is also the highest occupied molecular orbital (HOMO) of borylenes. However, contrary to their carbon analogs, borylenes have only one substituent and two empty p_π orbitals located on the boron atom. These comprise the two lowest unoccupied molecular orbitals (LUMO and LUMO+1) which are doubly degenerate in borylenes of $C_{\infty v}$ and C_{3v} symmetry. The electronic configuration of the singlet ground state is σ^2, while the configuration of the lowest excited triplet and singlet states can be described as $\sigma^1\pi^1$. The LUMO and LUMO+1 are no longer degenerate in borylenes of lower symmetry (C_{2v}, C_s) as a result of the interaction with the substituents.



Scheme 22. Orbitals of the lowest singlet state of borylene.

Energies of HOMO and LUMO of parent borylene, BH, as computed at the B3LYP/def2-TZVP level of theory, are -6.52 and -2.60 eV, respectively. Similarly to carbenes, σ-electron withdrawing substituents, F, Cl, or CF_3, lower the HOMO energy of borylenes compared to BH. The LUMO energy of haloborylenes is increased owing to the π electron donation from the lone pair of halogen to the empty p(B) orbitals, while the LUMO energy is decreased by CF_3. Electron donating substituents (CH_3, *t*Bu, $SiMe_3$) increase the energy of both HOMO and LUMO compared to BH. The methyl group elevates the energy of the LUMO due to the electron donation via hyperconjugation. The HOMO and LUMO energies of aminoborylenes are increased compared to BH due to the electron donation of the nitrogen lone pair into the empty p orbital of boron. Introduction of a phenyl or trimethylsilyl group results in an increase of the HOMO energy, but has nearly no influence on the energy of the LUMO. Introduction of the electron releasing groups on the phenyl ring increase, while electron withdrawing groups decrease the energies of both frontier molecular orbitals, compared to those of unsubstituted phenylborylene. The effect is stronger for substitution in para position.

Most substituents increase the HOMO-LUMO energy gap compared to BH (3.92 eV). Haloborylenes followed by aminoborylenes and alkylborylenes have the largest H-L gaps. Among all studied borylenes only two, phenylborylene and trimethylsilylborylene have H-L gaps smaller than parent borylene. EDG introduced in para position of arylborylenes only slightly increase, while EWG in para position considerably decrease the H-L gap compared to PhB (Table 1).

The singlet-triplet energy splitting of BH computed at the B3LYP/def2-TZVP level of theory underestimates somewhat the experimentally determined value[153] (calc. 26.4 kcal/mol; exp. 29.8 kcal/mol). In most cases, substitution increases the S-T gap compared to BH. Largest S-T gaps were obtained for haloborylenes (78.9 kcal/mol in BF) and aminoborylenes (> 44 kcal/mol) (see Table 1). A very small singlet-triplet energy separation

was found in $SiMe_3B$ where the singlet state is favored only by 8.2 kcal/mol over the triplet state. In the arylborylene series substitution affects the S-T gap more significantly when electron releasing or electron pulling group is placed in the para position. EDG increase while EWG decrease the gap relative to unsubstituted phenylborylene. The results are in agreement with trends observed in substituted phenyl(carbomethoxy)carbenes[154] and phenylcarbenes.[155, 156]

Table 1. B-R bond lengths (in Å) of borylenes in their lowest singlet and triplet states, energies of molecular orbitals (in eV), HOMO-LUMO energy gap (in eV), and singlet-triplet energy splitting (in kcal/mol) computed at the B3LYP/def2-TZVP+ZPVE level of theory.

Borylene	$d(B\text{-}R)^S$	$d(B\text{-}R)^T$	State	ε_{HOMO}	ε_{LUMO}	ε_{LUMO+1}	$\Delta E_{H\text{-}L}$	$\Delta E_{S\text{-}T}$
HB	1.233	1.192	^{3}П	-6.52	-2.60	-2.60	3.92	26.4
FB	1.265	1.315	^{3}П	-7.84	-1.33	-1.33	6.51	78.7
ClB	1.722	1.705	^{3}П	-7.28	-2.13	-2.13	5.14	53.8
MeB	1.530	1.546	^{3}A″	-6.00	-1.64	-1.64	4.36	37.7
***t*BuB**	1.545	1.576	^{3}A″	-5.78	-1.53	-1.53	4.25	36.6
CF_3B	1.650	1.589	^{3}A″	-7.44	-3.38	-3.38	4.06	28.1
$SiMe_3B$	2.115	2.012	^{3}A″	-5.27	-2.47	-2.47	2.80	8.2
NH_2B	1.372	1.369	^{3}B2	-6.20	-1.45	0.01	4.76	45.8
NHMeB	1.370	1.365	^{3}A′	-6.01	-1.36	0.12	4.65	44.6
NMe_2B	1.371	1.367	^{3}B2	-5.91	-1.16	0.10	4.75	45.9
PhB	1.529	1.478	^{3}B1	-5.81	-2.45	-1.60	3.36	30.8
***m*$SiMe_3$PhB**	1.527	1.478	^{3}A″	-5.71	-2.36	-1.52	3.35	30.9
***m*MePhB**	1.528	1.478	^{3}A″	-5.73	-2.38	-1.52	3.36	31.0
***m*OHPhB**	1.529	1.479	^{3}A″	-5.85	-2.47	-1.64	3.38	30.9
***m*OMePhB**	1.528	1.479	^{3}A″	-5.76	-2.38	-1.55	3.38	31.2
***m*NH_2PhB**	1.528	1.480	^{3}A	-5.66	-2.25	-1.43	3.40	31.4
***p*$SiMe_3$PhB**	1.528	1.475	^{3}A″	-5.72	-2.43	-1.52	3.29	30.3
***p*MePhB**	1.525	1.478	^{3}A′	-5.69	-2.30	-1.49	3.39	31.8
***p*OHPhB**	1.521	1.481	^{3}A″	-5.64	-2.14	-1.46	3.50	34.4
***p*OMePhB**	1.520	1.481	^{3}A″	-5.56	-2.07	-1.38	3.50	34.5
***p*NH_2PhB**	1.515	1.480	^{3}A′	-5.36	-1.82	-1.18	3.54	36.1
***m*FPhB**	1.534	1.478	^{3}A″	-6.02	-2.70	-1.81	3.32	29.8
***m*ClPhB**	1.534	1.477	^{3}A″	-6.03	-2.72	-1.84	3.32	29.8
***m*CF_3PhB**	1.535	1.477	^{3}A	-6.15	-2.88	-1.96	3.27	29.1
***m*CNPhB**	1.538	1.477	^{3}A″	-6.31	-3.07	-2.23	3.24	28.6
***m*NO_2PhB**	1.539	1.477	^{3}A″	-6.34	-3.30	-2.94	3.03	28.4
***p*FPhB**	1.527	1.484	^{3}B	-5.92	-2.49	-1.73	3.43	31.8
***p*ClPhB**	1.530	1.476	^{3}B1	-5.96	-2.64	-1.76	3.31	30.6
***p*CF_3PhB**	1.536	1.473	^{3}A	-6.17	-2.98	-1.97	3.19	27.9
***p*CNPhB**	1.538	1.468	^{3}B1	-6.30	-3.31	-2.11	2.99	26.4
***p*NO_2PhB**	1.541	1.465	^{3}B1	-6.38	-3.70	-2.18	2.67	24.7

Most of the triplet borylenes are of the same symmetry as their singlet counterparts. Exceptions are CH_3B, *t*BuB, CF_3B, and $SiMe_3B$ (C_{3v} symmetry of the singlet ground state) in which the symmetry of the triplet state is reduced to C_s due to the Jahn-Teller distortion. The

B-R bond is shorter in the triplet state of almost all studied borylenes. Exceptions are CH_3B, *t*BuB, and BF with notably elongated B-R bonds (see Table 1).

4.2 Excited States of Borylenes

Experimental and theoretical investigations concerning the excited states of borylenes were only performed on diatomic borylenes. Most of them involve the excited states of parent boylene (BH).[14, 153, 157-181] A number of studies concerning the excited states of chloroborylene (BCl),[182-194] fluoroborylene (BF),[175, 195-206] bromoborylene (BBr),[193, 207-212] and iodoborylene (BI)[213-218] are also available. No data, neither experimental nor theoretical, on the excited states of larger borylenes exist. To examine the influence of the substitution on the electronic excitations in borylenes a wide range of substituents was selected (see Scheme 21 in Chapter **4.1**).

The two lowest singlet-singlet electronic transitions are of n → π* type and involve the excitation from the non-bonding HOMO (sp orbital of boron) to the LUMO and LUMO+1 which mainly consist of empty p orbitals of boron and partially the orbitals of the substituent (Figure 1). Both TD-ωB97X and EOM-CCSD give similar trends of excitation energies and oscillator strengths upon substitution.

The lowest transition in diatomic borylenes is $X^1\Sigma^+ \rightarrow A^1\Pi$. The vertical excitation energies of HB (2.93 eV), FB (6.47 eV) and ClB (4.66 eV) calculated at the EOM-CCSD/aug-cc-pVTZ//B3LYP/def2-TZVP level of theory are about 0.1 eV higher than the experimental adiabatic energies of the S_1 state, 2.86, 6.34, 4.56 eV, respectively.[219] The excitation energies of methylborylene, *tert*-butylborylene, and trifluoromethylborylene are over 3 eV, and the lowest excitation energies of aminoborylenes are higher than 4 eV. The excitation energy of Me_3SiB (1.63 eV) is very low, almost in the near-infrared region (759 nm), and the absorption band is of low intensity (f = 0.003). The computed lowest excitation energy of phenylborylene is 2.85 eV. This value changes upon substitution with electron donating and electron withdrawing substituents (see Table 2). In the arylborylene series, excitation energies rise with the strength of the electron donating properties of the substituents. On the other hand, introduction of the electron withdrawing group decreases the excitation energy. The effects are stronger when substituents are placed in para position (Table 2).

The second transition also involves the excitation from HOMO mainly to the empty p orbital of boron (Figure 1). The excitation energies of aminoborylenes are in the range of 5.5-

5.8 eV (Table 2). The excitation energy of unsubstituted phenylborylene is 3.35 eV. The substitution of the phenyl ring of arylborylenes has hardly an influence on the excitation energies (3.32-3.38 eV) and oscillator strengths.

Table 2. Vertical excitation energies (E_{exc}, in eV) and oscillator strengths (f) of the lowest singlet-singlet electronic transition of substituted borylenes computed at the EOM-CCSD and TD-ωB97X levels of theory using the aug-cc-pVTZ basis set.

R	First excitation				Second excitation			
	ωB97X		EOM-CCSD		ωB97X		EOM-CCSD	
	E_{exc}	Osc. f	E_{exc}	Osc. f	E_{exc}	Osc. f	E_{exc}	Osc. f
HB	2.688	0.026	2.930	0.025				
FB	6.200	0.244	6.471	0.243				
ClB	4.434	0.068	4.661	0.065				
MeB	3.334	0.047	3.512	0.045				
***t*BuB**	3.188	0.031	3.303	0.028				
CF_3B	2.944	0.028	3.247	0.028				
$SiMe_3$B	1.421	0.003	1.634	0.003				
NH_2B	4.107	0.094	4.307	0.091	5.596	0.180	5.801	0.175
NHMeB	4.032	0.085	4.189	0.080	5.529	0.174	5.681	0.167
NMe_2B	4.142	0.080	4.272	0.077	5.420	0.156	5.513	0.144
PhB	2.735	0.023	2.845	0.021	3.193	0.042	3.352	0.042
***m*$SiMe_3$PhB**	2.740	0.021	2.833	0.020	3.187	0.040	3.337	0.039
***m*MePhB**	2.740	0.022	2.844	0.021	3.199	0.042	3.356	0.041
***m*OHPhB**	2.730	0.022	2.850	0.021	3.207	0.042	3.367	0.042
***m*OMePhB**	2.741	0.022	2.856	0.021	3.214	0.042	3.367	0.041
***m*NH_2PhB**	2.743	0.023	2.864	0.021	3.220	0.043	3.376	0.042
***p*$SiMe_3$PhB**	2.710	0.021	2.804	0.019	3.191	0.042	3.349	0.041
***p*MePhB**	2.791	0.023	2.886	0.022	3.192	0.043	3.347	0.042
***p*OHPhB**	2.905	0.026	2.998	0.024	3.182	0.043	3.335	0.042
***p*OMePhB**	2.907	0.026	3.000	0.024	3.182	0.043	3.334	0.042
***p*NH_2PhB**	2.982	0.027	3.051	0.025	3.179	0.044	3.324	0.043
***m*FPhB**	2.692	0.022	2.816	0.020	3.202	0.042	3.370	0.041
***m*ClPhB**	2.696	0.021	2.813	0.020	3.191	0.040	3.356	0.039
***m*CF_3PhB**	2.685	0.021	2.798	0.020	3.180	0.040	3.348	0.040
***m*CNPhB**	2.669	0.021	2.788	0.019	3.171	0.039	3.344	0.039
***m*NO_2PhB**	2.666	0.021	2.785	0.019	3.178	0.039	3.351	0.038
***p*FPhB**	2.816	0.024	2.929	0.023	3.183	0.042	3.345	0.041
***p*ClPhB**	2.729	0.022	2.839	0.020	3.185	0.042	3.348	0.041
***p*CF_3PhB**	2.617	0.020	2.740	0.019	3.184	0.042	3.354	0.041
***p*CNPhB**	2.540	0.018	2.672	0.017	3.181	0.041	3.353	0.041
***p*NO_2PhB**	2.505	0.017	2.646	0.017	3.184	0.041	3.359	0.041

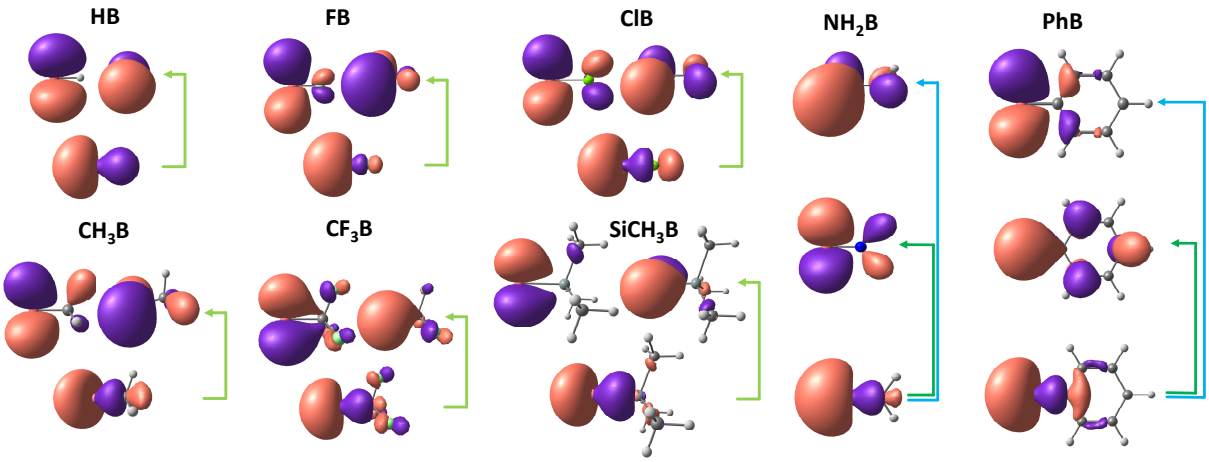


Figure 1. Natural transition orbitals of selected borylenes computed at the ωB97X/aug-cc-pVTZ level of theory. Light green arrows indicate the excitation in borylenes of $C_{\infty v}$ and C_{3v} symmetry. Dark green arrows indicate first excitation, while the blue ones second excitation in amino- and phenylborylene.

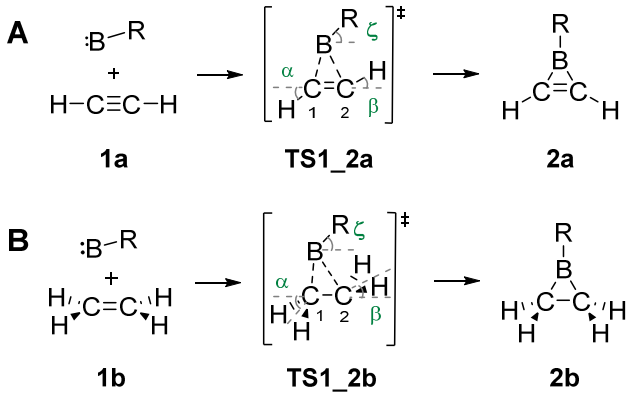
4.3 Reactivity of Borylenes towards Hydrocarbons

Despite the fact that borylenes have only one substituent, they are expected to follow the reactivity patterns of carbenes. In this section the reactivity of various substituted borylenes BR (where R = H, F, Cl, Br, CH_3, Ph, NH_2, NHMe, and NMe_2) towards some model hydrocarbons are examined by means of computational chemistry. Ethyne, ethene, and methane have been chosen as prototypical hydrocarbons. Additionally, the reaction mechanisms and the influence of the substitution on the reaction barriers and exothermicities are studied. The philicity of borylenes is studied following the analyses of carbenes performed by Houk et al.[95] In the course of the study, different conformers of the products and transition states were found but only those with lowest energies were taken into account.

4.3.1 Addition to Carbon-Carbon Double and Triple Bonds

The addition of borylene to ethyne results in the formation of borirene, while the reaction of borylene with ethene produces borirane (Scheme 23). Both addition reactions are highly exothermic, however the reaction energies for the formation of boriranes are lower. The barriers for the addition to CC triple and double bonds are lower than 10 kcal/mol for most of the borylenes studied here (Table 3). The exception is fluoroborylene with barrier heights larger than 10 kcal/mol. The reactions of parent borylene (BH) with ethyne and ethene proceed without barrier and are the most exothermic. The smallest barriers (less than 2 kcal/mol) and highest exothermicities (besides BH molecule) are found for the cycloadditions of the carbon substituted borylenes. In the halide series, exothermicity increases and reaction

barrier decreases from fluorine to bromine. Reactivity of aminoborylenes in terms of barrier heights and reaction energies for the addition to ethyne is similar to that of BCl, while in case of addition to ethene to BBr.



Scheme 23. Mechanisms of the addition of borylene to ethyne and ethene.

Table 3. Reaction barriers (in kcal/mol) and reaction energies (in kcal/mol) computed for the addition of borylenes RB to ethyne and ethene at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPVE level of theory.

R	Ethyne		Ethene	
	Barrier	Reaction energy	Barrier	Reaction energy
H	not existing	–96.1	not existing	–69.8
Ph[a]	1.0	–90.8	1.5[b]	–67.7
CH_3	1.6	–87.1	1.8	–62.7
Br	4.0	–75.1	4.0	–52.8
NH_2	5.5	–71.2	4.8	–55.4
NHMe	4.7	–71.3	3.7	–56.7
NMe_2	6.5	–71.0	6.1	–57.0
Cl	5.9	–70.9	6.5	–48.8
F	11.0	–53.2	13.6	–32.2

[a] Using the cc-pVTZ basis set. [b] With respect to TS1.

Geometries of most of the transition states for both addition reactions have C_s symmetry with R-B-C1-C2 atoms lying in the plane of symmetry, with the exception of BPh (for addition to both hydrocarbons) and $BNMe_2$ (only for addition to ethyne) that are of C_1 symmetry (Figures 2 and 3). The shortest B-C1 distances were computed for BF and the longest for BPh transition states. Two transition states were found for the addition of PhB to ethene (Figure 3), but only TS1 is discussed.

The largest tilt angles were obtained for the transition states of fluoroborylene (44.2° for ethyne and 48.5° for ethene) and the smallest for the transition states of phenylborylene and methylborylene (all in the range of 22-25°). The tilt angles of BBr, BCl, BNH_2, and BNHMe are larger than 30° for both types of transition states. In case of $BNMe_2$ transition

states, the tilt angles are similar to those of BF but most probably this is the consequence of the steric repulsion within the structures. The smallest α and β angles that reflect the distortions of HCC angles from linearity and CH_2 group from planarity (see Scheme 23) were obtained for BPh and BCH_3, and the largest for BF transition states. These distortions are larger for the transition states of ethyne. The smallest ratios of the BC1/BC2 distance were computed for the BF transition states (0.76 for ethyne and 0.72 for ethene) and the largest for the BPh transition states (0.88 for ethyne and 0.87 for ethene). For BCl, BBr, and BCH_3 transition states with ethyne the ratios are 0.80, 0.82, and 0.87 respectively and with ethene these ratios are 0.79, 0.81, and 0.86, respectively. Among aminoborylenes, the ratio values are 0.81 for BNH_2 and BNHMe, and 0.79 for $BNMe_2$ in the transition states with ethyne. The ratios for the transition states with ethene are 0.82 in case of BNH_2 and BNHMe, and 0.79 for $BNMe_2$.

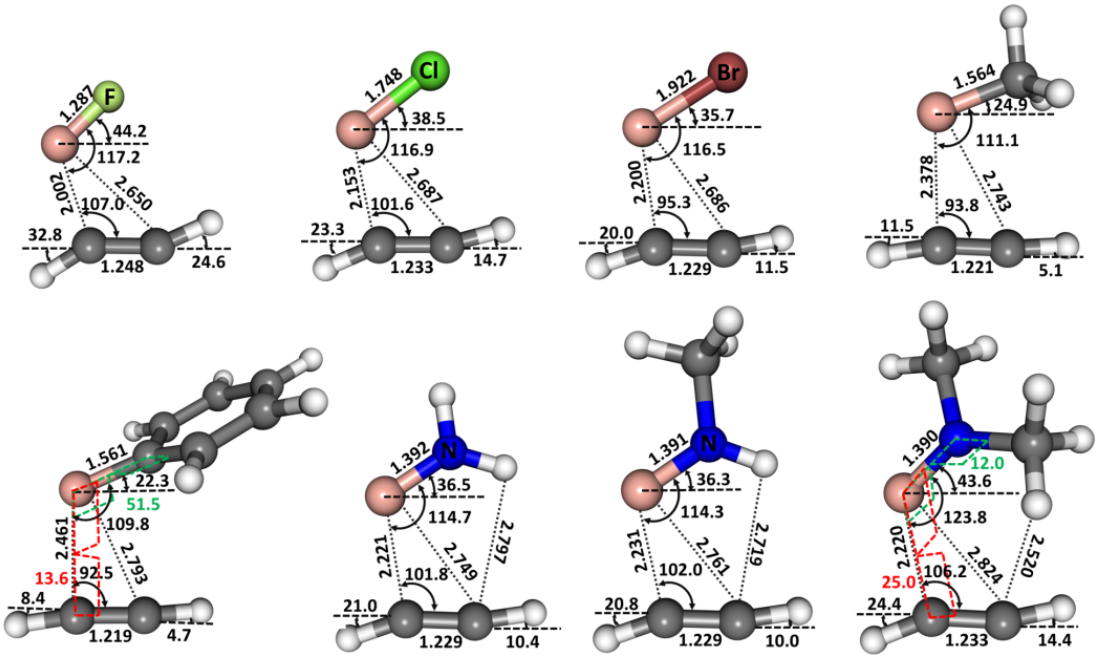


Figure 2. Geometries of the transition structures computed for the addition of borylenes BR to acetylene at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

The analysis of frontier molecular orbitals (Table 1) and the transition state parameters (tilt angle, ratio of carbon-boron distances, and distortion of the unsaturated organic substrate) of the addition reactions showed that the most nucleophilic borylene is BF, while the most electrophilic ones are parent borylene BH and phenylborylene. The reactivity in terms of computed barrier heights and exothermicities decreases for borylenes in the following order: BH > BPh > BCH_3 > BBr ≈ BNHMe > BNH_2 > BCl > $BNMe_2$ > BF.

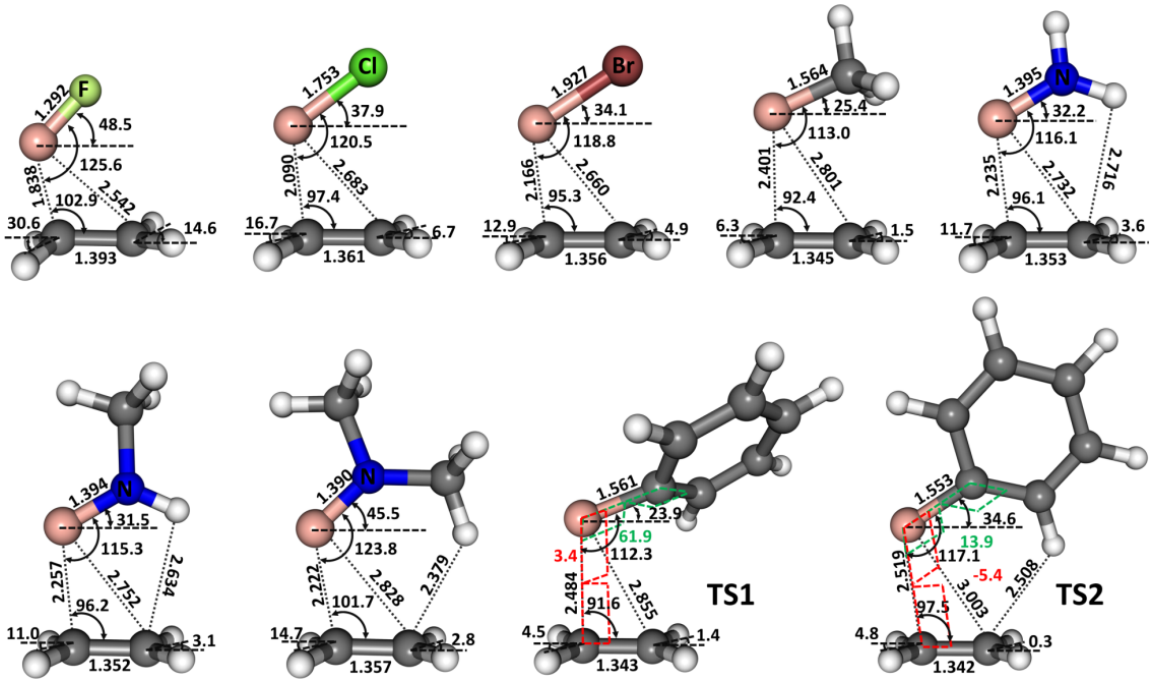
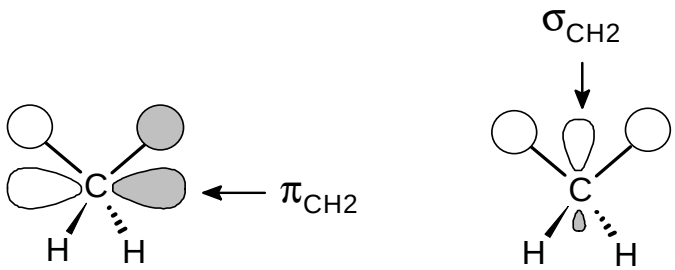


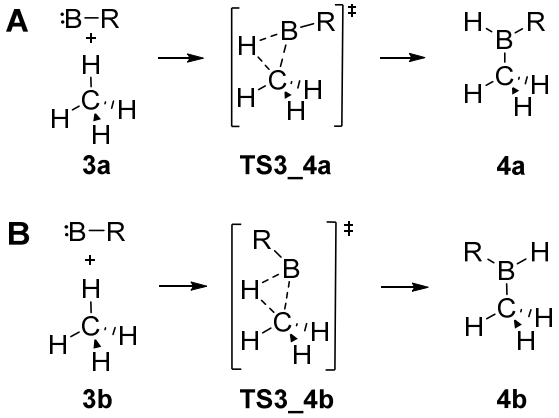
Figure 3. Geometries of the transition structures computed for the addition of borylenes BR to ethylene at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

4.3.2 Insertion into C-H Bond

According to Bach et al.[220] two approaches, σ_{CH2} and π_{CH2}, can be distinguished for the insertion of the singlet methylene (:CH_2) into the C-H bond of saturated hydrocarbons, based on frontier molecular orbital theory (Scheme 24). Also the insertion of borylene into methane can occur according to two approaches (Scheme 25 and Figures 4 and 5). Approach A of borylene insertion is termed π_{CH2} and approach B is termed inverted π_{CH2}. Borylene insertion following approach σ_{CH2} leads to a second order saddle point rather than to a transition state.



Scheme 24. Two possible approaches of carbene insertion into methane according to Bach et al.[220]



Scheme 25. Two approaches of insertion of borylene into a C–H bond of methane.

The insertion of borylene into the carbon-hydrogen bond of methane yields methylborane (Scheme 25). The insertion reactions are highly exothermic (Table 4). Significantly higher barriers were obtained for the insertions via approach B (Scheme 25). The barriers increase with decreasing reaction energies in case of both approaches. Contrary to addition reactions, insertions of parent borylene, BH, proceed with barriers. The highest barriers and smallest reaction energies were obtained for the BF insertions into methane. Among the aminoborylene series barriers heights are comparable.

Table 4. Reaction barriers (in kcal/mol) and reaction energies (in kcal/mol) computed for the insertion of borylenes RB into C-H bond of methane at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ +ZPE level of theory.

R	Barrier A	Barrier B	Reaction energy[b]
H	14.5	23.8	-77.0
Ph [a]	21.3	36.5	-74.2
CH_3	22.6	42.7	-69.0
NH_2	28.6	56.2	-65.8
NHMe	27.1	53.5	-66.9
NMe_2	30.7	54.9	-65.7
Br	33.8	53.8	-62.9
Cl	37.4	61.4	-59.9
F	53.1	86.2	-46.6

[a] Using the cc-pVTZ basis set. [b] Energy with reference to reaction product obtained via approach B.

Transition states of approaches A and B have different geometries (Scheme 25 and Figures 4 and 5). All transition states obtained via approach A are of C_s symmetry, except for phenylborylene and methylborylene. All transition states B are of C_1 symmetry. The distance between boron and hydrogen atoms in transition states A is shorter than in transition states B. The carbon-boron distance is shorter in transition states B, while the B-R bond is longer than in transition states of approach A.

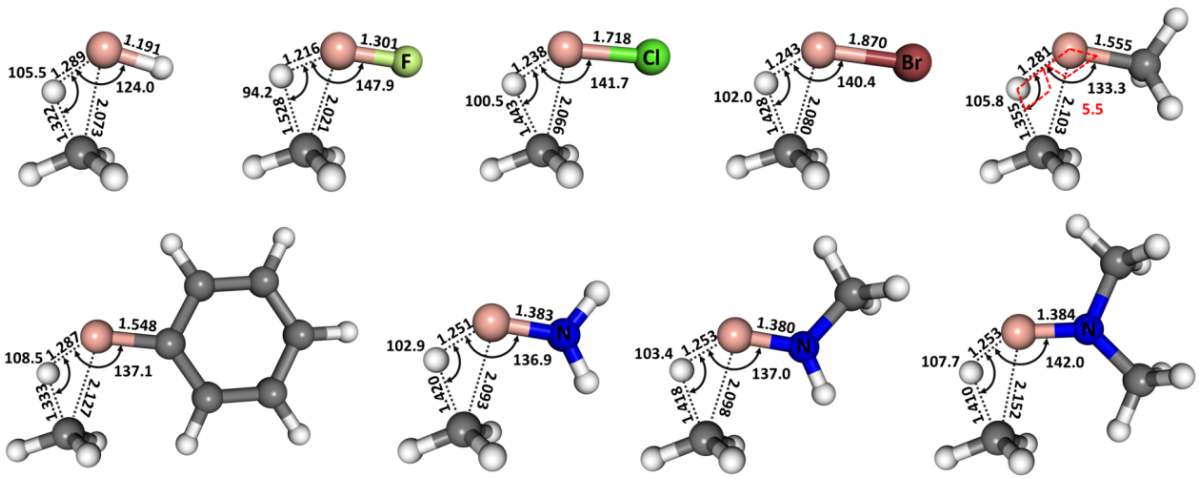


Figure 4. Geometries of the transition structures computed for the insertion of borylenes BR into a C–H bond of methane according to approach A at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

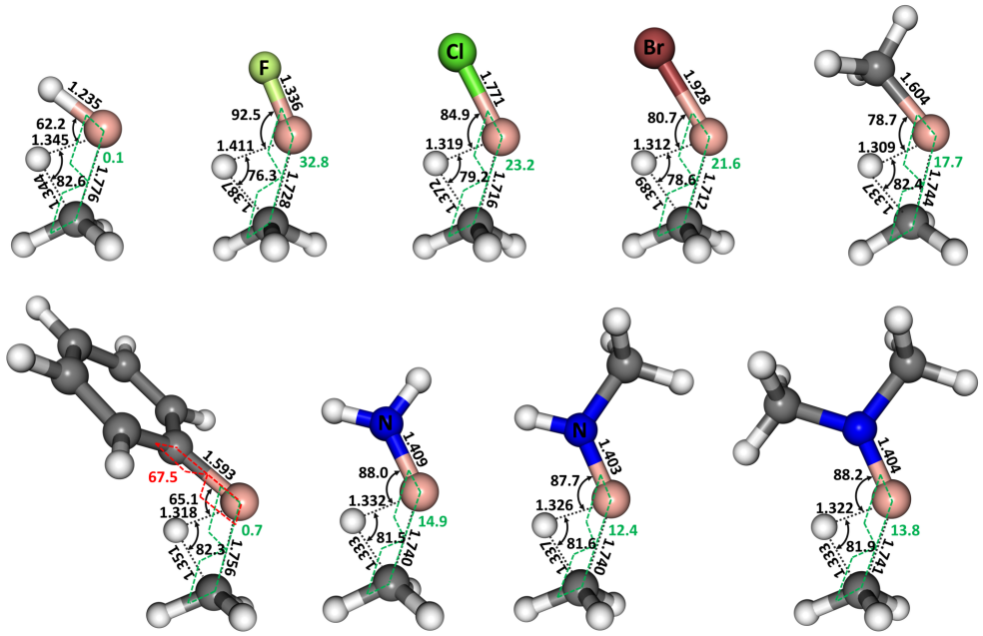
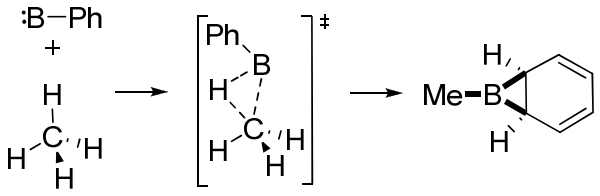


Figure 5. Geometries of the transition structures computed for the insertion of borylenes BR into a C–H bond of methane according to approach B at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

According to the IRC (intrinsic reaction coordinate) path computed at the MP2/cc-pVTZ level of theory the reaction of phenylborylene with methane according to approach B does not lead to methylphenylborane but to 7-methyl-7-boranorcaradiene (Scheme 26). Contrary to MP2 calculations, the IRC path computed at the B3LYP/6/-311+G** leads to the formation of the expected borane.



Scheme 26. Formation of 7-methyl-7-boranorcaradiene.

4.4 Van der Waals Complexes between Borylenes and Small Hydrocarbons

In addition to the transition states and products, van der Waals complexes corresponding to shallow minima on the potential energy surfaces can be found for the addition as well as for the insertion reactions examined in the proceeding section. This part concerns the borylene complexes with hydrocarbons involved in the aforementioned reactions. All of these complexes were found in the IRC profiles and their geometries were subsequently fully optimized at the SCS-MP2 level of theory.

4.4.1 Van der Waals Complexes of the Addition Reaction

Almost all van der Waals complexes in the addition reaction are of C_s symmetry (Figures 6 and 7) with binding energies in the range of 1-3 kcal/mol (Table 5). The borylene molecule only slightly affects the geometry of the hydrocarbon. The HC1C2 angle of ethyne is close to 180°. The B-C1 distances are longer than 3.3 Å. In the ethyne complexes borylene molecules shift in the direction of the hydrogen atom to possibly form a B···H interaction. The B···H distances are in the range of 2.8-3.2 Å (Figure 6). The least stable complexes are those involving the BF molecule, while the most strongly bound complexes are formed with aminoborylenes. This can be caused by the presence of the NH··π interaction in these complexes. Additionally, aminoborylenes form unusual complexes in which the borylene molecule is rotated by about 90° and is perpendicular to the organic substrate (Figure 8; these complexes are denoted as 'rotated' in the text and as '(rot)' in Tables 5 and 6) compared to regular complexes. These complexes arise from the pure NH··π interaction between borylene and the π system. Almost all of the rotated aminoborylene complexes are minima, except for the rotated $BNMe_2$-ethyne complex which is a first-order saddle point. All of the 'regular' aminoborylene-ethene complexes are also first-order saddle points. In the phenylborylene complex with ethene π··π stacking interaction dominates and borylene is twisted by about 42° with respect to the ethene molecule.

Table 5. Interaction energies (E_{rel} with respect to separated reactants in kcal/mol) of van der Waals complexes calculated at CCSD(T)/def2-QZVP//SCS-MP2/def2-QZVP (I) and CCSD(T)/aug-cc-pVTZ//SCS-MP2/def2-QZVP (II) level of theory.

Borylene	Method	Hydrocarbon			
		Ethyne	Ethene	Methane A	Methane B
BH	I			-0.9	-0.8
	II			-1.0	-1.0
BPh[a]	I	-1.8	-1.9	-1.5	-1.5
	II	-2.2	-2.4	-2.1	-2.0
BCH_3	I	-2.0	-1.5	-0.9	-0.8
	II	-2.1	-1.7	-1.0	-1.0
BBr	I	-1.2	-1.1	-0.7	-0.7
	II	-1.4	-1.3	-0.9	-0.9
BCl	I	-1.2	-1.0	-0.7	-0.6
	II	-1.4	-1.2	-0.9	-0.8
BF	I	-1.0	-0.9	-0.5	-0.5
	II	-1.2	-1.0	-0.7	-0.7
BNH_2	I	-2.7	-2.7	-1.1	-1.1
	II	-2.9	-3.0	-1.4	-1.3
BNH_2 (rot)	I	-2.8	-2.8		
	II	-3.1	-3.1		
BNHMe	I	-2.8	-2.8	-1.3	-1.3
	II	-3.1	-3.2	-1.6	-1.6
BNHMe (rot)	I	-2.8	-2.8		
	II	-3.2	-3.2		
$BNMe_2$	I	-2.8	-1.7	-0.9	-0.8
	II	-3.0	-2.0	-1.1	-1.0
$BNMe_2$ (rot)	I	-0.9	-2.1		
	II	-1.2	-2.4		

[a] energy calculated at the CCSD(T)/def2-TZVP//SCS-MP2/def2-QZVP level of theory.

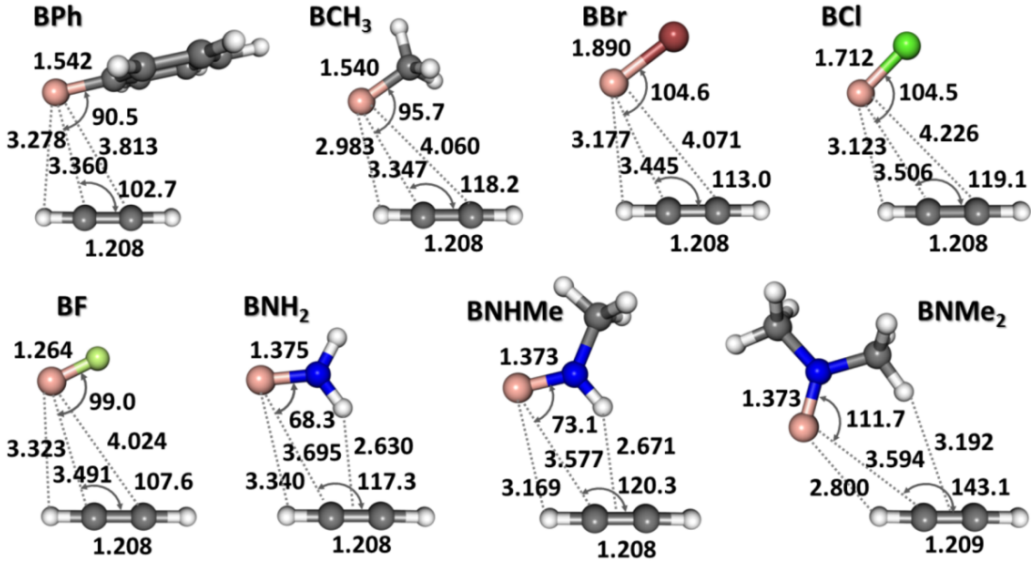


Figure 6. Geometries of borylene–ethyne complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths are given in Å, bond angles in degrees.

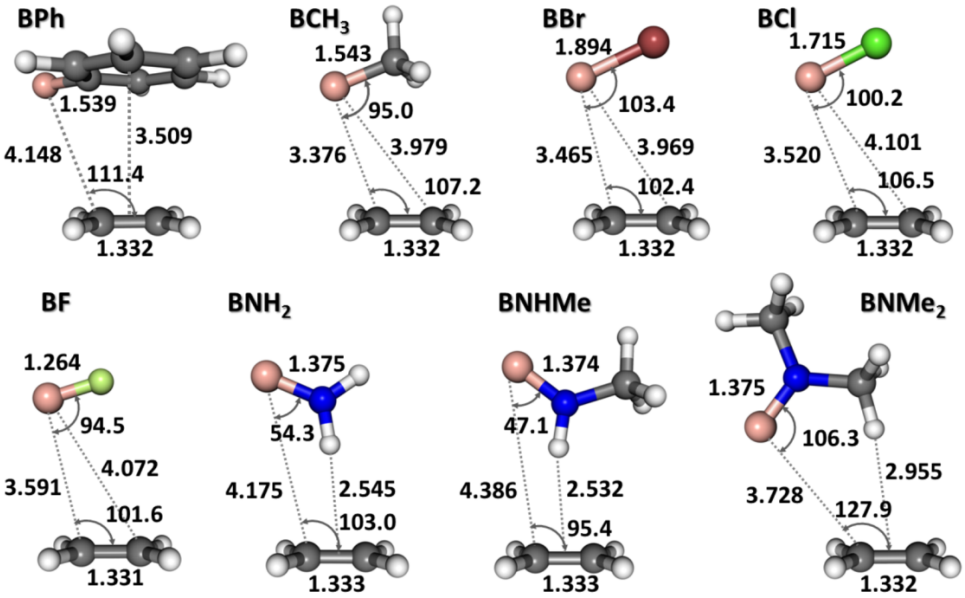


Figure 7. Geometries of borylene–ethene complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths are given in Å, bond angles in degrees. The depicted ethene–BNRR' complexes are saddle points.

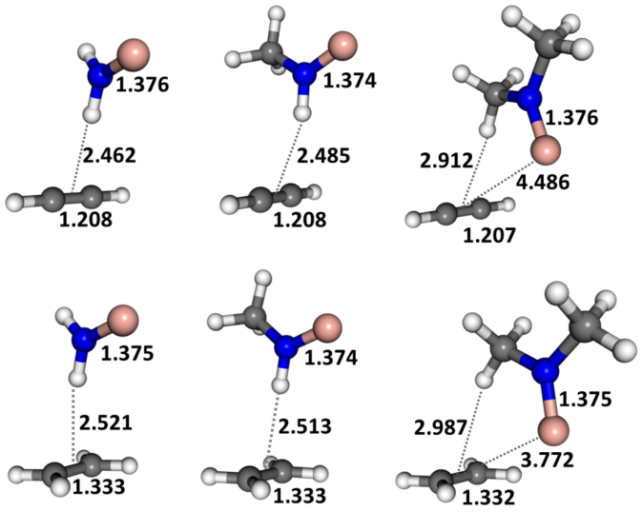


Figure 8. Geometries of other aminoborylene complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths are given in Å. All complexes except for ethyne–$BNMe_2$ are minima.

4.4.2 Van der Waals Complexes of the Insertion Reaction

Two types of van der Waals complexes of borylenes with methane were found (Figure 9). They differ by the orientation of the borylene towards the methane molecule. Almost all complexes B are of C_s symmetry and are saddle points. Exceptions are complexes of BNH_2 and BNHMe. Reduction of the symmetry produces the complexes A. Complexes of the insertion reaction are weaker than the ones found for the addition reactions and are stabilized by 0.7-2.1 kcal/mol relative to separate reactants (Table 5). The weakest are the complexes formed by haloborylenes. In the aminoborylene complexes the NH···C(methane) interaction

in present. CH···π interaction appears in phenylborylene complexes and most probably makes them energetically more stable than BH complexes.

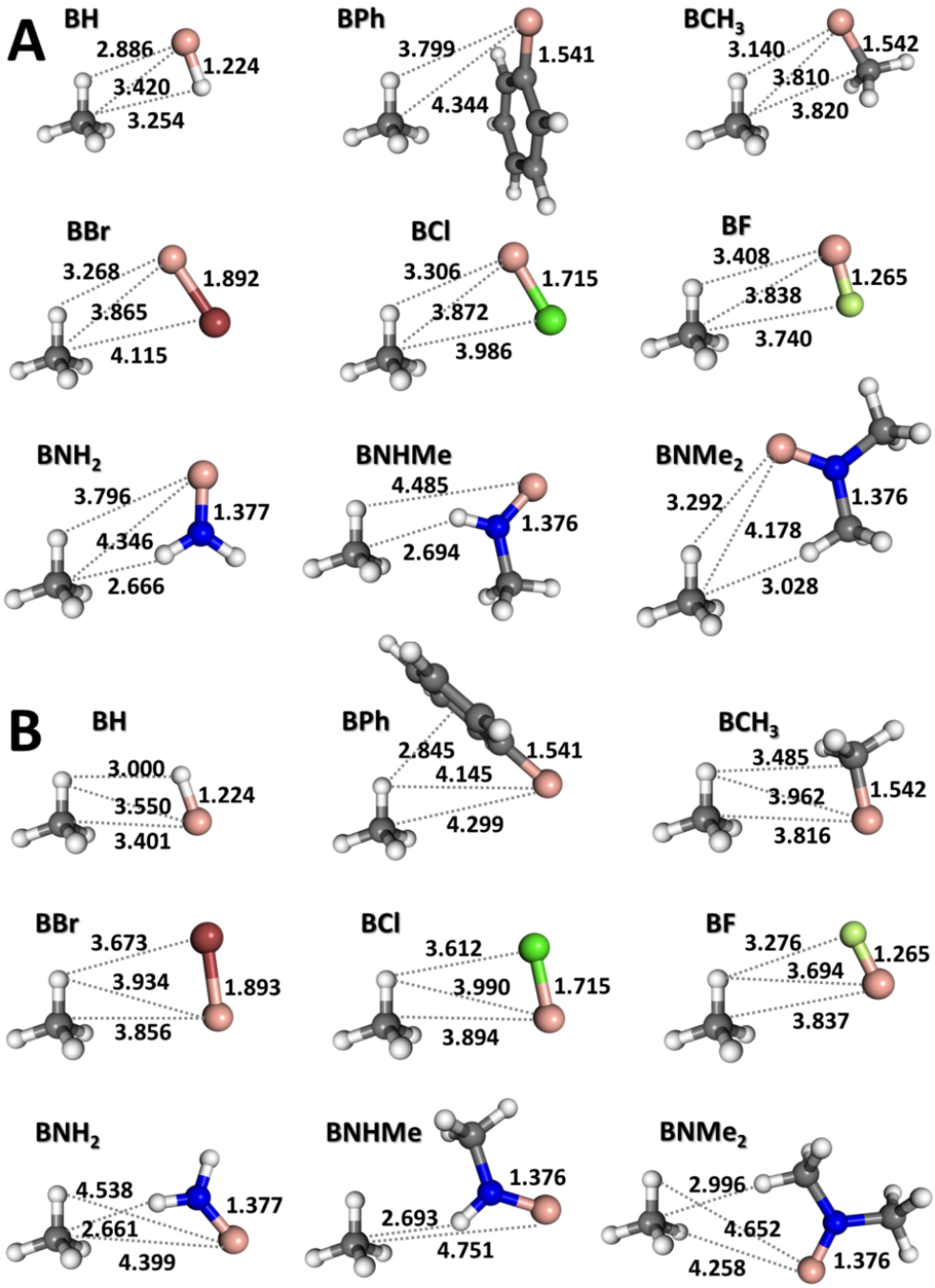


Figure 9. Geometries of borylene–methane complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths are given in Å.

4.4.3 Symmetry-Adapted Perturbation Theory (SAPT) Analysis

Symmetry-adapted perturbation theory allows to partition the interaction energy into the particular components which are the attractive electrostatic interaction energy (E_{elst}), induction (E_{ind}), and dispersion (E_{disp}), and the repulsive exchange interaction (E_{exch}). A detailed description of the SAPT method is given in the reviews by Szalewicz et al.[137, 138]

Table 6. Computed SAPT2+3 interaction energies (in kcal/mol) and their components. Computations were performed on the SCS-MP2/def2-QZVP geometries using aug-cc-pVTZ basis set.

Borylene	Ethyne					Ethene				
	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}^{SAPT}	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}^{SAPT}
BCH_3	-2.9	3.5	-0.7	-2.2	-2.3	-1.9	3.4	-0.7	-2.5	-1.7
BPh	-2.3	4.2	-0.6	-3.3	-2.1	-1.3	4.4	-0.4	-4.6	-1.9
BBr	-1.6	2.4	-0.5	-1.9	-1.6	-1.3	2.8	-0.5	-2.3	-1.3
BCl	-1.6	2.1	-0.4	-1.6	-1.5	-1.1	2.2	-0.4	-1.9	-1.2
BF	-1.4	1.8	-0.3	-1.3	-1.2	-1.0	1.6	-0.3	-1.3	-1.0
BNH_2	-3.3	3.5	-0.9	-2.2	-2.9	-3.2	3.9	-1.2	-2.2	-2.7
BNH_2 (R)	-3.6	4.0	-1.3	-2.1	-3.0	-3.4	4.1	-1.3	-2.3	-2.8
BNHMe	-3.4	3.8	-0.9	-2.5	-3.1	-3.2	4.1	-1.2	-2.6	-2.8
BNHMe (R)	-3.4	4.0	-1.1	-2.5	-3.0	-3.3	4.3	-1.3	-2.5	-2.8
$BNMe_2$	-3.8	4.0	-1.0	-2.4	-3.2	-1.9	2.9	-0.6	-2.3	-1.9
$BNMe_2$ (R)	-0.8	1.5	-0.3	-1.5	-1.1	-2.4	3.4	-0.6	-2.8	-2.4
Borylene	**Methane A**					**Methane B**				
	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}^{SAPT}	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}^{SAPT}
BH	-0.8	1.5	-0.4	-1.5	-1.0	-0.6	1.4	-0.3	-1.5	-1.0
BCH_3	-0.6	1.2	-0.2	-1.4	-1.0	-0.5	1.3	-0.2	-1.5	-0.9
BPh	-0.7	2.1	-0.2	-2.9	-1.6	-0.7	2.1	-0.2	-2.9	-1.6
BBr	-0.4	1.0	-0.1	-1.3	-0.9	-0.3	0.9	-0.1	-1.3	-0.8
BCl	-0.4	0.9	-0.1	-1.2	-0.8	-0.3	0.8	-0.1	-1.1	-0.7
BF	-0.3	0.6	-0.1	-0.8	-0.6	-0.3	0.5	-0.1	-0.8	-0.6
BNH_2	-0.8	1.3	-0.4	-1.3	-1.2	-0.8	1.3	-0.4	-1.3	-1.2
BNHMe	-0.7	1.4	-0.4	-1.8	-1.4	-0.7	1.4	-0.4	-1.7	-1.4
$BNMe_2$	-0.7	1.2	-0.2	-1.4	-1.1	-0.4	0.9	-0.2	-1.3	-0.9

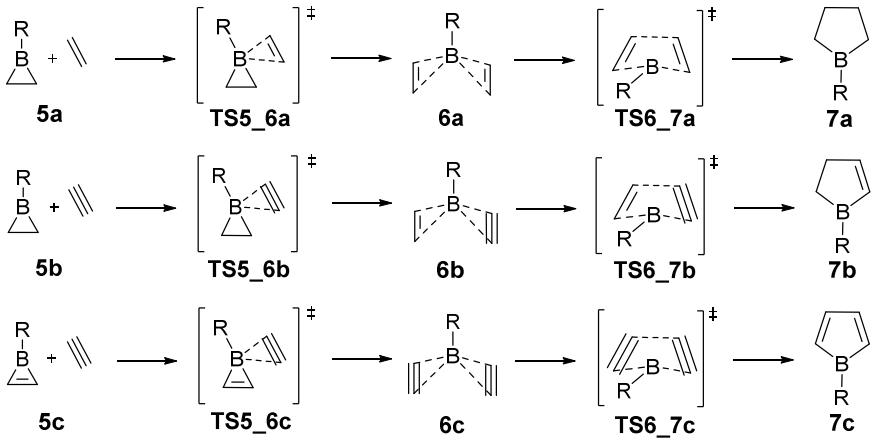
In almost all complexes formed by aminoborylenes with unsaturated hydrocarbons the electrostatic term has the largest contribution to the overall interaction energy. The exception is $BNMe_2$-ethene complex in which dispersion dominates (Table 6). In the haloborylene-ethyne complexes electrostatic and dispersive terms are almost equal. In the phenylborylene–ethyne complex dispersion interaction prevails. The dispersion energy has a greater contribution in all ethene complexes compared to ethyne complexes. Dispersion is the largest term in the overall interaction energies of organo- and haloborylene complexes with ethene. Induction is the smallest in all van der Waals complexes of the addition reactions. In methane

complexes the dispersion has the largest contribution to the attractive interaction. Induction, as in case of ethyne and ethene complexes, is the smallest component.

4.5 Reactions of Boriranes and Borirenes with Unsaturated Hydrocarbons

4.5.1 Ring Expansion Reactions

The reactions of three membered boron heterocycles (borirane and borirene) with unsaturated hydrocarbons (ethyne and ethene) are strongly exothermic (Table 7). These reactions are stepwise and proceed through unusual pentacoordinate boron intermediates (Scheme 27 and Figure 10A). Formation of most of the intermediates **6a** and **6b** involve very low (1 kcal/mol or less) or no barriers in case of the parent system (R = H). Exceptions are amino-substituted intermediates **6aNH$_2$** and **6bNH$_2$**. Barriers for their formation are about 11 kcal/mol and reactions are slightly endothermic. All transition states **TS5_6** (Figure 10B) are of C_s symmetry. The distances between the boron atom of borirane and carbon atoms of ethyne or ethene are in the range 2.15 – 2.65 Å.



Scheme 27. Reactions of boriranes and borirenes with ethene and ethyne.

Table 7. Energies of borirane reactions with ethyne and ethene relative to separate reactants (in kcal/mol) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory.

R	Borirane + ethyne					Borirane + ethene				
	vdW[a]	TS5_6b	6b	TS6_7b	7b	vdW[a]	TS5_6a	6a	TS6_7a	7a
F	-1.4	-0.6	-15.0	-14.5	-81.4	-1.4	-1.2	-14.4	-13.4	-61.9
Cl	-1.3	-0.1	-17.0	-15.9	-79.4	-1.5	-0.3	-17.4	-15.1	-59.4
H			-19.7	-17.6	-76.4			-21.3	-18.3	-56.0
Ph	-1.5	-0.1	-13.8	-12.9	-75.1	-2.2	-1.2	-16.0	-12.5	-55.2
Me	-1.8	-1.0	-14.1	-12.7	-75.3	-1.3	-0.7	-15.2	-13.6	-55.4
NH$_2$	-0.3	10.9	4.1	4.3	-74.5	-0.9	9.7	3.2	5.6	-56.0

[a] vdW refers to van der Waals complex formed between borirane and hydrocarbon.

Formation of intermediates **6c** in the reaction of borirenes with ethyne is endothermic. The reaction barriers are ranging from 13 (BF) to 18 (BCH_3) kcal/mol (Table 8). Intermediate **6c** with the amino group does not form upon the addition of ethyne. The **TS5_6c** of aminoborirene leads directly to aminoborole **7c** and the reaction with a barrier of 28 kcal/mol is strongly exothermic. Almost all transition states **TS5_6c** are of C_s symmetry with the exception of aminoborirene **TS5_6c** which is of C_1 symmetry.

Transition states **TS6_7** (Figure 10C) connect intermediates **6** with the five membered ring products **7**. The barriers for formation of **7** are very low (2 kcal/mol or less). Ring closure reactions are highly exothermic.

Table 8. Energies of borirene reactions with ethyne relative to separate reactants (in kcal/mol) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory.

R	vdW[a]	TS5_6c	6c	TS6_7c	7c
F	-0.4	12.5	10.6	10.3	-63.6
Cl	-1.1	12.9	9.8	10.2	-59.9
H	-0.2	13.7	12.3	13.4	-51.3
Ph	-0.7	15.2	12.7	13.5	-56.0
CH_3	-1.1	17.2	16.2	16.5	-53.7
NH_2	-1.7	26.3			-65.9

[a] van der Waals complex formed between borirene and ethyne

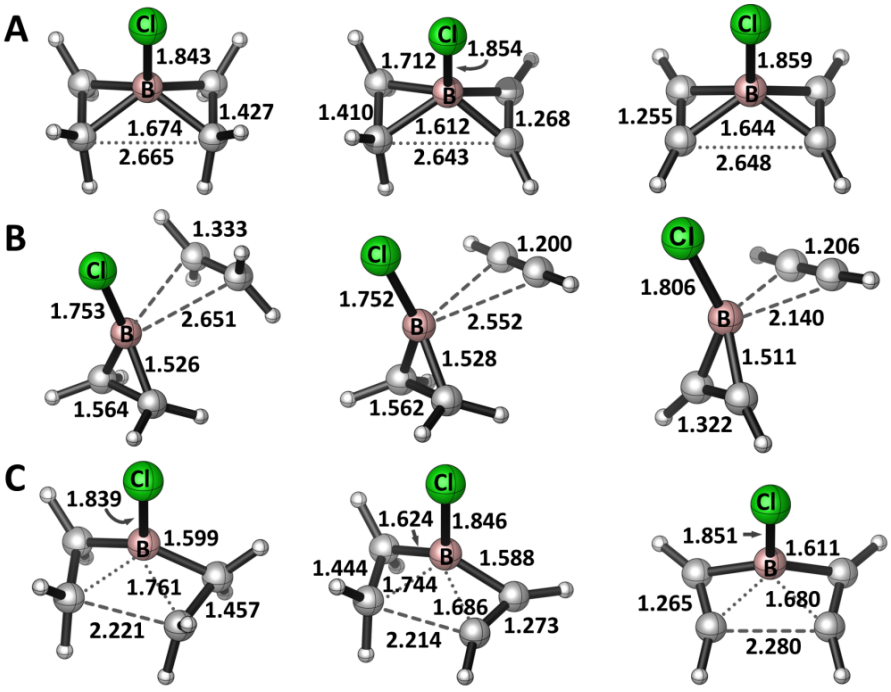
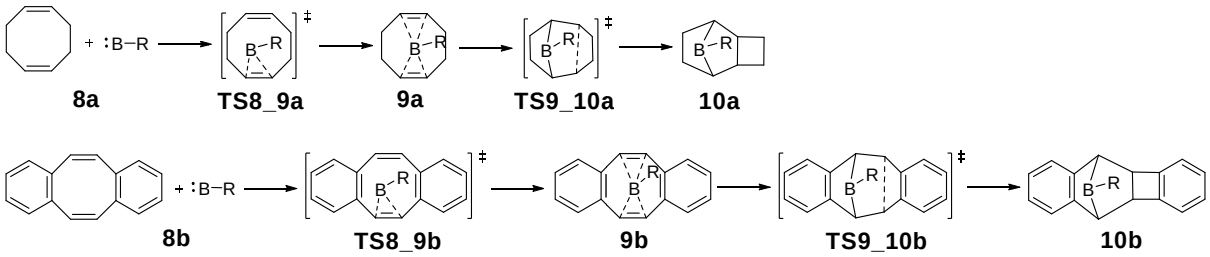


Figure 10. Optimized geometries (M06-2X/6-311+G**) of chloro-substituted intermediates **6** (A), transition states **TS5_6** (B), and **TS6_7** (C). Important distances are given in Å.

4.5.2 Reactions of Borylenes with Olefins

Intermediates **6** are shallow minima on the potential energy surfaces and are expected to be not detectable directly in experiments. The analogs of intermediate **6** could be formed, for instance, in the reaction of borylenes with dibenzo[*a*,*e*]cyclooctatetraene (DBCOT) or 1,5-cyclooctadiene (COD) (Scheme 28).



Scheme 28. Reactions of borylenes with 1,5-cyclooctadiene (top) and dibenzo[*a*,*e*]cycloocta-tetraene (bottom).

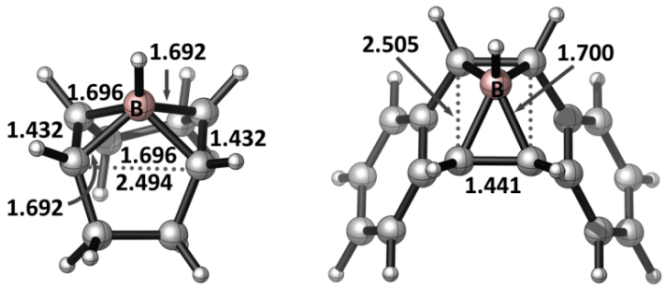


Figure 11. Computed geometries (M06-2X/6-311+G**) of intermediates **9aH** (left) and **9bH** (right). Important bond lengths and distances are given in Å.

The barriers for the formation of intermediates **9** do not exceed 5 kcal/mol (Table 9) and the reactions are highly exothermic. The structures of intermediates **9** are similar to that of intermediates **6**. Barriers for the cyclization of intermediates **9** to products **10** are considerably higher (10-16 kcal/mol) than the barriers for the formation of products **7**. The ring closure is endothermic for the reaction with DBCOT with the exception of amino derivative. The intramolecular cyclization of parent intermediate **9aH** is also endothermic. Heightened barriers for the cyclization to product **10**, compared to the formation of **7**, is most probably caused by the presence of strained four membered ring in the structure of **10**.

Table 9. Energies relative to separate reactants (in kcal/mol) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for the reactions of borylenes with COD and DBCOT.

R	Olefin	TS8_9	9	TS9_10	10
Cl	COD	3.5	-65.4	-54.4	-67.6
	DBCOT	3.9	-65.6	-51.1	-60.9
H	COD	not found	-90.5	-78.2	-85.3
	DBCOT	not found	-90.8	-74.3	-81.6
Me	COD	-0.1	-77.6	-67.7	-78.6
	DBCOT	0.0	-78.7	-65.4	-73.9
NH_2	COD	5.0	-51.8	-42.7	-72.9
	DBCOT	4.6	-53.9	-41.4	-66.1

4.5.3 Structure and Bonding of Intermediates 6

The CC bonds in parent **6aH** and **6cH** are elongated by about 0.1 Å compared to free hydrocarbons and are shorter by roughly 0.1 Å than in borirane or borirene. The B-C distances are in the range of 1.67-1.69 Å and are longer than in borirane (1.53 Å) or borirene (1.47 Å). The angle between the HCH plane and the C-C bond in **6aH** is smaller (22.9°) than in the corresponding borirane (33.6°). Similarly, the CCH angle in intermediate **6cH** (30°) is smaller than in borirene (41.2°). The HOMO of **6aH** and **6cH** involves the p orbital of boron and π* orbitals of the hydrocarbons (Figure 12). The LUMO comprises only antibonding π* orbitals of the hydrocarbons.

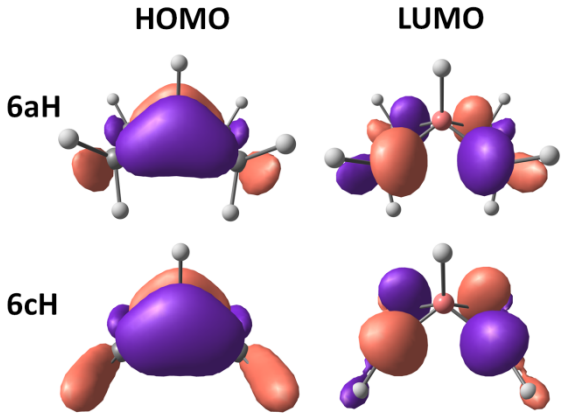
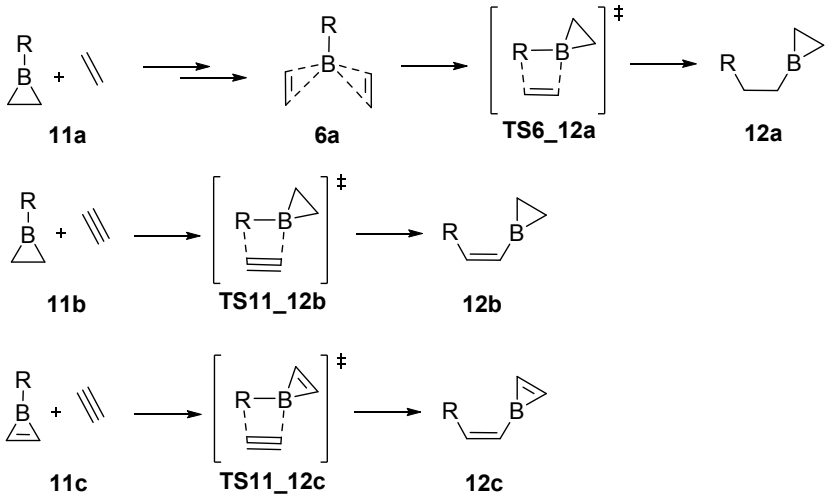


Figure 12. Frontier molecular orbitals of **6aH** and **6cH** computed at the M06-2X/6-311+G** level of theory.

4.5.4 Boration Reaction

In addition to the ring expansion reactions of three membered boron heterocycles, boration reactions of boriranes and borirenes were studied. The structures of transition states for boration of unsaturated hydrocarbons with boriranes or borirenes (Scheme 29 and Figure 13) resemble the structures of hydroboration of olefins with boranes.[221] In transition states **TS11_12** and **TS6_12** the B-R bond is parallel to the hydrocarbon (Figure 13).



Scheme 29. Schematic representation of boration reactions.

Boration of ethene by borirane starts with the intermediate **6a**, while in case of boration of ethyne, either by borirane or borirene, a van der Waals complex is formed in the first stage of the reaction. The formation of boration products **12** is exothermic in most cases (Table 10). Boration of ethyne by borirane has the lowest barriers, although the reaction barriers of boration are much higher than the barriers for the ring enlargement to product **7**. Owing to high reaction barriers, boration reactions are unlikely to take place.

Table 10. Reaction energies (with respect to separate reactants) in kcal/mol calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for boration (see Scheme 29).

R	Borirane + ethene			Borirane + ethyne			Borirene + ethyne		
	6a	TS6_12a	12a	vdW[b]	TS11_12b	12b	vdW[c]	TS11_12c	12c
H	-21.3	0.7	-31.9	-19.7*	4.9	-46.1	-0.1	34.6	-42.8
Cl	-17.4	19.6	1.5	-1.1	15.2	-13.1	-1.1	31.3	-14.6
Me	-15.2	25.1	-19.7	-0.9	22.5	-36.5	-0.2	48.9	-34.9
NH_2	-0.5	33.3	14.0	-0.7	31.1	-14.1	-1.5	40.0	-18.3

*starts with intermediate **6b**.

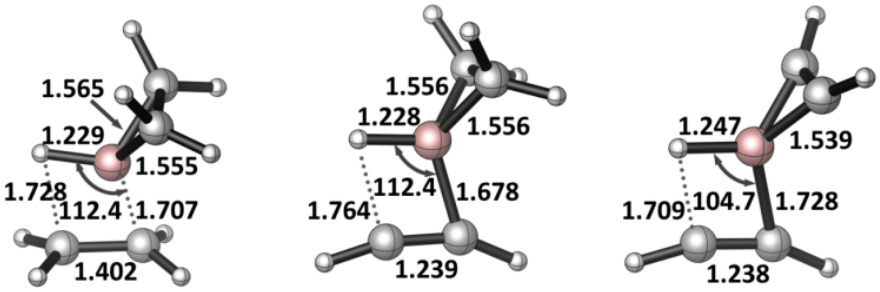
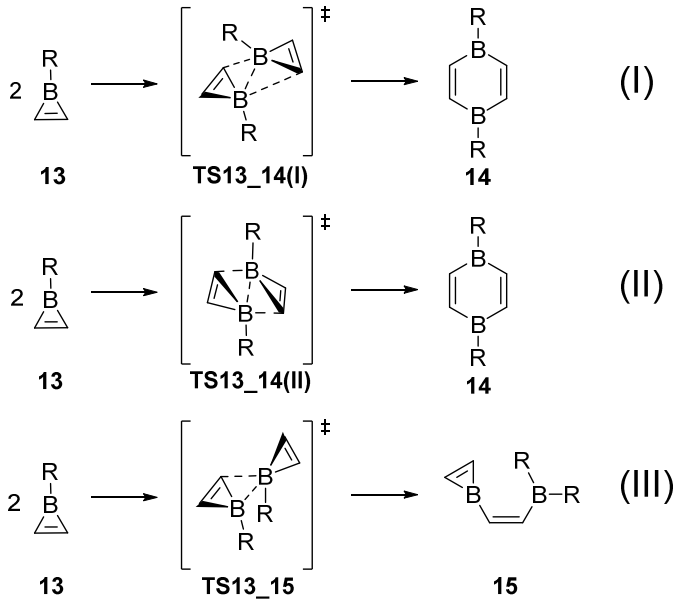


Figure 13. Optimized geometries (M06-2X/6-311+G**) of transition states **TS6_12aH** (left), **TS11_12bH** (middle), and **TS11_12cH** (right). Important distances are given in Å

4.6 Dimerization of Borirenes and Boriranes

Borirane and borirene were suggested by Timms to be possible intermediates in the formation of 1,4-dibora-2,5-cyclohexadienes and 1,4-dibora-2,5-cyclohexanes in his experiments with haloborylenes and unsaturated hydrocarbons.[7, 8] The dimerization of parent borirene was first studied by Schleyer and coworkers by computational means.[82]



Scheme 30. Dimerization pathways of borirenes.

Following Schleyer et al.,[82] computational investigations of the dimerization mechanism of chloro- and fluoroborirene, and of parent borirene as reference, were performed. Three low-energy pathways were identified (Scheme 30). In two of them (path I and II) 1,4-dibora-2,5-cyclohexadiene **14** is produced, as expected, while the third path is a boration reaction. The reaction barriers of all studied pathways are moderately high, ranging from 10.5 to 18.5 kcal/mol (Table 11). Computed transition states are of C_1 symmetry and resemble the structures obtained by Schleyer and coworkers (Figure 14). Path II is energetically favored, but boration is competitive.

Table 11. Energies relative to separate reactants (in kcal/mol) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for dimerization of borirenes (see Scheme 30 for pathways).

R	Path I		Path II		Path III	
	TS13_14(I)	14	TS13_14(II)	14	TS13_15	15
H	16.4	-55.7	10.7	-55.7	12.1	-27.7
Cl	18.5	-74.1	12.8	-74.1	16.7	-39.8
F	14.3	-81.2	10.5	-81.2	14.4	-52.6

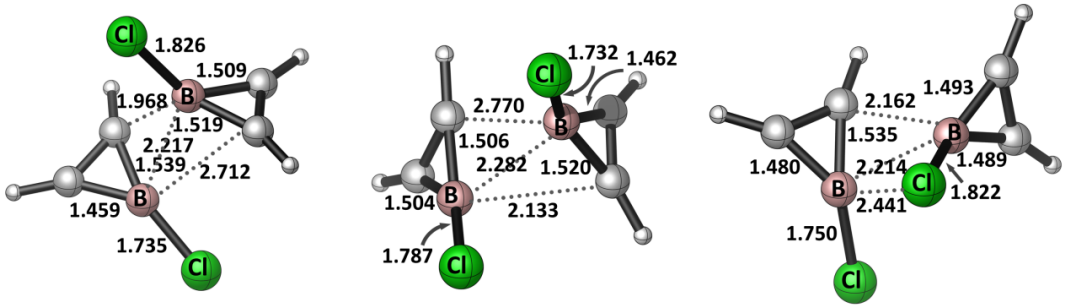
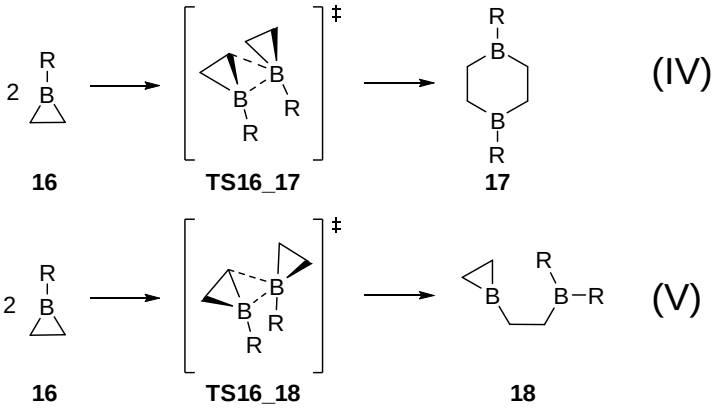


Figure 14. Optimized geometries (M062X/6-311+G**) of transition states **TS13_14(I)** (left), **TS13_14(II)** (middle), and **TS13_15** (right) formed by chloroborirene. Important distances are given in Å.

Additionally, dimerization reactions of boriranes were investigated for the first time. Two low-energy pathways were located (Scheme 31). Path IV leads to the formation of 1,4-dibora-2,5-cyclohexane, while the path V is a boration reaction. The structures of transition states of path IVand V (Figure 15) are similar to the transition states of path II and III found for dimerization of borirenes. Both types of borirane dimerization have extremely low barriers and dimerization of parent borirane to diboracyclohexane (path IV) proceeds without barrier (Table 12). The reaction energies are significantly more exothermic for dimerization of boriranes to diboracyclohexane than those of boration.



Scheme 31. Dimerization pathways of boriranes.

Table 12. Energies relative to separate reactants (in kcal/mol) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for dimerization of boriranes (see Scheme 31 for pathways).

R	Path IV			Path V		
	vdW^{IV}	TS16_17	17	vdW^{V}	TS16_18	18
H			-77.7	-1.9	-2.5	-38.8
Cl	-1.3	-0.6	-86.2	-1.9	0.1	-46.3
F	-1.0	-1.0	-92.1	-1.4	0.5	-57.3

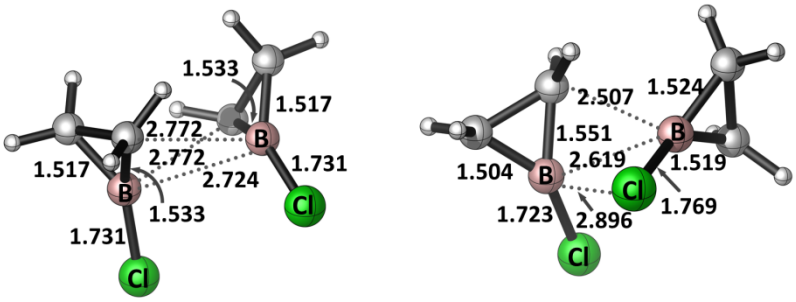


Figure 15. Optimized geometries (M06-2X/6-311+G**) of transition states **TS16_17** (A) and **TS16_18** (B) formed by chloroborirane. Important distances are given in Å.

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Reactivity of Borylenes toward Ethyne, Ethene, and Methane

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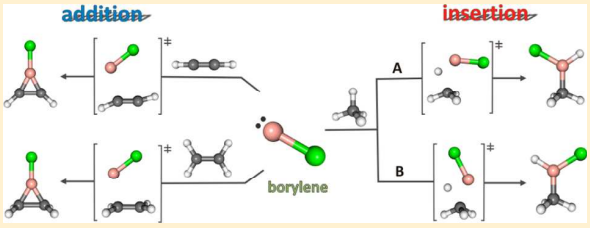
Supporting Information

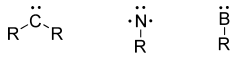
ABSTRACT: The electronic and geometric structure of various substituted borylenes BR (where R = H, F, Cl, Br, CH_3, Ph, NH_2, NHMe, and NMe_2) in their lowest singlet and triplet electronic states was investigated by computational means using hybrid density functional (B3LYP) and second-order Møller−Plesset perturbation theories combined with 6-311+G** and cc-pVTZ basis sets. The reactivity of singlet borylenes towards prototypical saturated and unsaturated hydrocarbons was examined by the MP2 method in conjugation with the cc-pVTZ basis set and also by coupled cluster [CCSD(T)] computations in combination with the aug-cc-pVTZ basis set. To study the energetics and the mechanism of the addition reaction of borylenes to unsaturated CC bonds, ethyne and ethene are chosen as model compounds. The insertion reaction of borylene into a C−H bond of methane was also investigated. The addition reactions of borylenes to multiple C−C bonds are strongly exothermic. In case of the BH molecule the reactions proceed without barrier and are the most exothermic. For the insertion reaction of borylenes into methane, two approaches could be identified. Again, the smallest reaction barriers and highest reaction energies were computed for the BH insertion, while the highest barriers and the smallest exothermicities were obtained for the BF molecule. On the basis of frontier molecular orbital energies, barrier heights, reaction energies, and transition state geometries BH is the most electrophilic borylene, followed by BPh, while aminoborylenes and BF are the most nucleophilic ones among the investigated derivatives. Accordingly, reactions of BH have the smallest barriers (if there is one at all) and the largest reaction energies, while the reactions of BF have the highest barriers and the smallest reaction energies.



1. INTRODUCTION

Neutral subvalent compounds of carbon and nitrogen, carbenes **1** and nitrenes **2**, are seminal reactive intermediates in organic chemistry. Their chemistry is well developed and summarized in numerous reviews and monographs.[1,2]

Chart 1



1 **2** **3**

The boron analogues of **1** and **2** are sometimes called borenes or boranediyls, but more commonly borylenes **3**. Similarly to **1** and **2**, free borylenes **3** are rather rare reactive intermediates. Seminal work by Timms in the 1960s has shown that BF formed by passing BF_3 over hot boron is readily reacting with alkynes.[3,4] The high-temperature reaction between BX_3 and boron was used to prepare a number of borylenes (X = H, F, Cl, Br, I) in the gas phase and to study their structure by microwave spectroscopy. Since then, occasional trapping reactions of borylenes have been reported. These involve the 1984 photogeneration of triphenylsilylborylene Ph_3SiB from $(Ph_3Si)_3B$ in organic glasses. Although it was not possible to observe the borylene directly by spectroscopy in this experiment, the reaction products isolated after warming the glass matrix to room temperature are in support of a transient borylene. In the absence of a trapping agent, the borylene inserts into the tertiary CH bond of glass forming 3-methylpentane or into the C−O bond of tetrahydrofuran. Photolysis in the presence of bis(trimethylsilyl)ethyne results in isolation of the corresponding borirene at room temperature.[5] Grigsby and Power concluded in their 1996 study of the metal reduction of arylboron dihalides with bulky substitution at the ortho positions of the phenyl ring that an intermediate borylene underwent intramolecular insertion into C−C σ bonds.[6] Similarly, reduction of chloroborane derivatives stabilized by N-heterocyclic carbenes (NHC) resulted in trapping products that were ascribed to result from NHC-stabilized borylenes that undergo C−H insertion reactions or [2 + 1] cycloaddition.[7−9] The barrier for the cycloaddition of BH•NHC to naphthalene was computed to be 2.6 kcal mol^{-1} using the B3LYP functional.[7] However, an alternative mechanism has recently been suggested to account for the trapping with naphthalene.[10] Ito et al. invoked the borylene TbtB (Tbt: 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) as a transient intermediate in the photoreaction of $TbtB(SeMe)_2$ with benzil and phenanthrenequinone that produced the boronic ester of 9,10-dihydroxyphenanthrene in both cases.[11] Very recently, a NHC-stabilized borylene was suggested as an intermediate in the photochemical isomerization of C,C-chelate $BMes_2$.[12]

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Stabilizing borylenes is possible either by transition metal centers or by nucleophilic carbenes. The transition metal chemistry of borylenes is well developed and a number of reviews are available.[13−18] Some of these complexes can be used for photochemical transfer of the borylene ligand onto organic substrates providing a convenient access to borirenes,[19−21] or 1,4-diboracyclohexadiene and 1,4-dibora-1,3-butadiene complexes.[22] Nucleophilic carbenes have also been used successfully to stabilize borylenes. While one NHC does not result in an isolable NHC-stabilized BH molecule,[7−9] use of two cyclic (alkyl)(amino)carbenes (CAAC) allowed isolation of $(CAAC)_2BH$.[23,24]

Direct spectroscopic observations of free organoborylenes BR are scarce: Andrews et al. observed by IR spectroscopy ethynylborylene formed by codeposition of boron atoms and ethyne in an argon matrix at 15 K.[25] More recently, one of us reported that the photoinduced decomposition of diazidophenylborane $PhB(N_3)_2$ yields inter alia phenylborylene that could be identified by comparison of its IR spectrum (and that of its $[D]_5$ isotopomer) with the computed vibrational spectra.[26] Phenylborylene was found to undergo photochemically induced insertion into an ortho-CH bond of the phenyl ring to give benzoborirene.[26]

The reactivity summarized above for borylenes BR is in line with expectations based on carbene chemistry. However, details of the reaction mechanisms, exothermicities of borylene reactions and barrier heights are not known. This prompted us to investigate by computational means (i) the influence of substitents [R = H, F, Cl, Br; R = CH_3; R = Ph; R = NH_2, $NHCH_3$, $NH(CH_3)_2$] on the electronic structure of borylenes BR, and (ii) the mechanisms for the reactions of these borylenes toward ethyne, ethene, and methane as prototypical representatives of alkynes, alkenes, and alkanes. The variation of frontier orbital energies, singlet/triplet energy splitting, exothermicities, barrier heights, and transition state geometries is discussed in terms of the change of philicity of the borylene.

2. COMPUTATIONAL DETAILS

The computations of HOMO/LUMO energies of borylene employed the B3LYP[27,28] hybrid density functional as implemented[29] in Gaussian 09[30] in combination with 6-311+G**[31] basis set. In addition, second-order Møller−Plesset perturbation theory (MP2)[32] was employed to optimize minima and transition structures using 6-311+G** and cc-pVTZ[33] basis sets. Harmonic vibrational frequencies were computed analytically and confirmed the nature of the stationary points as minima, or first or higher order saddle points. Energies were refined using coupled cluster theory employing singles, doubles and a perturbative estimate of triples excitations [CCSD(T)][34] in conjunction with cc-pVTZ and aug-cc-pVTZ[33] basis sets. The frozen core approximation was applied in MP2 and CCSD(T) calculations. Unscaled zero-point vibrational energy (ZPE) corrections from MP2/cc-pVTZ frequency calculations were included. Additionally, intrinsic reaction coordinate (IRC)[35,36] paths were calculated at the MP2/6-311+G** level of theory for each reaction. All energies were calculated relative to separated reactants.

3. RESULTS AND DISCUSSION

3.1. Geometry and Electronic Structure of Borylenes.

The electron lone pair of borylenes is best described by an sp orbital (see Figure 1). This comprises the highest occupied molecular orbital (HOMO) of borylenes. In addition, two empty p orbitals are available at boron, and these form a doubly degenerate set of lowest unoccupied molecular orbitals (LUMO and LUMO+1) in borylenes of $C_{\infty v}$ and C_{3v} symmetry. Therefore, the triplet state is $^3\Pi$ for these borylenes. For BCH_3 this state will be unstable with respect to a Jahn−Teller distortion into a $^3A'$ and a $^3A''$ state. While the latter is a minimum, the former is a first order saddle point that is 0.3 kcal mol^{-1} higher in energy at the B3LYP/6-311+G** level of theory. At lower symmetry (C_{2v} or C_s for R = Ph, NRR′), the degeneracy is lifted due to interaction with the substituent R. Two distinct triplet states are therefore available ($^3B_1$ and $^3B_2$ in C_{2v}, $^3A''$ and $^3A'$ in C_s, respectively), and their energetic order depends on the nature of the substituent (vide infra).[37]

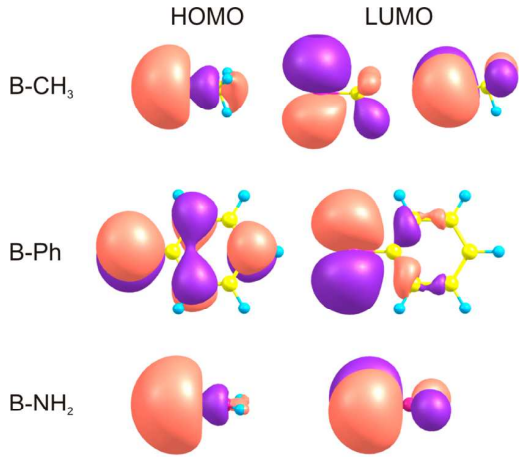


Figure 1. Molecular orbitals of borylenes in their singlet ground state as computed at the B3LYP/6-311+G** level of theory.

For several diatomic borylenes experimental bond lengths are available for their singlet states. The experimental r_e values compare reasonably well with the computed bond lengths (Table 1). The differences between experiment and theory are 0.015 Å or smaller. It should be noted that better agreement with experiment has been achieved previously using higher level CCSD(T) computations. Such computations are computationally very demanding for the larger borylenes and not deemed necessary as the present investigation aims at elucidating trends among substituted borylenes investigated here.[38]

Comparing the B−R bond distances of the lowest energy triplet states with the corresponding singlet states, it is observed that the bonds are shorter in the high spin states for all but two cases (Tables 1 and 2). These are BF and BCH_3.

In carbene chemistry, the concept of carbenic philicity is well established.[42−44] Depending on the substituents, the philicity can change from electrophilic over ambiphilic to nucleophilic. Inductively withdrawing substituents with free electron pairs (−I, +M), such as OR, NR_2, stabilize the singlet relative to the triplet state and enhance the nucleophilic character of the carbene.

Typical nucleophilic carbenes are dimethoxycarbene $C(OMe)_2$ and the diaminocarbenes $C(NR_2)_2$, including N-heterocyclic carbenes. As in borylenes only one position is available for substitution, a similarly strong stabilizing effect of +M substitutents as in carbenes is not expected. Yet, the behavior of borylenes BR is expected to parallel that of carbenes CR_2. One theoretical measure for carbene philicity is the energy of the frontier molecular orbitals (FMO). These were successfully used for rationalizing experimentally derived carbene selectivity indices m_{CXY}. Following common practice the FMO energies of the borylenes BR (Table 3) were

Table 1. Comparison of Computed and Experimental B–R (R = H, F, Cl, Br) Bond Distances (in Å) in Borylene Molecules in Their Lowest Energy Singlet (S) and Triplet (T) States

method	BH		BF		BCl		BBr	
	S	T ($^3\Pi$)	S	T($^3\Pi$)	S	T($^3\Pi$)	S	T($^3\Pi$)
B3LYP/6-311+G**	1.235	1.193	1.271	1.321	1.730	1.718	1.908	1.874
MP2/6-311+G**	1.230	1.187	1.273	1.324	1.710	1.710	1.890	1.866
MP2/cc-pVTZ	1.227	1.184	1.268	1.317	1.717	1.709	1.883	1.854
exp.[a]	1.232[b]		1.263[c]		1.715_9		1.888_2	

[a] r_e values taken from NIST Chemistry WebBook[39] unless noted otherwise. [b] r_e value taken from Fernando et al.[40] [c] r_e value taken from Cazzoli et al.[41]

Table 2. Comparison of Computed and Experimental B–R (*R* = C, N) Bond Distances (in Å) in Borylene Molecules in Their Lowest Energy Singlet (S) and Triplet (T) States at the B3LYP and MP2 Levels of Theory

method	BCH_3		BPh		BNH_2		BNHMe		$BNMe_2$	
	S	T ($^3A''$)	S	T ($^3B_1$)	S	T ($^3B_2$)	S	T ($^3A'$)	S	T ($^3B_2$)
B3LYP[a]	1.534	1.549	1.534	1.481	1.377	1.372	1.375	1.368	1.375	1.370
MP2[a]	1.545	1.559	1.547	1.513	1.384	1.383	1.383	1.379	1.383	1.380
MP2[b]	1.541	1.553	1.542	1.507	1.380	1.378	1.379	1.375	1.381	1.376

[a] 6-311+G**. [b] cc-pVTZ basis set.

computed at the B3LYP level of theory in conjunction with the 6-311+G** basis set.

Table 3. Molecular Orbital Energies (in eV), HOMO-LUMO Gap (in eV), and Singlet–triplet Energy Splitting (ΔE_{ST}, in kcal mol^{-1}) Computed at the B3LYP/6-311+G Level of Theory for Borylene Molecules B–R**

R	HOMO	LUMO	LUMO+1	$Gap_{H\text{-}L}$	ΔE_{ST}	state
H	−6.52	−2.62	−2.62	3.90	26.0	$^3\Pi$
F	−7.91	−1.47	−1.47	6.44	77.7	$^3\Pi$
Cl	−7.38	−2.17	−2.17	5.21	54.5	$^3\Pi$
Br	−7.31	−2.38	−2.38	4.93	50.1	$^3\Pi$
CH_3	−6.02	−1.66	−1.66	4.36	37.3	$^3A''$
Ph	−5.85	−2.48	−1.67	3.37	31.5	$^3B_1$
NH_2	−6.24	−1.50	−0.44	4.74	44.8	$^3B_2$
NHMe	−6.04	−1.45	−0.20	4.59	44.0	$^3A'$
NMe_2	−5.93	−1.23	−0.18	4.70	45.3	$^3B_2$

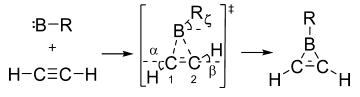
Compared to BH, the electronegativity of the fluorine atom results in a decrease of the HOMO energy: the B–F bond has an increased B(p) character and consequently the B(s) character of the lone pair at boron is increased. The energy of the LUMO is increased due to interaction with the lone pairs of fluorine. From fluorine to bromine, the HOMO energies increase while the LUMO energy drops, as expected. In the aminoborylenes the HOMO and LUMO energies are increased due to antibonding interaction with the fragment orbitals of the π donating NR_2 groups. The methyl group results in a significant upshift of the LUMO that is antibonding between B(p) and CH_3 fragment orbitals due to the electron-donating ability of CH_3 by hyperconjugation. However, the phenyl group only has a small influence on the LUMO energy. It shows a bonding interaction between the B(p) orbital and a π^* orbital of the phenyl ring. Thus, BPh has the second lowest LUMO energy among the borylenes investigated. On the basis of the FMO data, the BH followed by BPh are expected to be the most electrophilic borylenes, while BF is the one with the highest nucleophilic character.

The singlet–triplet energy splitting (ΔE_{ST}) of BH has previously been determined experimentally to 29.8 kcal mol^{-1} in favor of the singlet state.[45] The value (26 kcal/mol) computed at the B3LYP/6-311+G** underestimates this gap somewhat, but the accuracy is sufficient for analysis of the substituent effect on ΔE_{ST} (see Table 3). The singlet–triplet energy gap changes as expected. It increases to 78 kcal mol^{-1} for BF. In the halide series, ΔE_{ST} decreases from F to Br, similar to the behavior that is well established for the related carbenes. The aminoborylenes have ΔE_{ST} values that are larger than in BH but smaller by ca. 5 kcal mol^{-1} than in BBr.

Still smaller ΔE_{ST} values are computed for the organyl substituted borylenes. A ΔE_{ST} of 37 kcal mol^{-1} results for BCH_3 and this indicates that the hyperconjugative interaction favors the singlet more than the triplet state by roughly 11 kcal mol^{-1}. In the BPh molecule the degeneracy of the two p orbitals at boron is lifted due to overlap with the π system. The B(p_z) orbital of b_1 symmetry is lower in energy, and the $^3B_1$ state is preferred over the $^3B_2$ state (note that the HOMO is of a_1 symmetry). The singlet–triplet gap is only 32 kcal mol^{-1}, indicating that the phenyl ring results in the least stabilization of the singlet state among the substituents studied. Again, this finding is in agreement with the established trends in carbene chemistry.[46]

3.2. Reactivity of Borylenes. As mentioned in the preceding sections, we attempted to examine by computational means the reactivity of various substituted borylenes toward saturated and unsaturated hydrocarbons. Intramolecular reactions of BCH_3 and BNH_2 were studied previously.[47] In this part we give insight into the mechanisms of the reactions and describe the dependence of the energetics on the substitution pattern. Here we focus on the philicity of borylenes, also in terms of the geometry of transition states for addition reactions following earlier analyses for carbenes by Houk et al.[48] As in the case of carbene cycloaddition, the tilt angle ζ (see Schemes 1 and 2) is an important geometrical parameter reflecting the philicity of borylene. For the ideal

Scheme 1. Mechanism of Borylene Addition to Ethyne



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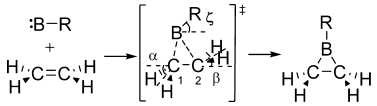
Scheme 2. Schematic Representation of Addition of Borylene to Ethene



nucleophile this angle would equal 90° and in case of ideal electrophile this angle would be 0°. The distortion of hydrogen atoms of ethyne (ethene) from linearity (planarity) in the transition state (given as α and β angles in Schemes 1 and 2) of the addition reaction is also discussed in terms of borylene philicity.[43,48] Another useful parameter for estimation of philicity employed by Houk et al.[48] and considered in this paper is the ratio of B−C1/B-C2 distances in the transition state. For electrophilic borylene, this ratio would increase and tend toward 1 while with increasing nucleophilic character this ratio would decrease.

During our study, we were able to locate different conformers (see the SI for more details) of the particular transition states and products but only those with the lowest energies were taken into account for determining the reaction energies and barrier heights. For all types of reactions, van der Waals complexes between borylene and organic substrate were found on the potential energy surfaces. As they do not play a significant role in the description of the reaction energetics, we only briefly report them. All of these complexes will be discussed extensively in a separate paper.

3.2.1. Addition to the C≡C Triple Bond of Ethyne. The addition of borylenes to a C≡C triple bond results in formation of a borirene (Scheme 1). The reaction is very strongly exothermic (Table 4, Figure 2). The exothermicity and

Table 4. Reaction Barriers (in kcal mol^{-1}) and Reaction Energies (in kcal mol^{-1}) Computed for the Addition of Borylenes BR to Ethyne at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ + ZPE Level of Theory

R	barrier	reaction energy
H	not existing	−96.1
Ph [a]	+1.0	−90.8
CH_3	+1.6	−87.1
Br	+4.0	−75.1
NH_2	+5.5	−71.2
NHMe	+4.7	−71.3
NMe_2	+6.5	−71.0
Cl	+5.9	−70.9
F	+11.0	−53.2

[a]Using the cc-pVTZ basis set.

the reaction barrier heights by and large follow the LUMO energies. BH and BPh show the highest exothermicity and the lowest barriers (there is no barrier for BH). Among the halides, the exothermicity decreases and the barrier increases from Br to F, as expected based on the LUMO energies. Aminoborylenes have LUMO energies similar to BF, but their reactivity in terms of barrier height and exothermicity is similar to that of BCl. The barrier is highest for the $BNMe_2$ molecule.

Most of the transition states are of C_s symmetry with atoms R−B−C1−C2 lying in the symmetry plane. Only the transition states of BPh and $BNMe_2$ are distorted to C_1 symmetry. Important dihedral angles for BPh and $BNMe_2$ TS are given in Figure 3. The shortest C1−B distance was calculated for the BF

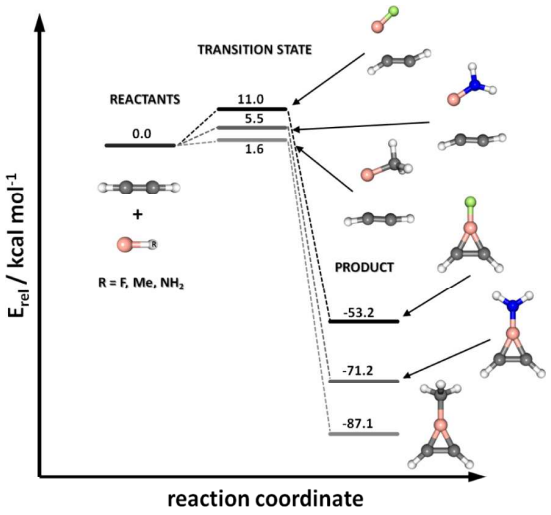


Figure 2. Selected reaction paths for borylene addition to ethyne calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPE level of theory.

transition state (2.002 Å) and the longest one for the BPh transition state (2.461 Å). Among aminoborylenes, the C−B distances are similar to that for the BBr TS, and the shortest distance was found for $BNMe_2$.

The largest value of the tilt angle was obtained for the BF transition state, 44.2°. Values of this angle diminish from F to Br. The smallest values were found for the BPh and BCH_3 transition states. Also, a large tilt angle was found for the $BNMe_2$ transition state and it is comparable to that computed for the BF molecule. The increase of the tilt angle from 36° in BNHMe to 44° in $BNMe_2$ may, however, be primarily a consequence of steric repulsion within the transition structure as barrier height and exotherimicity of the reaction hardly change.

The distortions of H−C−C angles of ethyne from linearity in the TS are smallest for the BPh molecule and largest for fluorine substituted borylene. In case of aminoborylenes, this distortion is similar to that of BBr for BNH_2 and BNHMe; for $BNMe_2$ it is larger, but this again is primarily attributed to steric interactions.

The smallest ratio of the BC1/BC2 distance was computed for BF (0.76) and the largest one (0.88) for the BPh transition state. For BCl, BBr, and BCH_3 transition states, the ratios equal to 0.80, 0.82, and 0.87, respectively. Among aminoborylenes, the ratio values amount to 0.81 for BNH_2, 0.81 for BNHMe and 0.79 for $BNMe_2$.

Interesting may be the finding of an intermediate in the reaction of fluoroborylene with ethyne at the MP2/6-311+G** level of theory. This intermediate corresponds to a shallow minimum: it is 0.02 kcal/mol lower in energy than the TS for its disappearance. Upon ZPE correction the energy of the intermediate becomes 0.5 kcal/mol higher than the TS. This species could not be obtained at the MP2/cc-pVTZ level of theory. For remaining borylenes intermediates in the addition reaction could not be found.

3.2.2. Addition to the C═C Double Bond of Ethene. The addition of borylenes to alkenes yields boriranes (Scheme 2). The reaction is significantly less exothermic than borirene formation.

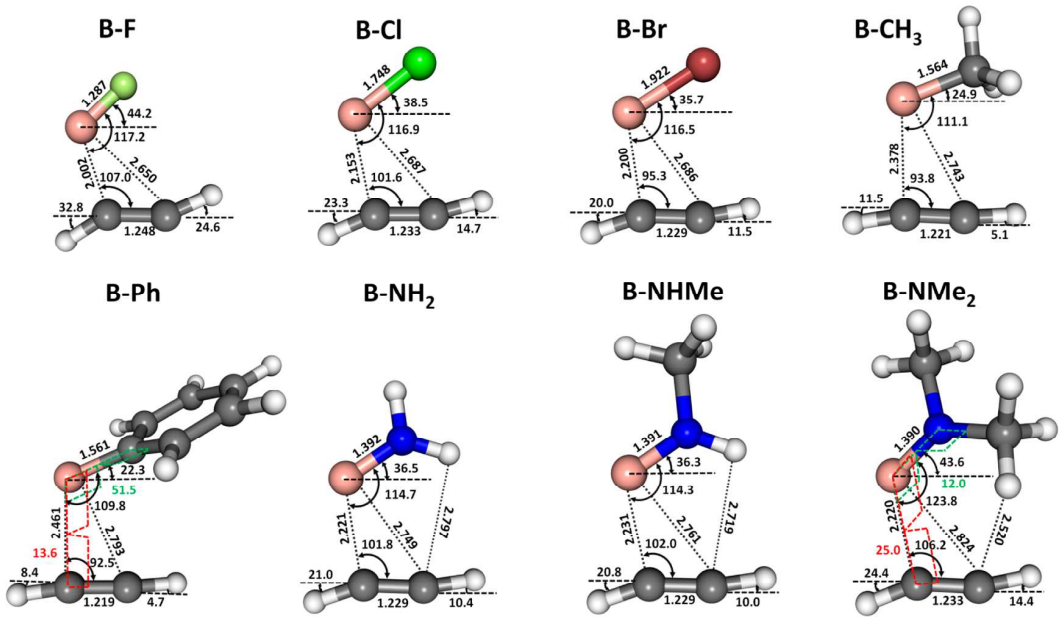


Figure 3. Geometries of the transition structures computed for the addition of borylenes BR to ethyne at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

The latter is an aromatic heterocycle isoelectronic to the cyclopropenylium cation and its formation thus may be more favorable than formation of the borirane molecule. The addition can proceed without barrier on the potential energy surface for the parent BH molecule. As found for addition to ethyne, the barrier increases and the exothermicity decreases among the halides from Br to F (Table 5, Figure 4). Similarly to ethyne addition, the carbon substituted borylenes have the lowest barriers and the largest exothermicities. The amino-borylenes, however, have reactivity parameters similar to those for BBr.

Table 5. Reaction Barriers (in kcal mol^{-1}) and Reaction Energies (in kcal mol^{-1}) Computed for the Addition of Borylenes BR to Ethene at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPVE Level of Theory

R	barrier	reaction energy
H	not existing	−69.8
Ph [a]	+1.5 [b]	−67.7
CH_3	+1.8	−62.7
Br	+4.0	−52.8
NH_2	+4.8	−55.4
NHMe	+3.7	−56.7
NMe_2	+6.1	−57.0
Cl	+6.5	−48.8
F	+13.6	−32.2

[a]Using the cc-pVTZ basis set. [b]With respect to TS1.

Two transition states were obtained at the MP2/cc-pVTZ level of theory for the reaction of phenylborylene with ethene. These differ by the relative orientation of the phenyl group (Figure 5). The energy difference between the two transition states is 0.2 kcal/mol without ZPE correction with TS1 being higher in energy. With ZPE correction these transition states become isoenergetic. TS1 is considered in the following discussion.

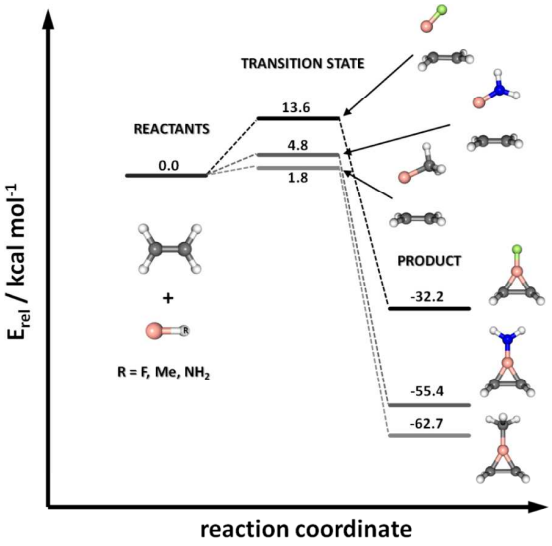


Figure 4. Selected reaction paths of borylene addition to CC double bond of ethene calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ+ZPE level of theory.

By analogy to reactions with ethyne most of the transition states have a plane of symmetry (C_s point group) except for the BPh transition state. In contrast to the addition to ethyne, the TS of $BNMe_2$ has a plane of symmetry. The shortest C1—B distance was also computed for BF and the longest one for the BPh transition state.

The largest tilt angle was found for the BF transition state just as for reactions with ethyne, and the smallest one for the BPh transition state. Aminoborylenes have tilt angles similar to BBr. Also, a large tilt angle was obtained for the $BNMe_2$ transition state, but as in the case of addition to CC triple bond, the increased value is likely a consequence of steric interaction between one methyl group and an ethene CH_2 fragment.

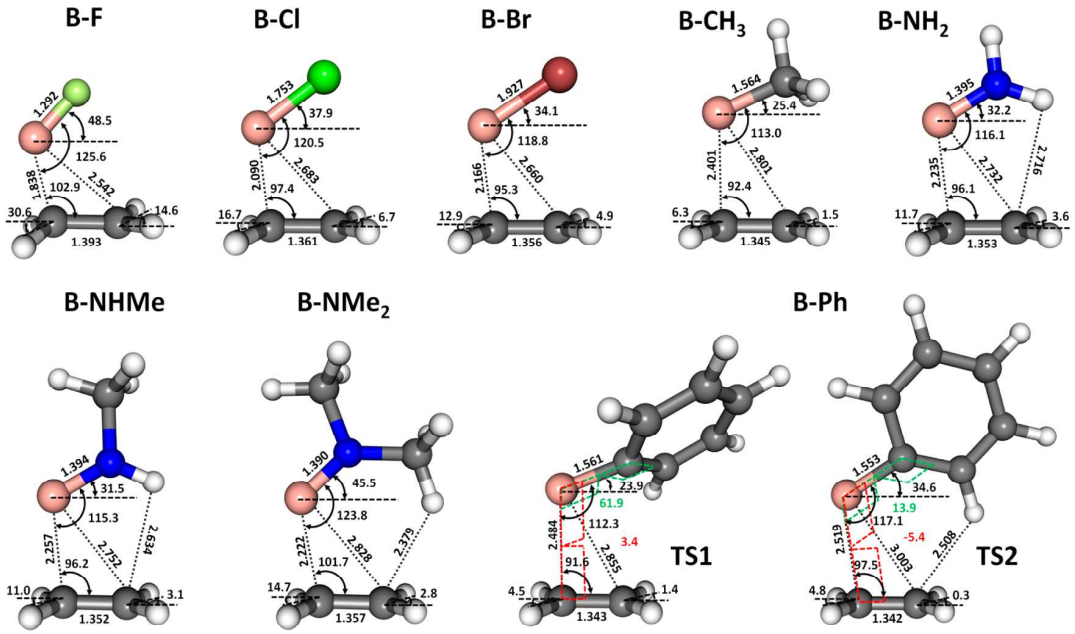


Figure 5. Geometries of the transition structures computed for the addition of borylenes BR to ethene at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles, and dihedral angles are given in degrees.

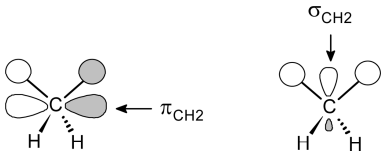
The greatest distortion from planarity of CH_2 groups of ethene in transition structures was obtained for the fluoroborylene TS and the smallest one for the phenylborylene TS. The CH_2 group distortions of the aminoborylene TSs are similar to the ones obtained for bromoborylene TS.

Also, for addition of borylenes to CC double bonds, the smallest ratio of the BC1/BC2 distance was found for the fluoroborylene transition state (0.72), while the largest ratio was obtained for the phenylborylene transition state with a value of 0.87. For the other haloborylenes, the ratios equal to 0.81 and 0.79 for BBr and BCl, respectively. The ratio equals 0.86 for BCH_3. In case of aminoborylenes, the ratios amount to 0.82 for BNH_2, 0.82 for BNHMe, and 0.79 for $BNMe_2$.

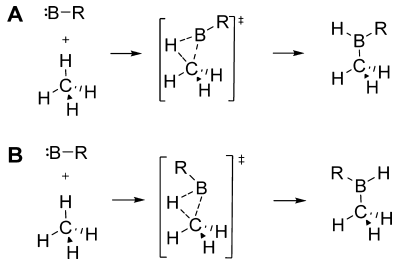
Similarly to the reaction of ethyne with fluoroborylene, an intermediate connecting two TSs on the PES of the BF reaction with ethene could be obtained, but now both at the MP2/6-311+G** and MP2/cc-pVTZ levels of theory. The intermediate lies just 0.6 kcal/mol (0.2 kcal/mol with ZPE) below the first transition state and 0.6 kcal/mol (0.4 kcal/mol with ZPE) below the transition state for ring closure.

3.2.3. Insertion into the C–H Bond of Methane. In their analysis of the insertion of singlet methylene (CH_2) into the C–H bonds of saturated hydrocarbons, Bach et al.[49] identified two approaches on the basis of frontier molecular orbital theory (FMO). Depending on the site of the attack of carbene on the hydrocarbon, σ_{CH2} and π_{CH2} approaches can be distinguished (Scheme 3). By analogy to carbenes, the insertion reaction of borylenes into the carbon–hydrogen bond of methane can also occur according to two approaches (Scheme 4, Figure 6). In

Scheme 3. Two Possible Approaches for Carbene Insertion into Methane According to Bach et al.[49]



Scheme 4. Two Approaches of Addition of Borylene to a Carbon–Hydrogen Bond of Methane



the terminology introduced by Bach et al.[49] approach A of borylene insertion follows a π_{CH2} fashion, whereas approach B is inverted π_{CH2}. Contrary to methylene, borylene insertion reaction according to the σ_{CH2} approach leads to a second order saddle point rather than to a transition state (see Supporting Information). The transition states obtained via the A approach are of C_s symmetry except for BPh and BCH_3 but the ones obtained for approach B are of C_1 symmetry. Higher barriers were computed for the reaction approach B shown in Scheme 4. For both approaches, the barrier decreases with increasing exothermicity (based on the most stable rotamer B for both approaches). In contrast to the addition reactions to multiple CC bonds, the CH insertion of BH has a barrier, but it is the smallest one among the studied borylenes. Again, the highest barrier occurs for the BF molecule due to the high electronegativity of fluorine. The barriers among aminoborylenes are of comparable heights with the largest value found for $BNMe_2$. The higher barrier for $BNMe_2$ than for other aminoborylenes is the consequence of steric repulsion.

For approach B, the reaction has a significantly larger barrier than for approach A. Differences in geometries of both

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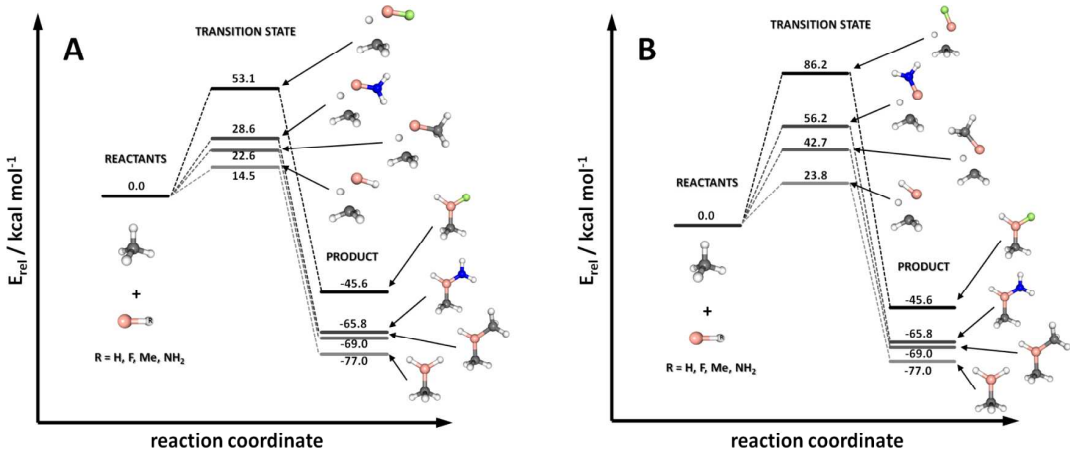


Figure 6. Selected reaction paths for borylene insertion into a C−H bond of methane calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ +ZPE level of theory.

Table 6. Reaction Barriers (in kcal mol^{-1}) and Reaction Energies (in kcal mol^{-1}) Computed for the Insertion of Borylenes BR to C−H Bond of Methane at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ +ZPE Level of Theory

R	barrier A	barrier B	reaction energy [b]
H	+14.5	+23.8	−77.0
Ph [a]	+21.3	+36.5	−74.2
CH_3	+22.6	+42.7	−69.0
NH_2	+28.6	+56.2	−65.8
NHMe	+27.1	+53.5	−66.9
NMe_2	+30.7	+54.9	−65.7
Br	+33.8	+53.8	−62.9
Cl	+37.4	+61.4	−59.9
F	+53.1	+86.2	−46.6

[a]Using the cc-pVTZ basis set. [b]Energy with reference to rotamer B.

transition states are notable (Figures 7 and 8). In the case of transition states A, the distances between boron and hydrogen atoms are smaller than in transition states found for approach B. According to IRC calculations (MP2/6-311+G**), the hydrogen atom from methane shifts toward the boron atom to form an almost linear BHR species soon after the TS. Then the HBR fragment bends and the boron−carbon distance diminishes until the boron−carbon bond is formed (Figure 9A). The carbon−boron distance, however, is shorter in the case of transition states B, while the B−R bond is longer than in transition states A. In reaction B, the formation of the hydrogen−boron and carbon−boron bond proceeds in a more synchronous fashion. At the same time, the CH_3 fragment rotates until rotamer B is formed (Figure 9B).

An interesting observation is that the reaction of phenylborylene with methane via approach B does not lead to methylphenylborane according to IRC computations at the MP2/6-311+G** and MP2/cc-pVTZ levels of theory (Scheme 5). The product obtained is 7-methyl-7-boranorcaradiene. At these levels of theory, the hydrogen atom shifts to one of the carbon atoms of the phenyl ring and the boron atom forms a bond with the carbon atom of methane. In the next stage of the reaction, two B−C bonds are formed. In contrast to MP2 calculations, the IRC path calculated at the B3LYP/6-311+G** level of theory leads to the expected methylphenylborane. The

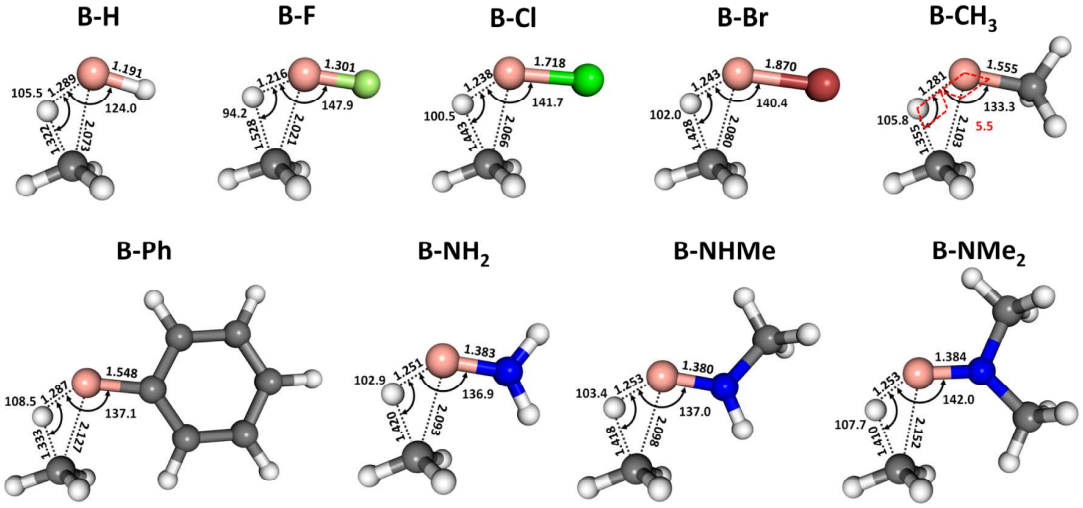


Figure 7. Geometries of the transition structures computed for the insertion of borylenes BR into a C−H bond of methane according to approach A at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles, and dihedral angles are given in degrees.

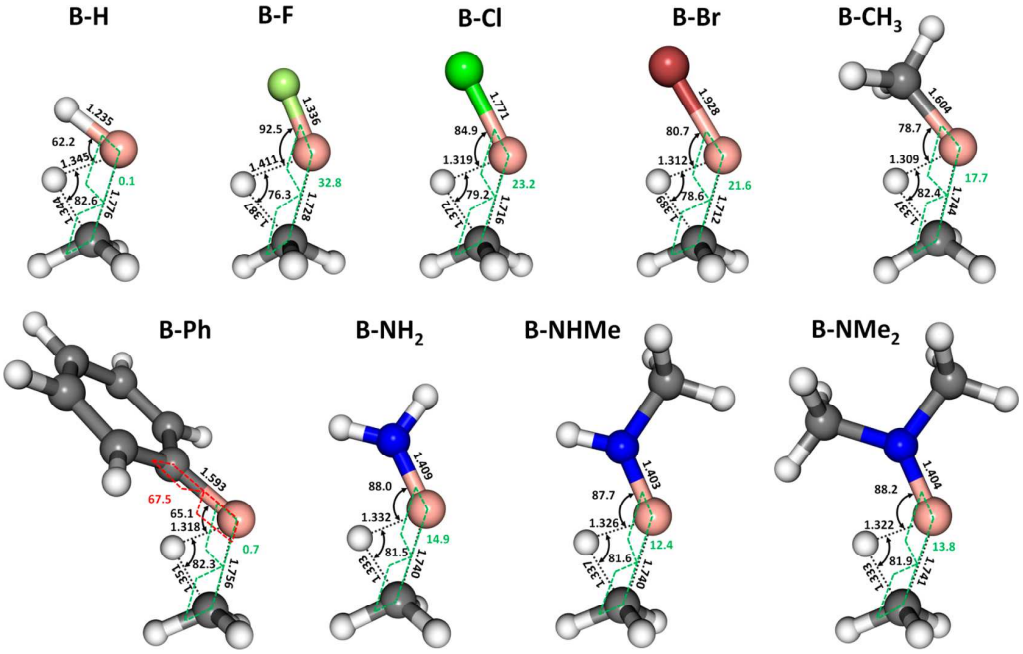


Figure 8. Geometries of the transition structures computed for the insertion of borylenes BR into a C−H bond of methane according to approach B at the MP2/cc-pVTZ level of theory. Important bond lengths are given in Å, bond angles, and dihedral angles are given in degrees.

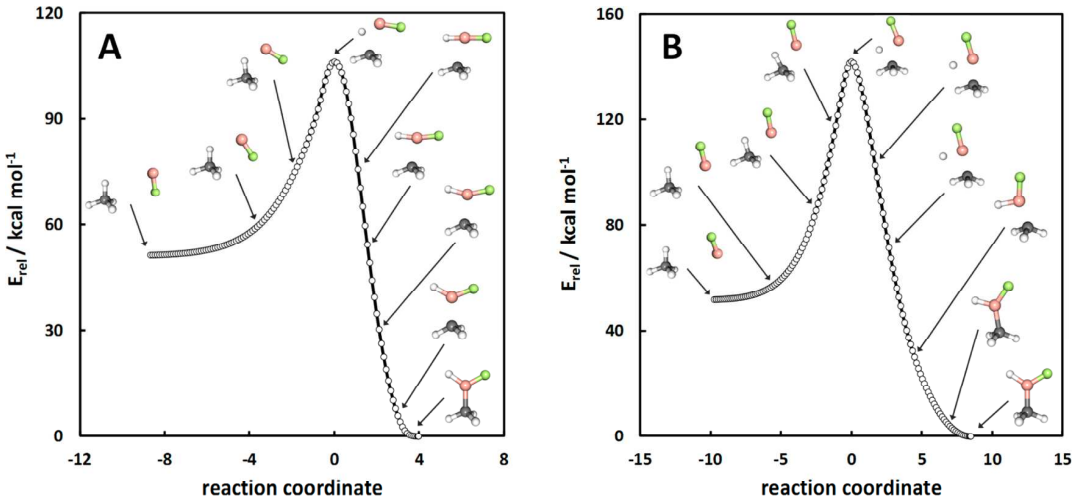
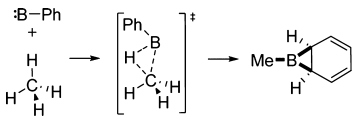


Figure 9. Calculated IRC reaction paths (MP2/6-311+G**) for the insertion of fluoroborylene into C−H bond for (A) approach A and (B) for approach B.

Scheme 5. Formation of 7-Methyl-7-boranorcaradiene



computed (MP2/6-311+G**) IRC path shows that reaction of methane with phenylborylene via approach A leads to methylphenylborane.

Finally, as expected the products of C−H insertion, $RBHCH_3$, are thermodynamically unstable with respect to dimerization. The formation of the dimers with two bridging hydrogen atoms becomes less favorable along the series H < Ph < CH_3 < Cl < Br < F < NH_2 < NHMe < NMe_2. The aminoborane derivatives prefer the formation of the B_2N_2 four membered ring motif, in agreement with NMR investigations of Me_2NBHMe (see Supporting Information for energy data).[50]

3.2.4. Comparison of the Borylenes. The reactivity in terms of computed barrier heights and exothermicities decreases for borylenes in the following order for addition reactions:

$$H > Ph > CH_3 > Br \approx NHMe > NH_2 > Cl > NMe_2 > F$$

The geometric parameters of the TS (tilt angle, ratio of carbon−boron distances, and distortion of the unsaturated organic substrate) are in line with increasing nucleophilicity along the above series of substituents. Considering the LUMO energies, aminoborylenes are comparable to BF, but the

barriers are larger and the exothermicities are smaller for BF. With respect to CH bond insertion, the above order changes inasmuch as the aminoborylenes are more reactive than the haloborylenes.

4. CONCLUSIONS

The computational study of the reactivity of various substituted borylenes BR (where R = H, Ph, CH_3, Br, Cl, F, NH_2, NHMe, NMe_2) performed at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ + ZPE level of theory showed that the reactions of borylenes with prototypical saturated (methane) and unsaturated (ethene and ethyne) hydrocarbons are strongly exothermic. The addition to the triple C≡C bond is the most exothermic process of all examined here. The addition of BH to multiple CC bonds proceeds without barrier, but on the other hand, the insertion of BH into the C−H bond of methane has the smallest reaction barrier. The largest reaction energies were obtained for the BH molecule, followed by BPh and BCH_3 for all type of reactions. The highest barriers and smallest exothermicities were computed for fluoroborylene. Among the halides, the barrier decreases and exothermicity increases from F to Br for both types of reactions. Aminoborylenes have the reaction energies and barrier heights comparable with those obtained for BBr.

The philicity of borylenes was analyzed on the basis of their FMO energies and the transition states geometries of addition reactions. The largest value of tilt angle ζ was found for the transition states of the BF addition to ethyne and ethene, while the smallest one for transition states of the BPh additions. The largest distortions from linearity/planarity of hydrogen atoms of ethyne/ethene were found for the BF and the smallest for BPh transition states. Also, the B−C1/B−C2 distance ratios are smallest for the BF and largest for the BPh transition states. This makes fluoroborylene the most nucleophilic and phenylborylene most electrophilic next to the BH among all studied borylenes. This conclusion is in agreement with the results of the analysis of frontier molecular orbital energies of substituted borylenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 30, geometries computed at the B3LYP/6-311+G** level, reaction energies and barrier heights at the B3LYP and MP2 levels, intrinsic reaction coordinates, energies of borane dimerizations, Cartesian coordinates of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Reactivity of Borylenes towards Ethyne, Ethene, and Methane.

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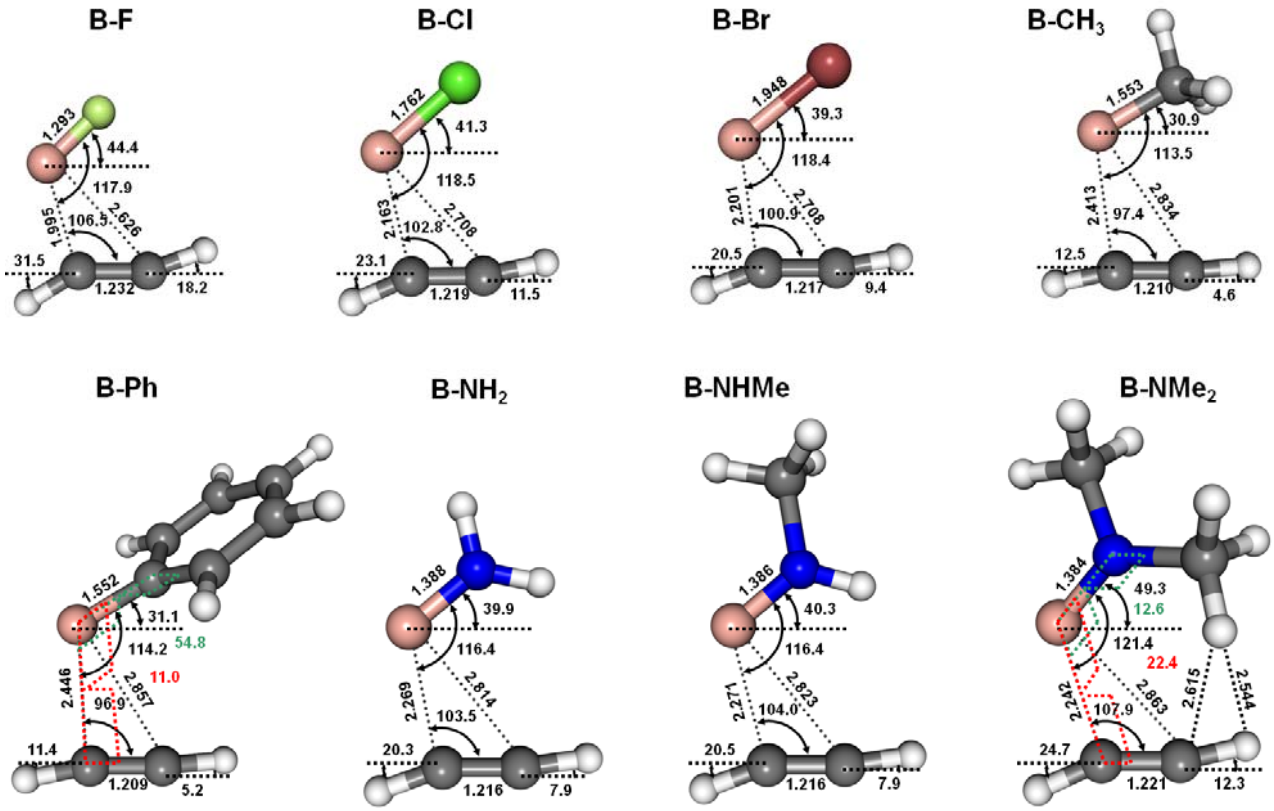

Figure S1. Geometries of the transition structures computed for the addition of borylene BR to acetylene at the B3LYP/6-311+G** level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

Table S1. Barrier heights and reaction energies (in kcal mol^{-1}) computed for the addition of borylenes BR to acetylene at the B3LYP and MP2 levels of theory. Zero-point energy corrections (ZPE) have been included.

R	Method	Barrier	Reaction energy
H	B3LYP[a]	not existing	-103.4
	MP2[a]	not existing	-101.7
	MP2[b]	not existing	-104.3
F	B3LYP[a]	+9.7	-59.8
	MP2[a]	+11.9	-57.1
	MP2[b]	+10.8	-58.1
Cl	B3LYP[a]	+5.8	-75.6
	MP2[a]	+6.6	-75.6
	MP2[b]	+4.9	-77.8
Br	B3LYP[a]	+4.8	-77.8
	MP2[a]	+4.7	-78.9
	MP2[b]	+3.1	-82.0
CH_3	B3LYP[a]	+2.6	-90.7
	MP2[a]	+2.2	-91.7
	MP2[b]	+0.8	-94.6
Ph	B3LYP[a]	+2.4	-93.9
	MP2[a]	+0.1	-96.2
	MP2[b]	-1.0	-98.7
NH_2	B3LYP[a]	+5.6	-75.1
	MP2[a]	+6.1	-74.9
	MP2[b]	+4.6	-77.2
NHMe	B3LYP[a]	+5.2	-74.7
	MP2[a]	+5.1	-74.8
	MP2[b]	+3.7	-77.2
NMe_2	B3LYP[a]	+7.7	-73.7
	MP2[a]	+6.8	-74.4
	MP2[b]	+5.4	-76.7

[a] using the 6-311+G** basis set; [b] using the cc-pVTZ basis set.

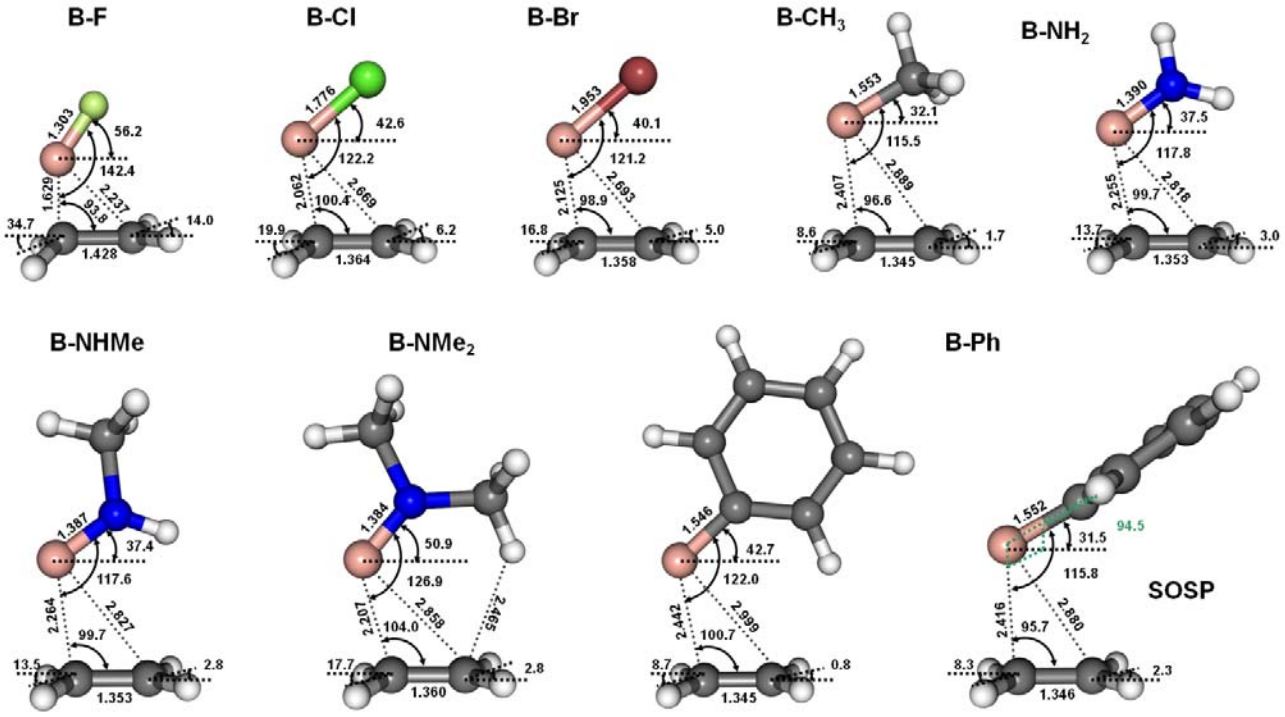

Figure S2. Geometries of the transition structures computed for the addition of borylenes BR to ethylene at the B3LYP/6-311+G** level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

Table S2. Barrier heights and reaction energies (in kcal mol^{-1}) computed for the addition of borylenes BR to ethylene at the B3LYP and MP2 levels of theory. Zero-point energy corrections (ZPE) have been included.

R	Method	Barrier	Reaction energy
H	B3LYP[a]	not existing	-75.1
	MP2[a]	not existing	-76.7
	MP2[b]	not existing	-79.5
F	B3LYP[a]	+15.8	-36.5
	MP2[a]	+15.8	-37.5
	MP2[b]	+14.6	-38.8
Cl	B3LYP[a]	+7.4	-51.5
	MP2[a]	+7.6	-54.9
	MP2[b]	+5.8	-57.1
Br	B3LYP[a]	+5.9	-53.3
	MP2[a]	+5.1	-57.8
	MP2[b]	+3.3	-61.0
CH_3	B3LYP[a]	+3.3	-64.5
	MP2[a]	+2.5	-68.8
	MP2[b]	+1.0	-71.6
Ph	B3LYP[a]	+3.4	-69.3
	MP2[a]	+1.17	-74.9
	MP2[b]	-0.4	-77.5
NH_2	B3LYP[a]	+5.8	-57.2
	MP2[a]	+5.6	-61.1
	MP2[b]	+4.1	-63.4
NHMe	B3LYP[a]	+5.2	-57.8
	MP2[a]	+4.3	-62.2
	MP2[b]	+2.8	-64.6
NMe_2	B3LYP[a]	+8.4	-57.2
	MP2[a]	+6.9	-62.5
	MP2[b]	+5.2	-64.7

[a] using the 6-311+G** basis set; [b] using the cc-pVTZ basis set.

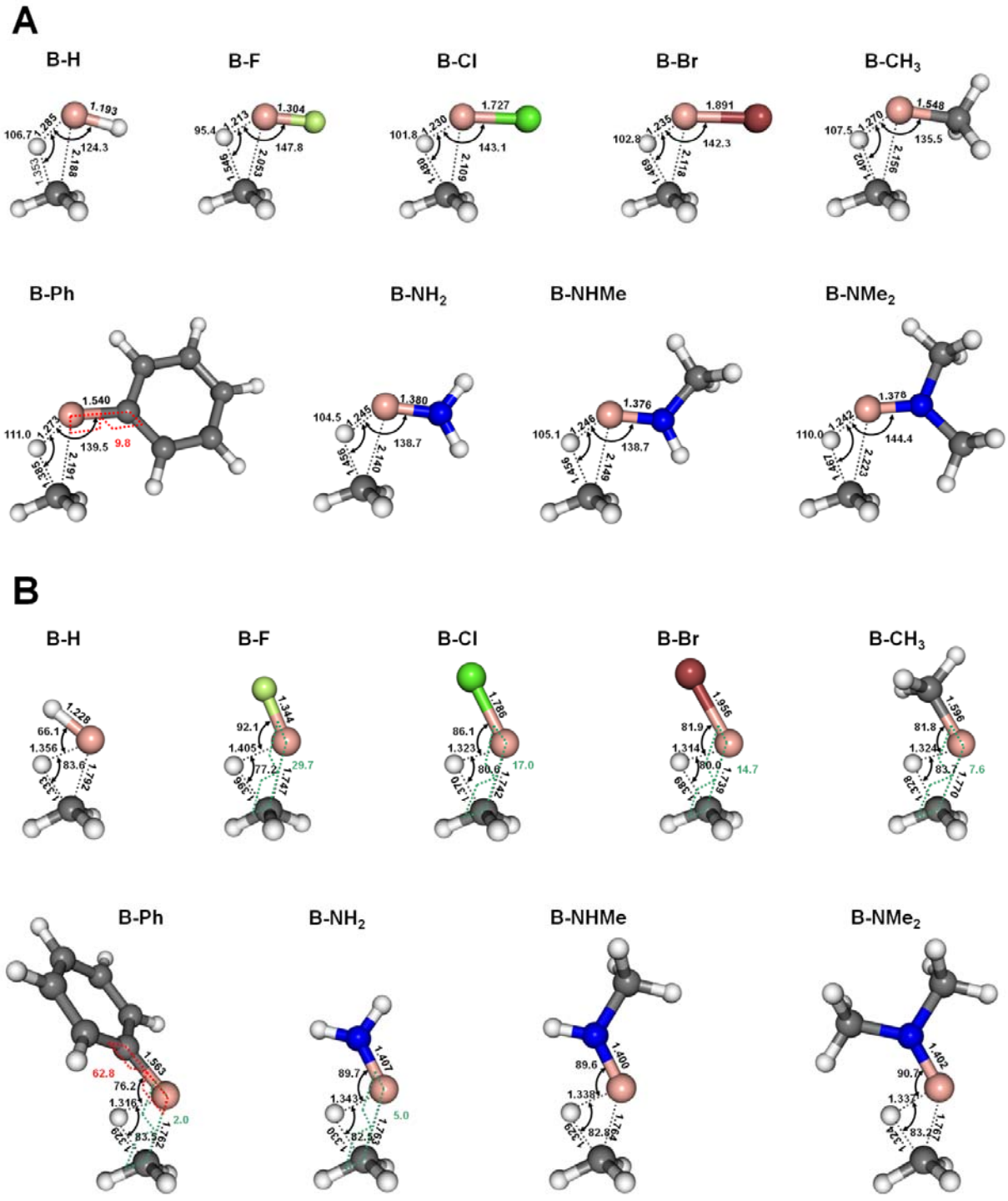

Figure S3. Geometries of the transition structures for the insertion of borylenes BR into a C-H bond of methane according to approaches A and B calculated at the B3LYP/6-311+G** level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

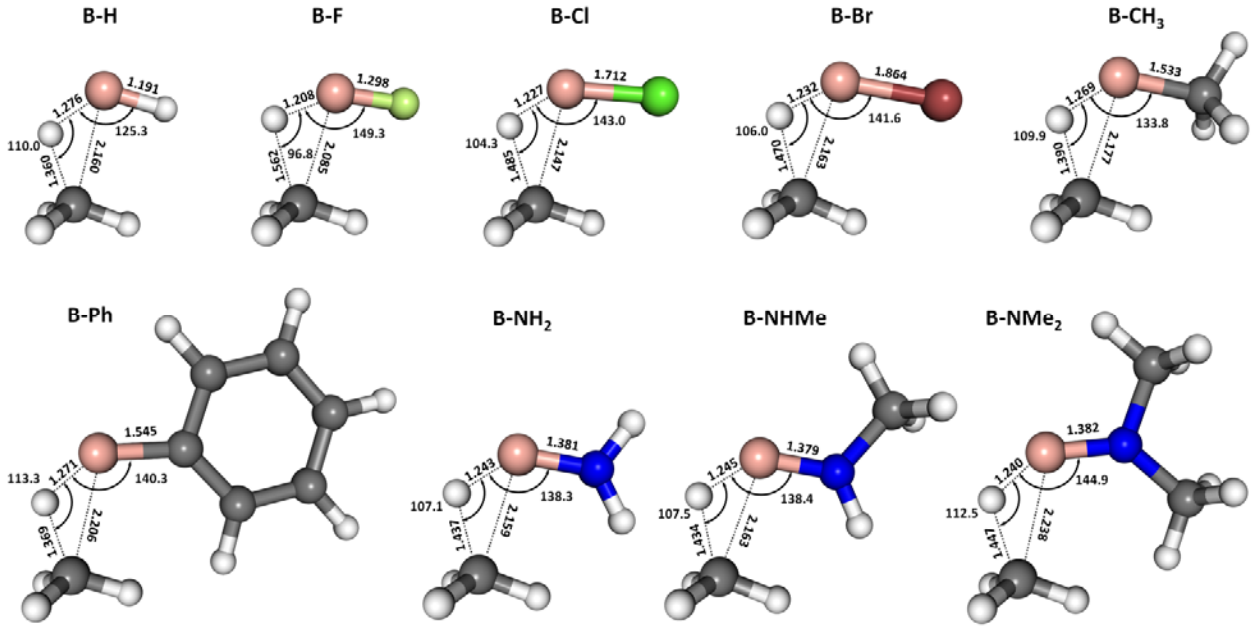

Figure S4. Geometries of the second-order saddle points computed for the insertion of borylene into C-H bond of methane at the MP2/cc-pVTZ level of theory. For the insertion of phenylborylene third-order saddle point was found. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

Table S3. Barrier heights, reaction energies, relative energies of SOSP and rotamers A (in kcal mol^{-1}) computed for the insertion of borylene into C-H bond of methane at the MP2 and B3LYP levels of theory. Zero-point energy corrections (ZPE) have been included.

R	Method	Barrier A	Barrier B	SOSP	Rotamer A	Reaction energy
H	B3LYP[a]	+10.9	+20.7			-82.3
	MP2[a]	+13.9	+22.9			-82.4
	MP2[b]	+12.2	+20.8	+14.9	-84.0	-84.1
F	B3LYP[a]	+48.6	+81.4			-50.4
	MP2[a]	+53.5	+89.3			-50.0
	MP2[b]	+52.6	+88.2	+54.3	-50.4	-50.6
Cl	B3LYP[a]	+35.7	+58.6			-62.7
	MP2[a]	+37.3	+63.2			-64.1
	MP2[b]	+35.4	+59.9	+37.6	-65.2	-65.5
Br	B3LYP[a]	+34.0	+52.7			-64.1
	MP2[a]	+34.5	+55.5			-66.5
	MP2[b]	+32.1	+52.4	+34.5	-67.9	-68.2
CH_3	B3LYP[a]	+21.6	+41.0			-70.9
	MP2[a]	+22.2	+42.4			-73.4
	MP2[b]	+20.4	+39.8	+22.3	-75.1	-75.3
Ph	B3LYP[a]	+20.4	+35.2			-75.5
	MP2[a]	+19.5	+33.7			-79.2
	MP2[b]	+17.6	+31.1	+20.8[c]	-80.4	-80.8
NH_2	B3LYP[a]	+26.8	+53.1			-67.2
	MP2[a]	+28.1	+56.3			-69.5
	MP2[b]	+26.7	+54.1	+28.5	-70.0	-71.0
NHMe	B3LYP[a]	+25.7	+51.0			-67.7
	MP2[a]	+26.6	+53.3			-70.3
	MP2[b]	+25.0	+51.2	+26.8	-70.9	-72.0
NMe_2	B3LYP[a]	+30.4	+53.7			-65.4
	MP2[a]	+30.4	+54.8			-68.8
	MP2[b]	+28.8	+52.5	+31.8	-70.6	-70.6

[a] using the 6-311+G** basis set; [b] using the cc-pVTZ basis set. [c] third-order saddle point.

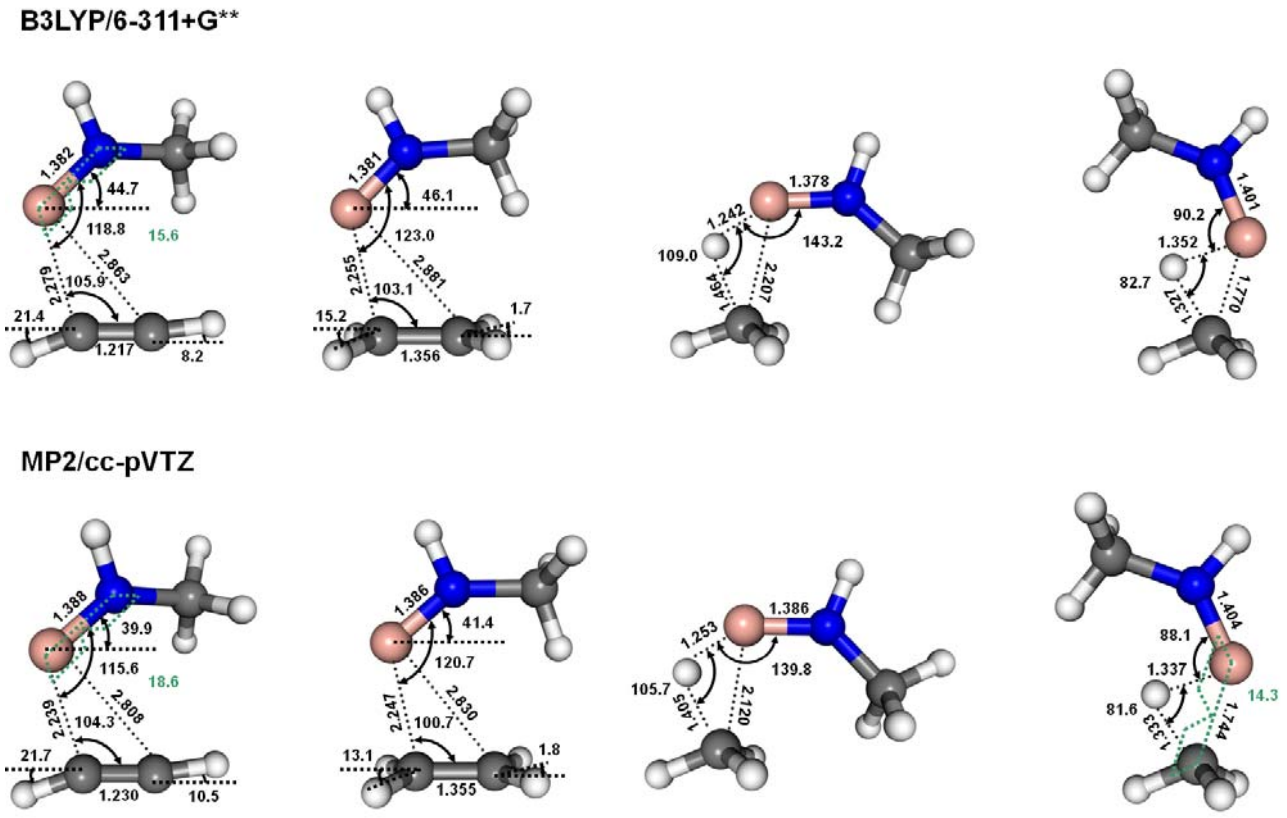

Figure S5. Geometries of the conformers of the transition states for the addition and insertion of the BNHMe. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

Table S4. Relative energies of the conformers of the transition states for the addition and insertion of the BNHMe calculated at the B3LYP and MP2 levels of theory. Zero-point energy corrections (ZPE) have been included.

Method	addition		insertion	
	C≡C	C=C	approach A	approach B
B3LYP/6-311+G**	6.1	6.8	29.0	52.1
MP2/cc-pVTZ	4.3	3.6	28.1	52.1

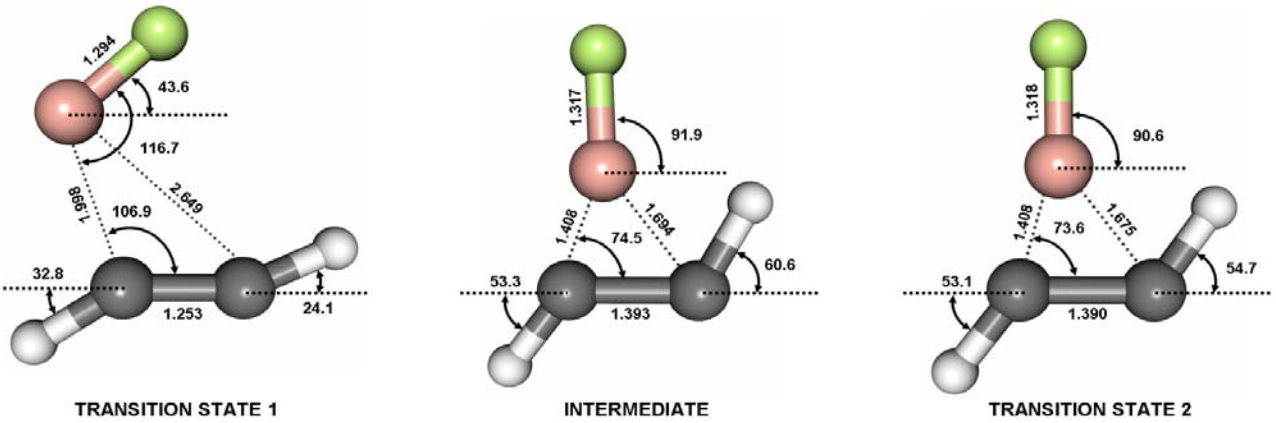

Figure S6. Geometries of the transition states and intermediate for the addition of fluoroborylene to acetylene calculated at the MP2/6-311+G** level of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

Table S5. Relative energies (in kcal mol^{-1}) of the transition states and intermediate for the addition reaction of fluoroborylene to acetylene calculated at the MP2/6-311+G** level of theory.

TS 1		intermediate		TS 2	
E	E+ZPE	E	E+ZPE	E	E+ZPE
10.9	11.9	-17.8	-14.8	-17.8	-15.3

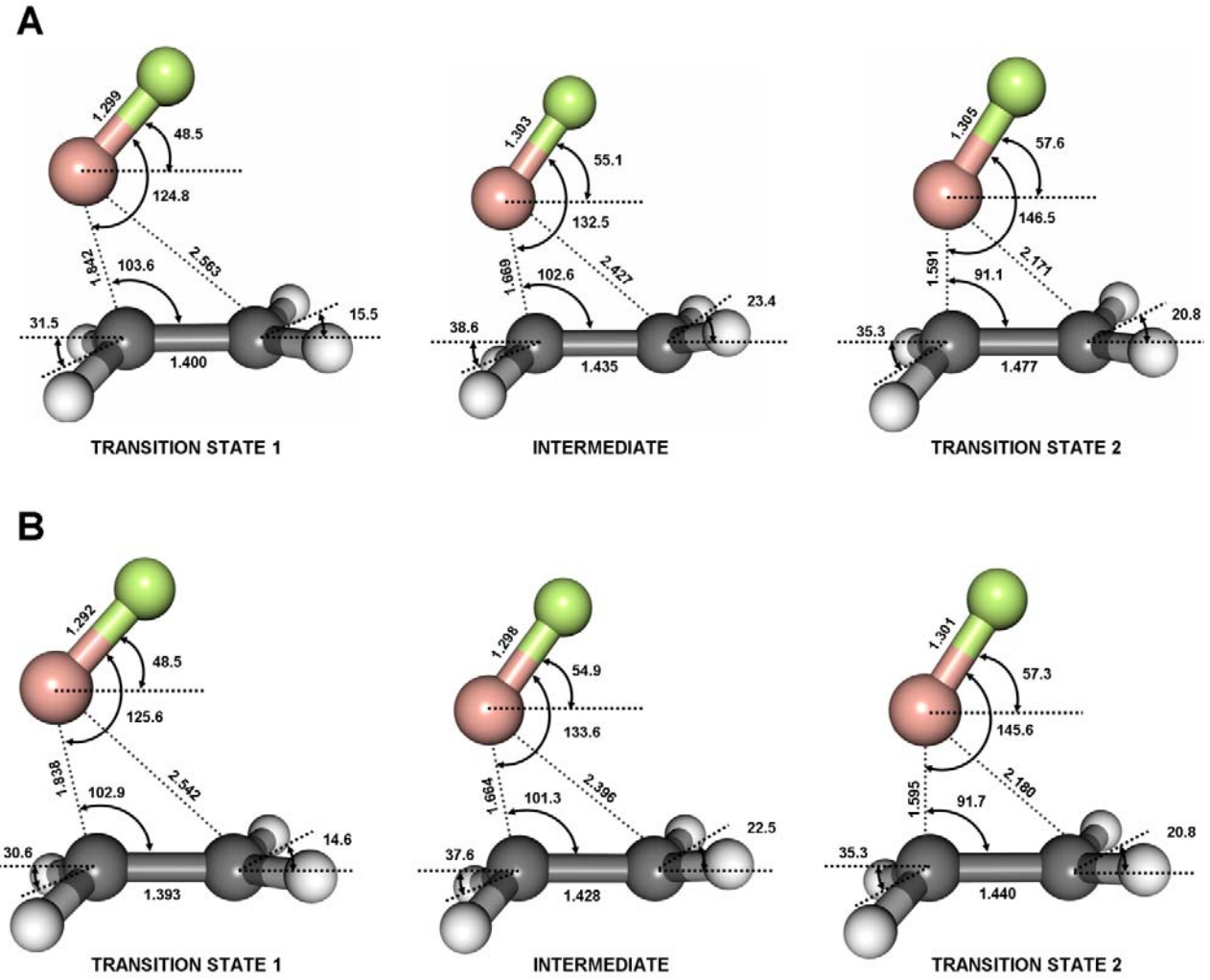

Figure S7. Geometries of the transition states and intermediate for the addition of fluoroborylene to acetylene calculated at the MP2/6-311+G** (A) and at the MP2/cc-pVTZ (B) levels of theory. Important bond lengths are given in Å, bond angles and dihedral angles are given in degrees.

Table S6. Transition state and intermediate energies (in kcal mol^{-1}) of the addition reaction of fluoroborylene to ethylene calculated at the MP2 level of theory.

Method	TS 1		intermediate		TS 2	
	E	E + ZPE	E	E + ZPE	E	E + ZPE
MP2/6-311+G**	14.7	15.8	14.2	15.7	15.2	16.6
MP2/cc-pVTZ	13.7	14.6	13.0	14.5	13.7	14.9

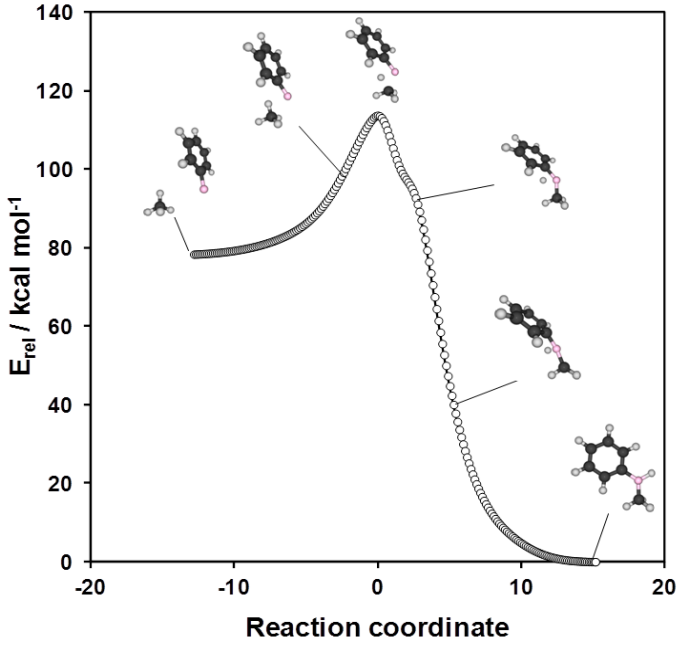

Figure S8. IRC path for the phenylborylene insertion into the C-H bond of methane via approach B calculated at the B3LYP/6-311+G** level of theory.

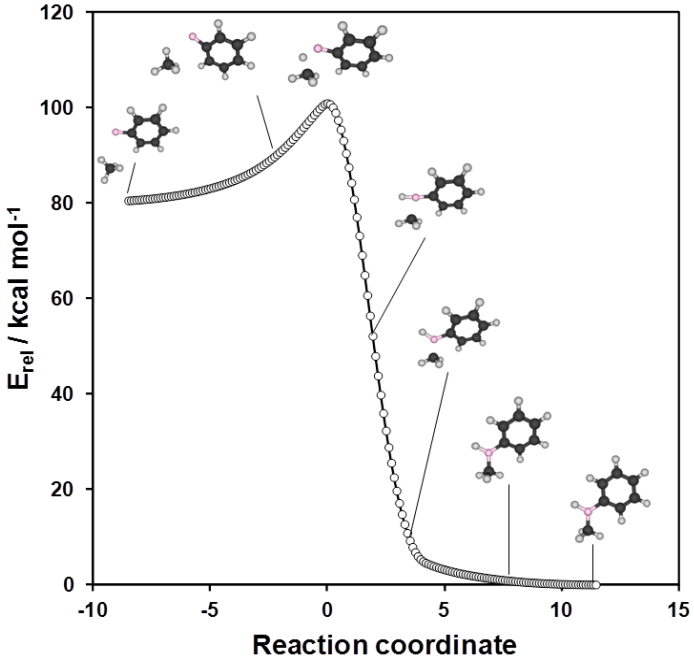

Figure S9. IRC path for the phenylborylene insertion into the C-H bond of methane via approach A calculated at the MP2/6-311+G** level of theory.

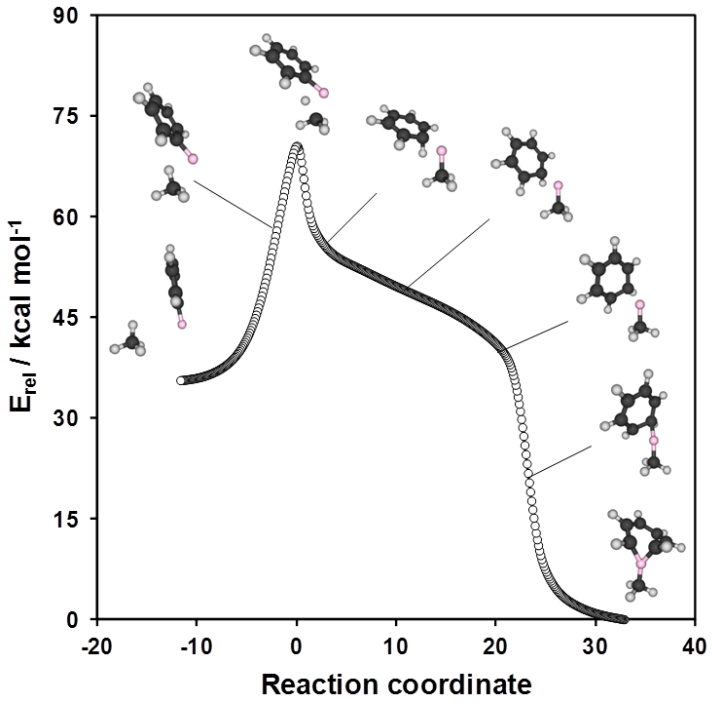

Figure S10. IRC path for the phenylborylene insertion into the C-H bond of methane via approach B calculated at the MP2/6-311+G** level of theory.

Table S7. Energies of borane dimerization (in kcal mol^{-1}) calculated at the MP2/6-311+G** level of theory.

R	H-bridged dimer		Halo- or BN-bridged dimer	
	E	E+ZPE	E	E+ZPE
H	-36.1	-30.1		
CH_3	-29.3	-24.0		
Ph	-26.5	-21.1		
Br	-21.0	-16.9	-5.8	-3.3
Cl	-19.6	-15.4	-5.7	-2.9
F	-11.3	-7.0	3.1	5.9
NH_2	10.5	12.9	-18.7	-14.2
NHMe	16.1	18.2	-23.2	-19.4
NMe_2	18.4	20.5	-25.9	-22.1

Geometries of all species given in Cartesian coordinates.

Total energies are given in hartree. Zero-point vibrational energies are given in kcal mol^{-1}. Values of imaginary frequencies are given for first or higher order saddle points (in cm^{-1}).

Hydrocarbons

	B3LYP/6-311+G**	MP2/cc-pVTZ
ethyne	E=-77.3566458 ZPE=16.96 C 0.000000000 0.000000000 0.599686000 C 0.000000000 0.000000000 -0.599686000 H 0.000000000 0.000000000 1.662817000 H 0.000000000 0.000000000 -1.662817000	E=-77.1591956 ZPE=16.65 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-77.1921839 C 0.000000000 0.000000000 0.605641000 C 0.000000000 0.000000000 -0.605641000 H 0.000000000 0.000000000 1.666853000 H 0.000000000 0.000000000 -1.666853000
ethene	E=-78.6155126 ZPE=31.87 C 0.000000000 0.000000000 0.664380000 C 0.000000000 0.000000000 0.664380000 H 0.000000000 0.922600000 1.235364000 H 0.000000000 -0.922600000 1.235364000 H 0.000000000 -0.922600000 -1.235364000 H 0.000000000 0.922600000 -1.235364000	E=-78.399306 ZPE=32.29 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-78.4436886 C 0.000000000 0.000000000 0.665890000 C 0.000000000 0.000000000 -0.665890000 H 0.000000000 0.922453000 1.228312000 H 0.000000000 -0.922453000 1.228312000 H 0.000000000 -0.922453000 -1.228312000 H 0.000000000 0.922453000 -1.228312000
methane	E=-40.5339328 ZPE=27.95 C 0.000000000 0.000000000 0.000000000 H 0.629834000 0.629834000 0.629834000 H -0.629834000 -0.629834000 0.629834000 H 0.629834000 -0.629834000 -0.629834000 H 0.629834000 0.629834000 -0.629834000	E=-40.4116665 ZPE=28.50 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-40.4408757 C 0.000000000 0.000000000 0.000000000 H 0.626572000 0.626572000 0.626572000 H -0.626572000 -0.626572000 0.626572000 H 0.626572000 -0.626572000 -0.626572000 H -0.626572000 0.626572000 -0.626572000

Singlet borylenes

Borylene	B3LYP/6-311+G**	MP2/cc-pVTZ
BH	E=-25.2975417 ZPE=3.35 B 0.000000000 0.000000000 0.205782000 H 0.000000000 0.000000000 -1.028911000	E=-25.2034572 ZPE=3.47 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-25.231457 B 0.000000000 0.000000000 0.204566000 H 0.000000000 0.000000000 -1.022829000
BF	E=-124.7014755 ZPE=1.94 B 0.000000000 0.000000000 -0.816758000 F 0.000000000 0.000000000 0.453755000	E=-124.4786396 ZPE=2.02 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-124.5097559 B 0.000000000 0.000000000 -0.815254000 F 0.000000000 0.000000000 0.452919000
BCl	E=-485.0167318 ZPE=1.17 B 0.000000000 0.000000000 -1.336563000	E=-484.415488 ZPE=1.23 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-484.4637003 B 0.000000000 0.000000000 -1.326769000

	Cl 0.000000000 0.000000000 0.393107000	Cl 0.000000000 0.000000000 0.390226000
BBr	E=-2598.9293707 ZPE=0.96 B 0.000000000 0.000000000 -1.669860000 Br 0.000000000 0.000000000 0.238551000	E=-2597.3851895 ZPE=1.01 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2597.4316771 B 0.000000000 0.000000000 -1.647608000 Br 0.000000000 0.000000000 0.235373000
BCH_3	E=-64.6621639 ZPE=21.84 B 0.000000000 0.000000000 -1.067046000 C 0.000000000 0.000000000 0.466377000 H 0.000000000 1.031490000 0.845656000 H 0.893296000 -0.515745000 0.845656000 H -0.893296000 -0.515745000 0.845656000	E=-64.4597355 ZPE=22.16 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-64.5066794 B 0.000000000 0.000000000 -1.070750000 C 0.000000000 0.000000000 0.470575000 H 0.000000000 1.027309000 0.843433000 H 0.889676000 -0.513655000 0.843433000 H -0.889676000 -0.513655000 0.843433000
BPh	E=-256.4419245 ZPE=57.08 B 0.000000000 0.000000000 -2.673492000 C 0.000000000 0.000000000 -1.139853000 C 0.000000000 1.214955000 -0.426535000 C 0.000000000 1.213156000 0.963727000 C 0.000000000 0.000000000 1.655371000 C 0.000000000 -1.213156000 0.963727000 C 0.000000000 -1.214955000 -0.426535000 H 0.000000000 2.156490000 -0.966863000 H 0.000000000 2.148971000 1.510965000 H 0.000000000 0.000000000 2.739845000 H 0.000000000 -2.148971000 1.510965000 H 0.000000000 -2.156490000 -0.966863000	E=-255.7826509 ZPE=57.36 CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-255.8746969 B 0.000000000 0.000000000 -2.676429000 C 0.000000000 0.000000000 -1.134662000 C 0.000000000 1.214082000 -0.426996000 C 0.000000000 1.212006000 0.963610000 C 0.000000000 0.000000000 1.655121000 C 0.000000000 -1.212006000 0.963610000 C 0.000000000 -1.214082000 -0.426996000 H 0.000000000 2.152578000 -0.968038000 H 0.000000000 2.145209000 1.509662000 H 0.000000000 0.000000000 2.736776000 H 0.000000000 -2.145209000 1.509662000 H 0.000000000 -2.152578000 -0.968038000
BNH_2	E=-80.768983 ZPE=15.76 B 0.000000000 0.000000000 -0.963098000 N 0.000000000 0.000000000 0.413412000 H 0.000000000 0.853848000 0.960804000 H 0.000000000 -0.853848000 0.960804000	E=-80.561385 ZPE=15.89 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-80.6017895 B 0.000000000 0.000000000 -0.964850000 N 0.000000000 0.000000000 0.415108000 H 0.000000000 0.850030000 0.959247000 H 0.000000000 -0.850030000 0.959247000
BNHMe	E=-120.083525 ZPE=34.40 B -1.351393000 0.748344000 0.000000000 N 0.000000000 0.496958000 0.000000000 H 0.630562000 1.293603000 0.000000000 C 0.630330000 -0.831087000 0.000000000 H 1.246719000 -0.967109000 0.891044000 H -0.149013000 -1.593293000 0.000000000 H 1.246719000 -0.967109000 -0.891044000	E=-119.7709978 ZPE=34.93 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-119.8321996 B -1.361828000 0.718056000 0.000000000 N 0.000000000 0.498880000 0.000000000 H 0.617872000 1.299925000 0.000000000 C 0.637513000 -0.817396000 0.000000000 H 1.251203000 -0.949129000 0.887338000 H -0.136217000 -1.579729000 0.000000000 H 1.251203000 -0.949129000 -0.887338000
$BNMe_2$	E=-159.4013691 ZPE=52.30 B 0.000000000 0.000000000 1.641862000 N 0.000000000 0.000000000 0.266776000 C 0.000000000 1.248513000 -0.495577000 C 0.000000000 -1.248513000 -0.495577000 H 0.890966000 -1.311437000 -1.128048000 H 0.000000000 -2.096807000 0.191185000 H -0.890966000 -1.311437000 -1.128048000	E=-158.986443 ZPE=53.15 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-159.0678377 B 0.000000000 0.000000000 1.648962000 N 0.000000000 0.000000000 0.268303000 C 0.000000000 1.237246000 -0.497652000 C 0.000000000 -1.237246000 -0.497652000 H 0.887374000 -1.290589000 -1.128141000 H 0.000000000 -2.087275000 0.180729000 H -0.887374000 -1.290589000 -1.128141000

	H 0.890966000 1.311437000 -1.128048000 H -0.890966000 1.311437000 -1.128048000 H 0.000000000 2.096807000 0.191185000	H 0.887374000 1.290589000 -1.128141000 H -0.887374000 1.290589000 -1.128141000 H 0.000000000 2.087275000 0.180729000

Triplet borylenes

Borylene	B3LYP/6-311+G**	MP2/cc-pVTZ
BH	E=-25.2560804 ZPE=3.72 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 0.198790000 H 0.000000000 0.000000000 -0.993951000	E=-25.166983 ZPE=3.88 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 0.197291000 H 0.000000000 0.000000000 -0.986454000
BF	E=-124.5776184 ZPE=1.82 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 -0.848917000 F 0.000000000 0.000000000 0.471621000	E=-124.3552534 ZPE=1.90 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 -0.846896000 F 0.000000000 0.000000000 0.470498000
BCl	E=-484.929899 ZPE=1.26 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 -1.327206000 Cl 0.000000000 0.000000000 0.390355000	E=-484.3319116 ZPE=1.32 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 -1.320307000 Cl 0.000000000 0.000000000 0.388326000
BBr	E=-2598.8495034 ZPE=1.06 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 -1.639268000 Br 0.000000000 0.000000000 0.234181000	E=-2597.3092177 ZPE=1.12 Electronic state: $^3\Pi$ B 0.000000000 0.000000000 -1.621976000 Br 0.000000000 0.000000000 0.231711000
BCH_3	E=-64.6027065 ZPE=22.27 Electronic state: $^3A''$ B -0.015550000 -1.079247000 0.000000000 C -0.015550000 0.469968000 0.000000000 H 1.059900000 0.716249000 0.000000000 H -0.444423000 0.930088000 0.897907000 H -0.444423000 0.930088000 -0.897907000	E=-64.405661 ZPE=22.81 Electronic state: $^3A''$ B -0.016117000 -1.080364000 0.000000000 C -0.016117000 0.472884000 0.000000000 H 1.055988000 0.709682000 0.000000000 H -0.439350000 0.927415000 0.894162000 H -0.439350000 0.927415000 -0.894162000
BPh	E=-256.391746 ZPE=56.49 Electronic state: $^3B_1$ B 0.000000000 0.000000000 -2.645090000 C 0.000000000 0.000000000 -1.164075000 C 0.000000000 1.221881000 -0.427174000 C 0.000000000 1.206750000 0.958208000 C 0.000000000 0.000000000 1.666152000 C 0.000000000 -1.206750000 0.958208000 C 0.000000000 -1.221881000 -0.427174000 H 0.000000000 2.171138000 -0.950655000 H 0.000000000 2.148738000 1.496227000 H 0.000000000 0.000000000 2.749442000 H 0.000000000 -2.148738000 1.496227000 H 0.000000000 -2.171138000 -0.950655000	E=-255.6998821 ZPE=59.13 Electronic state: $^3B_1$ C 0.000000000 1.196835000 -0.417083000 C 0.000000000 0.000000000 -1.134548000 C 0.000000000 -1.196835000 -0.417083000 C 0.000000000 -1.185604000 0.945709000 C 0.000000000 0.000000000 1.643993000 C 0.000000000 1.185604000 0.945709000 B 0.000000000 0.000000000 -2.641203000 H 0.000000000 -2.143412000 -0.939492000 H 0.000000000 -2.125107000 1.480695000 H 0.000000000 0.000000000 2.723432000 H 0.000000000 2.125107000 1.480695000 H 0.000000000 2.143412000 -0.939492000
BNH_2	E=-80.6975701 ZPE=16.50 Electronic state: $^3B_2$	E=-80.4947524 ZPE=16.89 Electronic state: $^3B_2$

	B 0.000000000 0.000000000 -0.963265000 N 0.000000000 0.000000000 0.409362000 H 0.000000000 0.843191000 0.975396000 H 0.000000000 -0.843191000 0.975396000	B 0.000000000 0.000000000 -0.965430000 N 0.000000000 0.000000000 0.412744000 H 0.000000000 0.840672000 0.968970000 H 0.000000000 -0.840672000 0.968970000
BNHMe	E=-120.0134553 ZPE=34.74 Electronic state: $^3A'$ B -1.332960000 0.800326000 0.000000000 N 0.000000000 0.490672000 0.000000000 H 0.697137000 1.231765000 0.000000000 C 0.612619000 -0.848852000 0.000000000 H 1.235805000 -0.989186000 0.889066000 H -0.179661000 -1.596611000 0.000000000 H 1.235805000 -0.989186000 -0.889066000	E=-119.7051579 ZPE=35.47 Electronic state: $^3A'$ B -1.344250000 0.777842000 0.000000000 N 0.000000000 0.488306000 0.000000000 H 0.677649000 1.238974000 0.000000000 C 0.621034000 -0.836168000 0.000000000 H 1.240953000 -0.972455000 0.885076000 H -0.164511000 -1.584406000 0.000000000 H 1.240953000 -0.972455000 -0.885076000
$BNMe_2$	E=-159.329145 ZPE=52.46 Electronic state: $^3B_2$ B 0.000000000 0.000000000 1.676736000 N 0.000000000 0.000000000 0.306694000 C 0.000000000 1.223468000 -0.514560000 C 0.000000000 -1.223468000 -0.514560000 H 0.887904000 -1.252641000 -1.156940000 H 0.000000000 -2.095405000 0.135973000 H -0.887904000 -1.252641000 -1.156940000 H 0.887904000 1.252641000 -1.156940000 H -0.887904000 1.252641000 -1.156940000 H 0.000000000 2.095405000 0.135973000	E=-158.9186341 ZPE=53.48 Electronic state: $^3B_2$ B 0.000000000 0.000000000 1.682184000 N 0.000000000 0.000000000 0.305687000 C 0.000000000 1.210319000 -0.515342000 C 0.000000000 -1.210319000 -0.515342000 H 0.884079000 -1.231040000 -1.155195000 H 0.000000000 -2.083614000 0.127076000 H -0.884079000 -1.231040000 -1.155195000 H 0.884079000 1.231040000 -1.155195000 H -0.884079000 1.231040000 -1.155195000 H 0.000000000 2.083614000 0.127076000

Transition states for the addition of borylenes BR to acetylene

R	B3LYP/6-311+G**	MP2/cc-pVTZ
F	E=-202.0438297 ZPE=19.65 U=382.6i C 0.443408000 -1.470896000 0.000000000 C 1.185856000 -0.487423000 0.000000000 B 0.000000000 1.116983000 0.000000000 H -0.449767000 -2.053481000 0.000000000 H 2.181435000 -0.096733000 0.000000000 F -1.278584000 0.923912000 0.000000000	E=-201.6222517 ZPE=19.69 U=513.3i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-201.6860112 C 0.439126000 -1.486418000 0.000000000 C 1.184918000 -0.486168000 0.000000000 B 0.000000000 1.127193000 0.000000000 H -0.496150000 -1.999274000 0.000000000 H 2.184452000 -0.112548000 0.000000000 F -1.270285000 0.923486000 0.000000000
Cl	E=-562.3651268 ZPE=18.74 U=333.4i C 1.605473000 -1.094038000 0.000000000 C 1.917465000 0.084802000 0.000000000 B 0.000000000 1.086390000 0.000000000 Cl -1.461403000 0.102685000 0.000000000 H 1.133991000 -2.048159000 0.000000000 H 2.572227000 0.925985000 0.000000000	E=-561.5680222 ZPE=18.60 U=397.6i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-561.6476079 C 1.553067000 -1.092330000 0.000000000 C 1.901415000 0.089979000 0.000000000 B 0.000000000 1.100020000 0.000000000 Cl -1.430125000 0.094640000 0.000000000 H 1.003092000 -2.002903000 0.000000000 H 2.582145000 0.908025000 0.000000000
Br	E=-2676.2792878 ZPE=18.47 U=305.0i C 0.988650000 -2.217865000 0.000000000 C -0.187546000 -2.528907000 0.000000000 B -1.141695000 -0.545893000 0.000000000	E=-2674.5404798 ZPE=18.30 U=341.1i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2674.6185614 C 0.994421000 -2.133259000 0.000000000 C -0.179020000 -2.497398000 0.000000000

	H 1.958952000 -1.781526000 0.000000000 H -1.057100000 -3.144494000 0.000000000 Br 0.000000000 1.032460000 0.000000000	B -1.158637000 -0.527702000 0.000000000 H 1.926739000 -1.622110000 0.000000000 H -1.025958000 -3.140880000 0.000000000 Br 0.000000000 1.005298000 0.000000000
CH_3	E=-142.0185568 ZPE=40.28 U=404.7i C -0.634501000 -1.363127000 0.000000000 C -1.461218000 -0.465245000 0.000000000 B 0.000000000 1.179397000 0.000000000 H 0.183684000 -2.041972000 0.000000000 H -2.416519000 0.007682000 0.000000000 C 1.516790000 0.811776000 0.000000000 H 2.079673000 1.752115000 0.000000000 H 1.813367000 0.242382000 0.889238000 H 1.813367000 0.242382000 -0.889238000	E=-141.6199034 ZPE=40.21 U=439.6i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-141.6984809 C -0.601482000 -1.299501000 0.000000000 C -1.477688000 -0.436452000 0.000000000 B 0.000000000 1.193409000 0.000000000 H 0.251375000 -1.933103000 0.000000000 H -2.435295000 0.026666000 0.000000000 C 1.503848000 0.734148000 0.000000000 H 2.106715000 1.643036000 0.000000000 H 1.764568000 0.153593000 0.886768000 H 1.764568000 0.153593000 -0.886768000
Ph	E=-333.7955996 ZPE=74.62 U=195.0i C 2.878236000 -0.672117000 0.840791000 C 3.433196000 0.054383000 0.049799000 B 1.420214000 1.144263000 -0.813133000 H 2.308524000 -1.262701000 1.516514000 H 4.097211000 0.607217000 -0.568941000 C 0.094187000 0.471005000 -0.369998000 C -0.904978000 1.337920000 0.111999000 C -2.173518000 0.857804000 0.430002000 C -2.470307000 -0.491026000 0.243361000 C -1.498773000 -1.362214000 -0.257929000 C -0.227914000 -0.887323000 -0.557919000 H -0.682710000 2.393601000 0.236105000 H -2.930577000 1.533221000 0.812567000 H -3.459943000 -0.865360000 0.481099000 H -1.737390000 -2.409416000 -0.408084000 H 0.523042000 -1.568474000 -0.944227000	E=-332.9445659 ZPE=74.67 U=158.7i CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-333.0618669 C 2.697038000 -0.681828000 0.826748000 C 3.386700000 0.000102000 0.087944000 B 1.436255000 1.227575000 -0.775441000 H 2.030399000 -1.222994000 1.452146000 H 4.108942000 0.519383000 -0.491969000 C 0.124101000 0.487218000 -0.367623000 C -0.886648000 1.341924000 0.105512000 C -2.150099000 0.845060000 0.418274000 C -2.426721000 -0.507025000 0.228637000 C -1.442229000 -1.363190000 -0.270552000 C -0.175225000 -0.871710000 -0.562083000 H -0.675420000 2.398021000 0.229640000 H -2.916772000 1.507228000 0.796770000 H -3.409602000 -0.894295000 0.460928000 H -1.666807000 -2.409873000 -0.425586000 H 0.586493000 -1.538648000 -0.945875000
NH_2	E=-158.1189528 ZPE=34.17 U=304.2i C -0.555501000 -1.526312000 0.000000000 C -1.340974000 -0.598329000 0.000000000 B 0.000000000 1.232222000 0.000000000 H 0.236089000 -2.236249000 0.000000000 H -2.267117000 -0.074157000 0.000000000 N 1.367748000 0.996450000 0.000000000 H 1.976273000 1.805458000 0.000000000 H 1.859366000 0.116537000 0.000000000	E=-157.7157025 ZPE=34.10 U=362.1i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-157.7876458 C -0.541259000 -1.472655000 0.000000000 C -1.346114000 -0.544223000 0.000000000 B 0.000000000 1.222787000 0.000000000 H 0.288377000 -2.136892000 0.000000000 H -2.284395000 -0.044728000 0.000000000 N 1.358772000 0.919278000 0.000000000 H 1.989730000 1.706013000 0.000000000 H 1.819120000 0.027991000 0.000000000
NHMe TS1	E=-197.4333006 ZPE=52.27 U=286.1i C 2.093636000 -0.983303000 0.000000000 C 2.166906000 0.230609000 0.000000000 B 0.000000000 0.910806000 0.000000000 N -0.959369000 -0.088926000 0.000000000 H 1.884238000 -2.025762000 0.000000000 H 2.598975000 1.203065000 0.000000000 C -2.387730000 0.242833000 0.000000000 H -0.744775000 -1.074474000 0.000000000 H -2.882557000 -0.152114000 0.891073000 H -2.494614000 1.329014000 0.000000000	E=-196.9258981 ZPE=52.54 U=337.9i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-197.0184601 C -1.196155000 -1.890603000 0.000000000 C 0.004420000 -2.151221000 0.000000000 B 0.920557000 -0.117230000 0.000000000 N 0.000000000 0.925892000 0.000000000 H -2.180119000 -1.488953000 0.000000000 H 0.895204000 -2.731030000 0.000000000 C 0.489924000 2.301063000 0.000000000 H -0.999136000 0.820919000 0.000000000 H 0.157301000 2.835388000 0.887527000 H 1.577524000 2.277757000 0.000000000

	H -2.882557000 -0.152114000 -0.891073000	H 0.157301000 2.835388000 -0.887527000
NHMe TS2	E=-197.4318103 ZPE=52.23 U=293.8i C -1.704626000 0.858658000 -0.116399000 C -1.919188000 -0.316106000 0.118298000 B 0.092724000 -1.369105000 -0.070716000 N 1.246312000 -0.607570000 -0.072178000 H -1.379759000 1.839368000 -0.366050000 H -2.470449000 -1.194067000 0.358380000 H 2.056392000 -1.199245000 -0.239257000 C 1.566875000 0.811383000 0.103895000 H 0.812578000 1.274270000 0.737239000 H 2.537742000 0.921722000 0.591203000 H 1.597324000 1.332866000 -0.857449000	E=-196.9249453 ZPE=52.56 U=340.4i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-197.017452 C -1.598235000 0.876131000 -0.143186000 C -1.879771000 -0.286671000 0.140772000 B 0.051983000 -1.395473000 -0.090046000 N 1.197276000 -0.611761000 -0.082838000 H -1.187257000 1.806450000 -0.450371000 H -2.477952000 -1.114777000 0.434328000 H 2.004132000 -1.201325000 -0.256014000 C 1.515754000 0.794353000 0.125758000 H 0.806444000 1.220639000 0.827074000 H 2.514098000 0.894364000 0.544344000 H 1.473193000 1.351468000 -0.809325000
NMe_2	E=-236.7469069 ZPE=70.0 U=315.1i C -2.433974000 0.453919000 0.325372000 C -2.276497000 -0.654269000 -0.162600000 B -0.083254000 -1.117342000 -0.123483000 N 0.864617000 -0.111415000 -0.053248000 H -2.352172000 1.397568000 0.809065000 H -2.590177000 -1.568066000 -0.610659000 C 2.240629000 -0.555901000 0.211309000 C 0.716215000 1.330260000 -0.237497000 H 2.611656000 -0.113725000 1.141753000 H 2.264121000 -1.641920000 0.310057000 H 2.900402000 -0.261575000 -0.611387000 H 0.847865000 1.859982000 0.713200000 H 1.471873000 1.696210000 -0.940449000 H -0.267857000 1.554094000 -0.640931000	E=-236.1384042 ZPE=70.68 U=365.8i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-236.2511505 C -2.338387000 0.469824000 0.349436000 C -2.239201000 -0.643641000 -0.170675000 B -0.082060000 -1.166390000 -0.107259000 N 0.829149000 -0.118119000 -0.055427000 H -2.170609000 1.384577000 0.864909000 H -2.593872000 -1.523570000 -0.651353000 C 2.208369000 -0.526771000 0.213214000 C 0.667998000 1.310228000 -0.257856000 H 2.566541000 -0.057708000 1.130285000 H 2.254265000 -1.606679000 0.332555000 H 2.854747000 -0.231340000 -0.613785000 H 0.755991000 1.847589000 0.688725000 H 1.445971000 1.673816000 -0.930519000 H -0.299448000 1.514256000 -0.701246000

Intermediate and transition states of BF addition to acetylene

	MP2/6-311+G**	
BF TS1	E=-201.5076815 ZPE=19.60 U=523.1i C 0.440638000 -1.481703000 0.000000000 C 1.188400000 -0.476006000 0.000000000 B 0.000000000 1.130606000 0.000000000 H -0.493120000 -2.005425000 0.000000000 H 2.191738000 -0.100099000 0.000000000 F -1.274761000 0.910972000 0.000000000	
BF TS2	E=-201.5533317 ZPE=21.00 U=389.3i C -0.187425000 -1.376061000 0.000000000 C 1.017813000 -0.684158000 0.000000000 B 0.000000000 0.288366000 0.000000000 H -1.193214000 -0.910373000 0.000000000 H 2.009347000 -1.110513000 0.000000000 F -0.644273000 1.437819000 0.000000000	
BF INT	E=-201.5533672 ZPE=21.51 C -0.215162000 -1.392182000 0.000000000	

	C 0.996833000 -0.705536000 0.000000000 B 0.000000000 0.288436000 0.000000000 H -1.177349000 -0.813029000 0.000000000 H 1.983801000 -1.139457000 0.000000000 F -0.610720000 1.455180000 0.000000000	

Transition states for the addition of borylenes BR to ethylene

R	B3LYP/6-311+G**	MP2/cc-pVTZ
F	E=-203.2937041 ZPE=35.02 U=357.4i C 1.170461000 -0.270610000 0.000000000 C 0.247592000 -1.360786000 0.000000000 B 0.000000000 0.861986000 0.000000000 F -1.294317000 1.008125000 0.000000000 H 1.781421000 -0.106761000 0.886683000 H 1.781421000 -0.106761000 -0.886683000 H -0.211150000 -1.690582000 0.923222000 H -0.211150000 -1.690582000 -0.923222000	E=-202.8561694 ZPE=35.27 U=394.6i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-202.9332829 C 1.145778000 -0.352082000 0.000000000 B 0.000000000 1.084955000 0.000000000 F -1.290590000 1.018935000 0.000000000 C 0.277521000 -1.441609000 0.000000000 H 1.711633000 -0.136062000 0.898063000 H 1.711633000 -0.136062000 -0.898063000 H -0.173875000 -1.780460000 0.922235000 H -0.173875000 -1.780460000 -0.922235000
Cl	E=-563.6221787 ZPE=34.13 U=297.7i C 1.820009000 0.107094000 0.000000000 C 1.405684000 -1.192204000 0.000000000 B 0.000000000 1.076801000 0.000000000 H 2.180329000 0.574854000 0.909379000 H 2.180329000 0.574854000 -0.909379000 H 1.175173000 -1.712019000 0.922316000 H 1.175173000 -1.712019000 -0.922316000 Cl -1.533245000 0.200058000 0.000000000	E=-562.8072095 ZPE=34.53 U=362.0i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-562.8986737 C 1.833919000 0.090809000 0.000000000 C 1.340850000 -1.178233000 0.000000000 B 0.000000000 1.093812000 0.000000000 H 2.190521000 0.547928000 0.912032000 H 2.190521000 0.547928000 -0.912032000 H 1.078468000 -1.673674000 0.923743000 H 1.078468000 -1.673674000 -0.923743000 Cl -1.505094000 0.194528000 0.000000000
Br	E=-2677.5371628 ZPE=33.87 U=269.1i C 0.306512000 -2.430622000 0.000000000 C -1.010363000 -2.097546000 0.000000000 B 1.140114000 -0.475865000 0.000000000 H 0.808552000 -2.732152000 0.912279000 H 0.808552000 -2.732152000 -0.912279000 H -1.547287000 -1.911185000 0.922394000 H -1.547287000 -1.911185000 -0.922394000 Br 0.000000000 1.109572000 0.000000000	E=-2675.7807715 ZPE=34.30 U=296.0i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2675.8706322 C 0.281215000 -2.432519000 0.000000000 C -1.002673000 -1.997649000 0.000000000 B 1.163937000 -0.454333000 0.000000000 H 0.770686000 -2.733984000 0.914942000 H 0.770686000 -2.733984000 -0.914942000 H -1.516154000 -1.773069000 0.923673000 H -1.516154000 -1.773069000 -0.923673000 Br 0.000000000 1.081908000 0.000000000
CH_3	E=-143.2749961 ZPE=55.33 U=192.8i C 1.418893000 -0.569959000 0.000000000 C 0.430661000 -1.482851000 0.000000000 B 0.000000000 1.373983000 0.000000000 H 1.898483000 -0.244813000 0.914850000 H 1.898483000 -0.244813000 -0.914850000 H 0.000749000 -1.857027000 0.922670000 H 0.000749000 -1.857027000 -0.922670000 C -1.526983000 1.088682000 0.000000000 H -2.040370000 2.058603000 0.000000000 H -1.846760000 0.529963000 -0.888187000 H -1.846760000 0.529963000 0.888187000	E=-142.8600253 ZPE=56.10 U=196.5i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-142.9501652 C 1.440539000 -0.547850000 0.000000000 C 0.399406000 -1.399162000 0.000000000 B 0.000000000 1.373283000 0.000000000 H 1.919187000 -0.237554000 0.916703000 H 1.919187000 -0.237554000 -0.916703000 H -0.044838000 -1.742761000 0.923432000 H -0.044838000 -1.742761000 -0.923432000 C -1.518167000 0.997664000 0.000000000 H -2.073269000 1.938074000 0.000000000 H -1.803050000 0.426113000 -0.885180000 H -1.803050000 0.426113000 0.885180000

Ph TS1	E=-335.0538471 ZPE=90.13 U=146.3i C 3.457713000 -0.101711000 0.000000000 C 2.965095000 -1.353392000 0.000000000 B 1.392077000 1.200000000 0.000000000 H 3.748419000 0.398100000 0.915148000 H 3.748419000 0.398100000 -0.915148000 H 2.750096000 -1.878871000 0.924185000 H 2.750096000 -1.878871000 -0.924185000 C 0.000000000 0.526594000 0.000000000 C -0.380696000 -0.831861000 0.000000000 C -1.721485000 -1.194709000 0.000000000 C -2.714164000 -0.210736000 0.000000000 C -2.366356000 1.138243000 0.000000000 C -1.022358000 1.502341000 0.000000000 H 0.382519000 -1.598594000 0.000000000 H -1.999910000 -2.242693000 0.000000000 H -3.759528000 -0.499726000 0.000000000 H -3.137345000 1.900426000 0.000000000 H -0.749652000 2.553517000 0.000000000	E=-334.1838925 ZPE=90.49 U=141.4i CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-334.3122185 C 0.921839000 1.339070000 0.047256000 C -0.014130000 0.425362000 -0.467630000 C 0.362486000 -0.920517000 -0.607296000 C 1.629698000 -1.342263000 -0.224068000 C 2.537372000 -0.428235000 0.316593000 C 2.184269000 0.912065000 0.453934000 B -1.329896000 1.093185000 -0.975792000 C -3.353272000 0.112213000 0.078674000 C -2.604981000 -0.686079000 0.857700000 H -3.755989000 -0.230752000 -0.863436000 H -3.656831000 1.096488000 0.400961000 H -2.334419000 -1.684357000 0.545239000 H -2.225308000 -0.346850000 1.811088000 H -0.337228000 -1.635375000 -1.021602000 H 1.912892000 -2.380016000 -0.337112000 H 3.520086000 -0.761569000 0.621662000 H 2.891969000 1.620030000 0.863240000 H 0.654624000 2.386790000 0.127941000
Ph TS2[a]	E=-335.0529296 ZPE=89.72 U=187.2i; 23.6i C 3.344969000 -0.002696000 -0.003127000 C 2.687830000 0.013531000 1.171189000 B 1.365585000 -0.017946000 -1.387614000 H 3.699226000 0.905606000 -0.474662000 H 3.696065000 -0.924073000 -0.451068000 H 2.391034000 0.942037000 1.645594000 H 2.387920000 -0.901442000 1.669329000 C 0.010459000 -0.007357000 -0.630766000 C -0.658726000 -1.213629000 -0.352237000 C -1.936033000 -1.205799000 0.199177000 C -2.571566000 0.006830000 0.470087000 C -1.929395000 1.212397000 0.183344000 C -0.652026000 1.206103000 -0.367722000 H -0.175597000 -2.161296000 -0.570492000 H -2.439500000 -2.141745000 0.414930000 H -3.568818000 0.012353000 0.895749000 H -2.427776000 2.153802000 0.386823000 H -0.163556000 2.148209000 -0.597810000	E=-334.1842106 ZPE=90.70 U=102.2i CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-334.3126722 C 3.443804000 -0.370506000 0.064595000 C 3.026114000 0.903761000 0.120495000 B 1.180562000 -1.444854000 -0.193949000 H 3.758710000 -0.824006000 -0.863023000 H 3.571234000 -0.963617000 0.957817000 H 2.947254000 1.505848000 -0.774124000 H 2.750760000 1.363375000 1.059317000 C -0.059345000 -0.514165000 -0.097546000 C -0.237552000 0.880044000 -0.132241000 C -1.510662000 1.430710000 -0.052825000 C -2.629124000 0.602752000 0.068077000 C -2.477144000 -0.780758000 0.102947000 C -1.202149000 -1.334391000 0.015522000 H 0.621799000 1.527329000 -0.224021000 H -1.637251000 2.504420000 -0.081713000 H -3.616865000 1.038975000 0.133167000 H -3.343819000 -1.420953000 0.194053000 H -1.078276000 -2.411785000 0.034135000
NH_2	E=-159.3787589 ZPE=49.81 U=251.3i C 0.357319000 -1.498720000 0.000000000 C 1.310764000 -0.538690000 0.000000000 H 1.806000000 -0.234653000 0.913235000 H -0.063351000 -1.879742000 0.924340000 H -0.063351000 -1.879742000 -0.924340000 H 1.806000000 -0.234653000 -0.913235000 B 0.000000000 1.296765000 0.000000000 N -1.376999000 1.110777000 0.000000000 H -1.953026000 1.943241000 0.000000000 H -1.901781000 0.250749000 0.000000000	E=-158.9577022 ZPE=50.38 U=293.9i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-159.0412863 C -1.254472000 0.760197000 0.000000000 C -1.297050000 -0.591668000 0.000000000 H -1.430476000 -1.148695000 0.914776000 H -1.202033000 1.316521000 0.925566000 H -1.202033000 1.316521000 -0.925566000 H -1.430476000 -1.148695000 -0.914776000 B 0.916894000 -0.898474000 0.000000000 N 1.696212000 0.258152000 0.000000000 H 2.694826000 0.115727000 0.000000000 H 1.421365000 1.222757000 0.000000000
NHMe TS1	E=-198.6932844 ZPE=67.85 U=228.1i C 1.803831000 -1.234350000 0.000000000 C 2.096278000 0.086681000 0.000000000	E=-198.1682535 ZPE=68.75 U=256.2i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-198.272416 C 1.945308000 0.779721000 0.000000000 C 2.019454000 -0.570001000 0.000000000

	B 0.000000000 0.941876000 0.000000000 N -1.058748000 0.045517000 0.000000000 H 2.350488000 0.608826000 0.913343000 H 1.653918000 -1.781618000 0.924442000 H 1.653918000 -1.781618000 -0.924442000 H 2.350488000 0.608826000 -0.913343000 C -2.443284000 0.527717000 0.000000000 H -0.949771000 -0.956766000 0.000000000 H -2.977775000 0.187371000 0.890808000 H -2.433201000 1.619319000 0.000000000 H -2.977775000 0.187371000 -0.890808000	B -0.207418000 -0.934964000 0.000000000 N -0.999799000 0.211354000 0.000000000 H 2.159554000 -1.124416000 -0.915276000 H 1.884099000 1.335144000 -0.925624000 H 1.884099000 1.335144000 0.925624000 H 2.159554000 -1.124416000 0.915276000 C -2.451549000 0.058130000 0.000000000 H -0.661801000 1.157257000 0.000000000 H -2.892951000 0.507293000 -0.887374000 H -2.683196000 -1.005052000 0.000000000 H -2.892951000 0.507293000 0.887374000
NHMe TS2	E=-198.6915095 ZPE=67.80 U=241.3i C 1.483485000 -1.105968000 0.000000000 C 1.917822000 0.178251000 0.000000000 B 0.000000000 1.364292000 0.000000000 N -1.248621000 0.774150000 0.000000000 C -1.816443000 -0.576145000 0.000000000 H 2.242209000 0.661019000 0.912513000 H 1.285467000 -1.637633000 0.924182000 H 1.285467000 -1.637633000 -0.924182000 H 2.242209000 0.661019000 -0.912513000 H -1.955352000 1.508125000 0.000000000 H -2.433468000 -0.738060000 0.888365000 H -2.433468000 -0.738060000 -0.888365000 H -1.001897000 -1.296110000 0.000000000	E=-197.3491924 ZPE=68.62i U=276.2i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-198.2704388 C 1.427514000 -1.063611000 0.000000000 C 1.912382000 0.201281000 0.000000000 B 0.000000000 1.380219000 0.000000000 N -1.228224000 0.737195000 0.000000000 C -1.776827000 -0.611229000 0.000000000 H 2.233466000 0.676147000 0.914245000 H 1.211001000 -1.579388000 0.925207000 H 1.211001000 -1.579388000 -0.925207000 H 2.233466000 0.676147000 -0.914245000 H -1.941078000 1.462724000 0.000000000 H -2.387930000 -0.780869000 0.884888000 H -2.387930000 -0.780869000 -0.884888000 H -0.952840000 -1.314612000 0.000000000
NMe_2	E=-238.0057917 ZPE=85.53 U=260.2i C -0.353425000 -2.392090000 0.000000000 C 0.978960000 -2.118700000 0.000000000 B 1.071126000 0.086120000 0.000000000 N 0.000000000 0.962502000 0.000000000 H 1.560194000 -2.181018000 0.910543000 H -0.914050000 -2.477824000 0.924164000 H -0.914050000 -2.477824000 -0.924164000 H 1.560194000 -2.181018000 -0.910543000 C 0.384067000 2.385871000 0.000000000 C -1.447976000 0.754795000 0.000000000 H -0.012235000 2.883505000 0.891112000 H 1.469960000 2.477844000 0.000000000 H -0.012235000 2.883505000 -0.891112000 H -1.897181000 1.216487000 0.886624000 H -1.897181000 1.216487000 -0.886624000 H -1.668802000 -0.307511000 0.000000000	E=-237.3794252 ZPE=86.69 *U*=292.9i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-237.5037308 C -0.363285000 -2.319774000 0.000000000 C 0.979324000 -2.122578000 0.000000000 B 1.108029000 0.095657000 0.000000000 N 0.000000000 0.934873000 0.000000000 H 1.550782000 -2.185959000 0.913059000 H -0.920172000 -2.373729000 0.925141000 H -0.920172000 -2.373729000 -0.925141000 H 1.550782000 -2.185959000 -0.913059000 C 0.365010000 2.357130000 0.000000000 C -1.438469000 0.732111000 0.000000000 H -0.040014000 2.843365000 0.888109000 H 1.446502000 2.462932000 0.000000000 H -0.040014000 2.843365000 -0.888109000 H -1.881043000 1.196253000 0.883335000 H -1.881043000 1.196253000 -0.883335000 H -1.661228000 -0.326516000 0.000000000

[a] second-order saddle point at the B3LYP/6-311+G** level of theory

Intermediate and transition states for the BF addition to ethylene

	MP2/6-311+G**	MP2/cc-pVTZ
BF TS1	E=-202.7346035 ZPE=35.10 U=393.2i C 1.145322000 -0.345512000 0.000000000 B 0.000000000 1.096680000 0.000000000 F -1.296459000 1.014779000 0.000000000 C 0.284884000 -1.450310000 0.000000000 H 1.714983000 -0.131643000 0.902031000 H 1.714983000 -0.131643000 -0.902031000 H -0.171534000 -1.789093000 0.925757000 H -0.171534000 -1.789093000 -0.925757000	

BF TS2	E=-202.7338762 ZPE= 35.40 U=449.4i C 1.184608000 -0.252625000 0.000000000 C 0.239769000 -1.347988000 0.000000000 B 0.000000000 0.809772000 0.000000000 F -1.291259000 0.998993000 0.000000000 H 1.795604000 -0.101073000 0.890402000 H 1.795604000 -0.101073000 -0.890402000 H -0.258068000 -1.616988000 0.926395000 H -0.258068000 -1.616988000 -0.926395000	E=-202.8561545 ZPE=35.53 U=409.9i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-202.9283327 C 1.179043000 -0.255613000 0.000000000 C 0.241912000 -1.348379000 0.000000000 B 0.000000000 0.817894000 0.000000000 F -1.288079000 0.997326000 0.000000000 H 1.787277000 -0.102431000 0.886339000 H 1.787277000 -0.102431000 -0.886339000 H -0.253788000 -1.618297000 0.921886000 H -0.253788000 -1.618297000 -0.921886000
BF INT	E=-202.7355429 ZPE=35.62 C 1.128668000 -0.251482000 0.000000000 C 0.308475000 -1.428886000 0.000000000 B 0.000000000 0.978062000 0.000000000 F -1.303199000 0.977594000 0.000000000 H 1.734317000 -0.071767000 0.889465000 H 1.734317000 -0.071767000 -0.889465000 H -0.181349000 -1.731453000 0.922621000 H -0.181349000 -1.731453000 -0.922621000	E=-202.8571577 ZPE=35.73 C 1.132990000 -0.256976000 0.000000000 C 0.297584000 -1.414684000 0.000000000 B 0.000000000 0.962334000 0.000000000 F -1.297484000 0.978229000 0.000000000 H 1.735553000 -0.077524000 0.885810000 H 1.735553000 -0.077524000 -0.885810000 H -0.188600000 -1.715363000 0.919208000 H -0.188600000 -1.715363000 -0.919208000

Transition states for the insertion of borylenes BR into a C-H bond of methane via approach A

R	B3LYP/6-311+G**	MP2/cc-pVTZ
H	E=-65.8156923 ZPE=32.27 U=1007.2i C -0.042387000 -0.799727000 0.000000000 H 0.543659000 -0.960390000 0.902667000 H -0.940999000 -1.419150000 0.000000000 H -0.828768000 0.301660000 0.000000000 H 0.543659000 -0.960390000 -0.902667000 B -0.042387000 1.318033000 0.000000000 H 1.148709000 1.246472000 0.000000000	E=-65.5971697 ZPE=32.86 U=1065.0i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-65.650662 C -0.042722000 -0.779853000 0.000000000 H 0.544530000 -0.932706000 0.899892000 H -0.928900000 -1.412130000 0.000000000 H -0.835901000 0.278082000 0.000000000 H 0.544530000 -0.932706000 -0.899892000 B -0.042722000 1.293613000 0.000000000 H 1.145683000 1.210512000 0.000000000
F	E=-165.1564254 ZPE=28.91 U=1519.8i C -1.055049000 -0.871727000 0.000000000 B 0.000000000 0.889536000 0.000000000 F 1.211411000 0.407384000 0.000000000 H -0.618934000 -1.291615000 0.908420000 H -2.141825000 -0.968746000 0.000000000 H -1.192715000 0.668199000 0.000000000 H -0.618934000 -1.291615000 -0.908420000	E=-164.804487 ZPE=29.29 U=1566.2i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-164.8640009 C -1.048992000 -0.847109000 0.000000000 B 0.000000000 0.880460000 0.000000000 F 1.203861000 0.386390000 0.000000000 H -0.605429000 -1.259123000 0.905332000 H -2.131788000 -0.952737000 0.000000000 H -1.198154000 0.673827000 0.000000000 H -0.605429000 -1.259123000 -0.905332000
Cl	E=-525.4926038 ZPE=28.35 U=1359.2i C -1.841162000 -0.014702000 0.000000000 B 0.000000000 1.013905000 0.000000000 Cl 1.084908000 -0.329296000 0.000000000 H -1.698956000 -0.597728000 0.908590000 H -2.805827000 0.496728000 0.000000000 H -1.192718000 1.315455000 0.000000000 H -1.698956000 -0.597728000 -0.908590000	E=-524.7691015 ZPE=28.71 U=1401.4i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-524.8434428 C -1.794360000 -0.004875000 0.000000000 B 0.000000000 1.018333000 0.000000000 Cl 1.058559000 -0.334543000 0.000000000 H -1.627171000 -0.580540000 0.906160000 H -2.772569000 0.474802000 0.000000000 H -1.202436000 1.311092000 0.000000000 H -1.627171000 -0.580540000 -0.906160000

Br	E=-2639.4078271 ZPE=28.05 U=1348.2i C -0.566706000 -2.247670000 0.000000000 B 1.008163000 -0.831362000 0.000000000 Br 0.000000000 0.768424000 0.000000000 H 0.890573000 -2.060379000 0.000000000 H -0.376584000 -3.323220000 0.000000000 H -1.077284000 -1.934197000 0.908433000 H -1.077284000 -1.934197000 -0.908433000	E=-2637.7439297 ZPE=28.45 U=1375.7i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2637.8170014 C -0.562720000 -2.185720000 0.000000000 B 1.009218000 -0.823956000 0.000000000 Br 0.000000000 0.749967000 0.000000000 H 0.859509000 -2.058373000 0.000000000 H -0.419320000 -3.266223000 0.000000000 H -1.054979000 -1.845068000 0.906057000 H -1.054979000 -1.845068000 -0.906057000
CH_3	E=-105.162061 ZPE=50.05 U=1172.3i C 1.461969000 -0.204477000 0.000086000 B -0.364393000 0.941027000 -0.014773000 H 1.343006000 -0.697758000 -0.963578000 H 2.462817000 0.218096000 0.105290000 H 0.897382000 1.078955000 0.027191000 H 1.220904000 -0.856299000 0.838013000 C -1.345873000 -0.256443000 -0.009030000 H -2.365800000 0.059200000 -0.239452000 H -1.072763000 -1.094572000 -0.661434000 H -1.360159000 -0.647233000 1.021497000	E=-104.8393712 ZPE=50.96 U=1186.2i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-104.9119778 C 1.412533000 -0.208634000 -0.000040000 B -0.338823000 0.955708000 -0.018540000 H 1.275818000 -0.671497000 -0.973467000 H 2.431390000 0.156035000 0.122367000 H 0.936492000 1.058923000 0.041759000 H 1.127806000 -0.864028000 0.817576000 C -1.312221000 -0.257162000 -0.010841000 H -2.321968000 0.041801000 -0.279656000 H -1.010470000 -1.119616000 -0.607014000 H -1.346825000 -0.585384000 1.036417000
Ph	E=-296.9425655 ZPE=84.53 U=1128.5i C 3.208556000 -0.399862000 0.103895000 B 1.736420000 1.205761000 -0.128656000 H 2.977634000 -0.998575000 -0.775182000 H 4.280264000 -0.202729000 0.164799000 H 2.982649000 0.956353000 -0.065001000 H 2.838957000 -0.831642000 1.031286000 C 0.388594000 0.464163000 -0.060906000 C -0.727503000 1.330259000 0.003008000 C -2.028910000 0.840338000 0.064711000 C -2.249990000 -0.534888000 0.042720000 C -1.168569000 -1.415999000 -0.032927000 C 0.129787000 -0.924091000 -0.077145000 H -0.551478000 2.400264000 0.003220000 H -2.866259000 1.526599000 0.120997000 H -3.262065000 -0.923032000 0.081806000 H -1.343130000 -2.486151000 -0.052264000 H 0.949544000 -1.629411000 -0.126514000	E=-296.1654501 ZPE=85.35 U=1126.3i CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-296.2780856 C -2.592466000 1.800590000 0.000000000 B -0.483300000 2.078515000 0.000000000 H -2.669094000 1.210846000 0.907851000 H -3.319590000 2.611472000 0.000000000 H -1.609379000 2.701562000 0.000000000 H -2.669094000 1.210846000 -0.907851000 C 0.000000000 0.607561000 0.000000000 C 1.408792000 0.515645000 0.000000000 C 2.058641000 -0.714994000 0.000000000 C 1.310563000 -1.889572000 0.000000000 C -0.083656000 -1.827107000 0.000000000 C -0.730396000 -0.597006000 0.000000000 H 1.981674000 1.434194000 0.000000000 H 3.139050000 -0.758615000 0.000000000 H 1.808192000 -2.850162000 0.000000000 H -0.663528000 -2.740200000 0.000000000 H -1.810594000 -0.583212000 0.000000000
NH_2	E=-121.2617424 ZPE=44.61 U=1248.0i C -1.186102000 -0.815915000 0.000000000 B 0.000000000 0.965635000 0.000000000 N 1.237827000 0.356601000 0.000000000 H -0.784668000 -1.254639000 0.912508000 H -2.276517000 -0.841780000 0.000000000 H -1.201694000 0.640145000 0.000000000 H -0.784668000 -1.254639000 -0.912508000 H 2.073400000 0.921937000 0.000000000 H 1.425970000 -0.639913000 0.000000000	E=-120.9319485 ZPE=45.26 U=1291.3i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-120.9984386 C -1.164787000 -0.770538000 0.000000000 B 0.000000000 0.968108000 0.000000000 N 1.217804000 0.312366000 0.000000000 H -0.753107000 -1.197641000 0.910185000 H -2.251918000 -0.817933000 0.000000000 H -1.209942000 0.649095000 0.000000000 H -0.753107000 -1.197641000 -0.910185000 H 2.068514000 0.847202000 0.000000000 H 1.363660000 -0.686960000 0.000000000
NHMe TS1	E=-160.5712607 ZPE=62.36 *U*=1270.7i	E=-160.1425681 ZPE=63.31 *U*=1274.1i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-160.2297748

	C 0.909747000 -1.970539000 0.000000000 B -0.733995000 -0.586728000 0.000000000 N 0.000000000 0.576951000 0.000000000 C -0.597263000 1.914500000 0.000000000 H 1.392423000 -1.624234000 0.912774000 H 0.806974000 -3.056429000 0.000000000 H -0.537704000 -1.817191000 0.000000000 H 1.392423000 -1.624234000 -0.912774000 H 1.014911000 0.586885000 0.000000000 H -0.295983000 2.475953000 -0.889462000 H -1.681990000 1.814515000 0.000000000 H -0.295983000 2.475953000 0.889462000	C 0.920460000 -1.903786000 0.000000000 B -0.733468000 -0.613271000 0.000000000 N 0.000000000 0.556063000 0.000000000 C -0.612579000 1.879021000 0.000000000 H 1.378123000 -1.528061000 0.910737000 H 0.882303000 -2.991481000 0.000000000 H -0.496226000 -1.843270000 0.000000000 H 1.378123000 -1.528061000 -0.910737000 H 1.011857000 0.571906000 0.000000000 H -0.321442000 2.441734000 -0.885750000 H -1.691238000 1.758003000 0.000000000 H -0.321442000 2.441734000 0.885750000
NHMe TS2	E=-160.5712607 ZPE=62.36 *U*=1270.7i C 0.694127000 -1.729514000 0.000000000 B 1.216346000 0.414797000 0.000000000 N 0.000000000 1.063032000 0.000000000 H 1.743909000 -0.709560000 0.000000000 H 1.479727000 -2.486818000 0.000000000 H 0.102238000 -1.788892000 0.912131000 H 0.102238000 -1.788892000 -0.912131000 H 0.099469000 2.070817000 0.000000000 C -1.408327000 0.653113000 0.000000000 H -1.918810000 1.038097000 -0.887403000 H -1.486493000 -0.429651000 0.000000000 H -1.918810000 1.038097000 0.887403000	E=-160.1375175 ZPE=63.23 *U*=1307.2i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-160.2252617 C -1.674669000 -0.474951000 -0.000663000 B -0.432137000 1.242306000 0.002619000 N 0.815901000 0.640542000 -0.003444000 H -1.644940000 0.929415000 0.008464000 H -2.761435000 -0.419990000 0.033398000 H -1.341042000 -0.931086000 -0.928409000 H -1.285060000 -0.964297000 0.887304000 H 1.568983000 1.309875000 0.004377000 C 1.284586000 -0.743629000 0.001269000 H 2.366006000 -0.753747000 -0.101120000 H 1.026290000 -1.248343000 0.929795000 H 0.861067000 -1.305676000 -0.826435000
NMe_2	E=-199.8862166 ZPE=79.77 *U*=1275.8i C 0.602040000 -2.310674000 0.000000000 B 1.179990000 -0.164610000 0.000000000 N 0.000000000 0.547594000 0.000000000 C -1.398647000 0.112044000 0.000000000 C 0.115099000 2.014735000 0.000000000 H 1.670041000 -1.305457000 0.000000000 H 1.371974000 -3.084337000 0.000000000 H 0.009568000 -2.356807000 0.912543000 H 0.009568000 -2.356807000 -0.912543000 H -0.368904000 2.433375000 0.889532000 H 1.166352000 2.296813000 0.000000000 H -0.368904000 2.433375000 -0.889532000 H -1.912498000 0.501654000 0.885570000 H -1.912498000 0.501654000 -0.885570000 H -1.475602000 -0.970206000 0.000000000	E=-199.351209 ZPE=81.05 *U*=1298.8i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-199.4588231 C 0.610286000 -2.228076000 0.000000000 B 1.206136000 -0.160041000 0.000000000 N 0.000000000 0.519622000 0.000000000 C -1.388057000 0.081229000 0.000000000 C 0.086219000 1.980770000 0.000000000 H 1.686456000 -1.316859000 0.000000000 H 1.339464000 -3.037210000 0.000000000 H 0.019718000 -2.241111000 0.911346000 H 0.019718000 -2.241111000 -0.911346000 H -0.407215000 2.384315000 0.886118000 H 1.129278000 2.280074000 0.000000000 H -0.407215000 2.384315000 -0.886118000 H -1.897439000 0.472210000 0.882384000 H -1.897439000 0.472210000 -0.882384000 H -1.466694000 -0.997527000 0.000000000

Transition states for the insertion of borylenes BR into a C-H bond of methane via approach B

R	B3LYP/6-311+G**	MP2/cc-pVTZ
H	E=-65.7995212 ZPE=31.94 U=863.54i C 0.106547000 -0.688257000 0.000000000 H -0.701670000 -1.446132000 0.000000000 H 0.720979000 -0.865540000 0.882121000 H -0.895748000 0.190454000 0.000000000 H 0.720979000 -0.865540000 -0.882121000 B 0.106547000 1.103451000 0.000000000 H -1.016555000 1.599046000 0.000000000	E=-65.5827349 ZPE=32.39 U=888.8i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-65.6350102 C -0.689093000 0.002471000 -0.000028000 H -1.289029000 0.925369000 -0.000923000 H -0.962747000 -0.572858000 0.879745000 H 0.350335000 0.854858000 -0.000259000 H -0.963448000 -0.575053000 -0.878132000 B 1.062893000 -0.285627000 -0.000052000 H 1.684982000 0.780995000 -0.000003000

F	E=-165.1042898 ZPE=29.02 U=1375.9i C -1.449163000 0.036899000 -0.004238000 B 0.239861000 -0.407372000 -0.028661000 F 1.485501000 0.097158000 0.002830000 H -1.981501000 0.943459000 -0.361600000 H -1.628671000 -0.063152000 1.068998000 H -0.334448000 0.874255000 -0.065283000 H -1.929218000 -0.813515000 -0.498853000	E=-164.748329 ZPE=29.61 U=1522.4i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-164.8118554 C -1.436246000 0.034309000 -0.005847000 B 0.235794000 -0.401367000 -0.034557000 F 1.475647000 0.093991000 0.004198000 H -1.972413000 0.920481000 -0.389889000 H -1.594067000 -0.015227000 1.073791000 H -0.342345000 0.885016000 -0.073014000 H -1.933492000 -0.835202000 -0.440799000
Cl	E=-525.4563562 ZPE=28.58 U=1089.2i C -1.996784000 0.097576000 -0.001426000 B -0.386169000 -0.565910000 -0.018431000 Cl 1.284113000 0.067308000 0.001126000 H -2.356631000 1.126166000 -0.219075000 H -2.262466000 -0.145206000 1.027932000 H -0.768133000 0.699610000 -0.061681000 H -2.531136000 -0.580708000 -0.665607000	E=-524.7309714 ZPE=29.28 U=1147.8i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-524.8060053 C -1.969656000 0.095942000 -0.002681000 B -0.386517000 -0.564650000 -0.027792000 Cl 1.267703000 0.065714000 0.002068000 H -2.323609000 1.100788000 -0.294028000 H -2.176743000 -0.043648000 1.058784000 H -0.742829000 0.703627000 -0.086824000 H -2.557251000 -0.630310000 -0.558041000
Br	E=-2639.3782956 ZPE=28.26 U=1017.9i C -2.537438000 0.126621000 -0.001514000 B -0.976256000 -0.638384000 -0.015325000 Br 0.860286000 0.035002000 0.000418000 H -2.815109000 1.182320000 -0.196513000 H -2.838140000 -0.124116000 1.016421000 H -1.250441000 0.646267000 -0.054395000 H -3.100428000 -0.497336000 -0.694441000	E=-2637.7125338 ZPE=28.95 U=1037.2i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2637.7858651 C -2.495492000 0.124024000 -0.002785000 B -0.961314000 -0.635996000 -0.024900000 Br 0.845921000 0.034304000 0.000866000 H -2.770320000 1.154725000 -0.283188000 H -2.724018000 -0.015282000 1.054522000 H -1.212393000 0.650016000 -0.083925000 H -3.120991000 -0.554251000 -0.576498000
CH_3	E=-105.1314962 ZPE=50.26 U=938.9i C -1.529111000 0.091029000 -0.000503000 B 0.095631000 -0.610765000 -0.015421000 C 1.522275000 0.103865000 -0.002466000 H -1.889459000 1.142886000 -0.089415000 H -1.879209000 -0.293095000 0.956502000 H -0.322748000 0.645275000 -0.038919000 H -2.012094000 -0.478642000 -0.791695000 H 2.329854000 -0.630900000 -0.041811000 H 1.680570000 0.816867000 -0.825940000 H 1.655947000 0.682070000 0.926203000	E=-104.8093112 ZPE=51.47 U=952.5i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-104.880752 C 1.505752000 0.096620000 -0.001260000 B -0.079049000 -0.629735000 -0.040708000 C -1.503429000 0.107597000 -0.006314000 H 1.836034000 1.133855000 -0.202464000 H 2.086323000 -0.557074000 -0.643552000 H 0.282229000 0.627108000 -0.101027000 H 1.758440000 -0.138866000 1.031454000 H -2.310440000 -0.612853000 -0.112623000 H -1.600212000 0.549540000 0.994888000 H -1.671068000 0.921667000 -0.717694000
Ph	E=-296.9187753 ZPE=84.41 U=827.9i C 3.285352000 0.120894000 0.356092000 B 1.926160000 -0.443260000 -0.612667000 C 0.424837000 -0.184106000 -0.265210000 H 3.312742000 0.682807000 1.316592000 H 3.801034000 0.727816000 -0.386745000 H 1.972504000 0.151977000 0.560196000 H 3.844946000 -0.801420000 0.498173000 C -0.451273000 -1.281996000 -0.095904000 C -1.803860000 -1.086861000 0.166221000 C -2.344443000 0.198178000 0.201328000	E=-296.1433519 ZPE=85.00 U=951.7i CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-296.2532249 C 3.148751000 0.136576000 0.429759000 B 1.959351000 -0.453848000 -0.718630000 C 0.445555000 -0.196656000 -0.296279000 H 2.998798000 0.647486000 1.399105000 H 3.712187000 0.806013000 -0.214123000 H 1.799808000 0.072030000 0.478878000 H 3.742961000 -0.755506000 0.603407000 C -0.427757000 -1.287729000 -0.096788000 C -1.774274000 -1.081652000 0.183016000 C -2.304178000 0.207847000 0.214866000

	C -1.504742000 1.295657000 -0.004895000 C -0.142882000 1.114920000 -0.205906000 H -0.064092000 -2.290211000 -0.189508000 H -2.447305000 -1.948588000 0.309003000 H -3.404293000 0.344027000 0.374125000 H -1.912807000 2.300752000 0.010713000 H 0.488532000 1.989025000 -0.339573000	C -1.464313000 1.298746000 -0.011147000 C -0.106710000 1.105705000 -0.233286000 H -0.044266000 -2.296038000 -0.183473000 H -2.419841000 -1.934961000 0.343687000 H -3.358031000 0.360544000 0.401064000 H -1.864279000 2.303927000 0.005814000 H 0.533467000 1.968722000 -0.382052000
NH_2	E=-121.2206627 ZPE=45.19 U=1117.2i C 1.502979000 0.055613000 0.000008000 B -0.175622000 -0.483585000 -0.006143000 N -1.459654000 0.091385000 0.000184000 H 1.968561000 1.070158000 -0.060877000 H 1.905383000 -0.518470000 -0.830949000 H 0.366532000 0.745620000 -0.015121000 H 1.839449000 -0.390752000 0.932352000 H -2.259485000 -0.525881000 0.005839000 H -1.742627000 1.063882000 -0.001866000	E=-120.8898336 ZPE=46.26 U=1215.i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-120.9560772 C 1.487130000 0.057922000 -0.000465000 B -0.164149000 -0.490761000 -0.019459000 N -1.447288000 0.091052000 0.000656000 H 1.932676000 1.058190000 -0.178710000 H 1.961397000 -0.620802000 -0.701272000 H 0.343147000 0.740352000 -0.047212000 H 1.756955000 -0.244471000 1.006856000 H -2.243077000 -0.524490000 0.018889000 H -1.722120000 1.060125000 -0.003057000
NHMe TS1	E=-160.5366907 ZPE=62.72 U=1063.6i C 1.257422000 1.837914000 0.000000000 B 0.000000000 0.601098000 0.000000000 N -0.084113000 -0.796344000 0.000000000 H 2.372972000 1.772607000 0.000000000 H 0.978341000 2.402946000 0.885471000 H 1.334833000 0.511560000 0.000000000 H 0.978341000 2.402946000 -0.885471000 C -1.369098000 -1.508713000 0.000000000 H 0.691892000 -1.449884000 0.000000000 H -1.466307000 -2.140614000 0.890053000 H -2.164919000 -0.765235000 0.000000000 H -1.466307000 -2.140614000 -0.890053000	E=-160.1021356 ZPE=64.08 U=1167.7i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-160.1889248 C -2.204146000 -0.069935000 0.002438000 B -0.488909000 -0.362116000 -0.023026000 N 0.685497000 0.405379000 -0.004889000 C 2.010094000 -0.214392000 0.004755000 H -2.789944000 0.861359000 -0.137252000 H -2.437296000 -0.456024000 0.989527000 H -1.169450000 0.775998000 -0.030092000 H -2.561829000 -0.775987000 -0.738973000 H 0.751565000 1.413554000 0.001746000 H 2.565622000 0.067466000 0.899849000 H 1.866161000 -1.290159000 -0.005959000 H 2.585551000 0.082684000 -0.872647000
NHMe TS2	E=-160.535067 ZPE=62.79 U=1077.4i C -1.054228000 1.755746000 0.000000000 B -0.951293000 -0.011038000 0.000000000 N 0.040416000 -1.000092000 0.000000000 H -0.280093000 2.561185000 0.000000000 H -1.665951000 1.911351000 0.884783000 H 0.000000000 0.949595000 0.000000000 H -1.665951000 1.911351000 -0.884783000 H -0.316068000 -1.948086000 0.000000000 C 1.507669000 -0.988292000 0.000000000 H 1.909065000 -1.489731000 0.887546000 H 1.909065000 -1.489731000 -0.887546000 H 1.862841000 0.045174000 0.000000000	E=-160.1006492 ZPE=64.11 U=1181.7i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-160.1874644 C -1.998291000 0.299582000 -0.000614000 B -0.604352000 -0.748641000 -0.017095000 N 0.791758000 -0.603291000 -0.000111000 H -2.104962000 1.389803000 -0.175717000 H -2.358336000 0.094552000 1.002823000 H -0.696991000 0.584460000 -0.043394000 H -2.655277000 -0.191998000 -0.710028000 H 1.298635000 -1.476484000 0.017350000 C 1.699363000 0.539271000 -0.000047000 H 2.314422000 0.556289000 0.900276000 H 2.360454000 0.519375000 -0.867002000 H 1.115076000 1.457124000 -0.034087000
NMe_2	E=-199.8495652 ZPE=80.12 U=1049.3i C -2.455756000 -0.087437000 0.000003000 B -0.772882000 -0.625475000 -0.000017000 N 0.512242000 -0.065775000 0.000002000 H -2.919788000 0.930230000 -0.000078000 H -2.824366000 -0.598538000 0.885195000 H -1.320859000 0.594091000 -0.000060000	E=-199.3146126 ZPE=81.76 U=1181.7i CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-199.4213844 C -2.431019000 -0.081906000 0.002453000 B -0.781331000 -0.636226000 -0.023534000 N 0.502250000 -0.067627000 -0.007828000 H -2.865411000 0.926864000 -0.159321000 H -2.712307000 -0.401444000 1.000919000 H -1.279299000 0.588678000 -0.034099000

	H -2.824489000 -0.598728000 -0.885027000 C 1.678910000 -0.965032000 0.000002000 C 0.949211000 1.337936000 0.000000000 H 2.298966000 -0.789898000 0.888578000 H 1.329005000 -1.993192000 0.000019000 H 2.298947000 -0.789923000 -0.888592000 H 1.559380000 1.556528000 0.885002000 H 1.559386000 1.556527000 -0.884998000 H 0.088345000 2.007896000 -0.000002000	H -2.903631000 -0.740583000 -0.718150000 C 1.668447000 -0.954771000 0.005106000 C 0.941645000 1.326095000 0.000577000 H 2.271771000 -0.772739000 0.898181000 H 1.323571000 -1.981470000 -0.000974000 H 2.294045000 -0.769254000 -0.871747000 H 1.530645000 1.537286000 0.896305000 H 1.571632000 1.534802000 -0.867347000 H 0.085452000 1.995871000 -0.020113000

Second-order saddle points for the insertion of borylenes BR into a C-H bond of methane

R		MP2/cc-pVTZ
H		E=-65.5919709 ZPE=32.36 U=1204.9i; 326.2i C -0.039148000 -0.819540000 0.000000000 H -0.481253000 -1.248523000 0.896166000 H -0.481253000 -1.248523000 -0.896166000 H -0.793925000 0.311309000 0.000000000 H 1.035789000 -0.918727000 0.000000000 B -0.039148000 1.340383000 0.000000000 H 1.151264000 1.319790000 0.000000000
F		E=-164.8014889 ZPE=29.09 U=1553.2i; 178.4i C 1.064760000 -0.909612000 0.000000000 B 0.000000000 0.883352000 0.000000000 F -1.223251000 0.450556000 0.000000000 H 1.649456000 -1.092081000 0.899558000 H 0.136725000 -1.477607000 0.000000000 H 1.185067000 0.647672000 0.000000000 H 1.649456000 -1.092081000 -0.899558000
Cl		E=-524.7650336 ZPE=28.36 U=1401.6i; 202.5i C -1.873922000 -0.046955000 0.000000000 B 0.000000000 1.000976000 0.000000000 Cl 1.103464000 -0.308159000 0.000000000 H -2.457647000 0.132740000 0.900839000 H -2.457647000 0.132740000 -0.900839000 H -1.196096000 1.273781000 0.000000000 H -1.403969000 -1.023703000 0.000000000
Br		E=-2637.7396617 ZPE=28.07 U=1385.3i; 205.7i C -0.567947000 -2.283264000 0.000000000 B 1.003563000 -0.797330000 0.000000000 Br 0.000000000 0.772918000 0.000000000 H 0.879173000 -2.023126000 0.000000000 H -0.559596000 -2.893604000 0.901144000 H -1.370111000 -1.555551000 0.000000000 H -0.559596000 -2.893604000 -0.901144000
CH_3		E=-104.835748 ZPE=50.56 U=1267.3i; 209.6i C -1.286386000 -0.734196000 0.000000000 B 0.000000000 1.022341000 0.000000000 H -1.892758000 -0.836668000 0.897839000

		H -1.892758000 -0.836668000 -0.897839000 H -1.213953000 0.653689000 0.000000000 H -0.449090000 -1.421383000 0.000000000 C 1.353657000 0.261626000 0.000000000 H 2.200804000 0.941918000 0.000000000 H 1.422065000 -0.388586000 0.877388000 H 1.422065000 -0.388586000 -0.877388000
Ph[a]		E=-296.1594926 ZPE=84.77 U=1243.9i; 238.4i, 68.0i C -2.673853000 1.957822000 0.000000000 B -0.469301000 2.039626000 0.000000000 H -3.114472000 2.381898000 0.899687000 H -3.114472000 2.381898000 -0.899687000 H -1.539921000 2.724881000 0.000000000 H -2.731630000 0.879801000 0.000000000 C 0.000000000 0.568010000 0.000000000 C 1.411541000 0.488787000 0.000000000 C 2.074664000 -0.734226000 0.000000000 C 1.339407000 -1.916786000 0.000000000 C -0.054918000 -1.868438000 0.000000000 C -0.715191000 -0.645452000 0.000000000 H 1.975621000 1.412690000 0.000000000 H 3.155454000 -0.765408000 0.000000000 H 1.846848000 -2.872194000 0.000000000 H -0.625887000 -2.786974000 0.000000000 H -1.794939000 -0.653020000 0.000000000
NH_2		E=-120.9284354 ZPE=44.87 U=1315.9i; 205.7i C -1.199298000 -0.833824000 0.000000000 B 0.000000000 0.961289000 0.000000000 N 1.252410000 0.378196000 0.000000000 H -1.794777000 -0.971329000 0.899681000 H -1.794777000 -0.971329000 -0.899681000 H -1.190919000 0.603541000 0.000000000 H -0.323967000 -1.475586000 0.000000000 H 2.064924000 0.970546000 0.000000000 H 1.468436000 -0.606720000 0.000000000
NHMe		E=-160.1391566 ZPE=62.93 U=1301.0i; 201.4i C 0.946751000 -1.976990000 0.000000000 B -0.708717000 -0.585282000 0.000000000 N 0.000000000 0.597825000 0.000000000 C -0.651220000 1.903214000 0.000000000 H 1.015173000 -2.583957000 0.899884000 H 1.015173000 -2.583957000 -0.899884000 H -0.477408000 -1.808479000 0.000000000 H 1.685238000 -1.181510000 0.000000000 H 1.009109000 0.644408000 0.000000000 H -0.375454000 2.472905000 -0.885914000 H -1.725976000 1.751978000 0.000000000 H -0.375454000 2.472905000 0.885914000
NMe_2		E=-199.3454561 ZPE=80.42 U=1326.8i; 232.9i C 0.541206000 -2.384142000 0.000000000 B 1.146636000 -0.229552000 0.000000000 N 0.000000000 0.542277000 0.000000000 C -1.425514000 0.248760000 0.000000000 C 0.223426000 1.991603000 0.000000000 H 1.590783000 -1.387439000 0.000000000

		H 0.871496000 -2.897642000 0.900229000 H -0.530399000 -2.236316000 0.000000000 H 0.871496000 -2.897642000 -0.900229000 H -0.231046000 2.437494000 0.886421000 H 1.289377000 2.193928000 0.000000000 H -0.231046000 2.437494000 -0.886421000 H -1.890611000 0.689672000 0.882964000 H -1.890611000 0.689672000 -0.882964000 H -1.617328000 -0.814724000 0.000000000

[a] third-order saddle point

Borirenes

R	B3LYP/6-311+G**	MP2/cc-pVTZ
H	E=-102.8282664 ZPE=26.15 C 0.000000000 0.675387000 -0.379854000 B 0.000000000 0.000000000 0.927292000 C 0.000000000 -0.675387000 -0.379854000 H 0.000000000 1.490238000 -1.091051000 H 0.000000000 -1.490238000 -1.091051000 H 0.000000000 0.000000000 2.103893000	E=-102.5389506 ZPE=26.42 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-102.5868426 C 0.000000000 0.678858000 -0.380521000 C 0.000000000 -0.678858000 -0.380521000 B 0.000000000 0.000000000 0.929562000 H 0.000000000 1.486875000 -1.093641000 H 0.000000000 -1.486875000 -1.093641000 H 0.000000000 0.000000000 2.105729000
F	E=-202.1595732 ZPE=22.80 C 0.000000000 0.682025000 -1.020937000 B 0.000000000 0.000000000 0.275110000 F 0.000000000 0.000000000 1.600126000 C 0.000000000 -0.682025000 -1.020937000 H 0.000000000 1.470172000 -1.762717000 H 0.000000000 -1.470172000 -1.762717000	E=-201.7374392 ZPE=23.07 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-201.7937824 C 0.000000000 0.685852000 -1.021892000 C 0.000000000 -0.685852000 -1.021892000 B 0.000000000 0.000000000 0.279909000 F 0.000000000 0.000000000 1.600251000 H 0.000000000 1.463113000 -1.769551000 H 0.000000000 -1.463113000 -1.769551000
Cl	E=-562.4999739 ZPE=21.93 C 0.000000000 0.678494000 -1.576680000 C 0.000000000 -0.678494000 -1.576680000 B 0.000000000 0.000000000 -0.277856000 Cl 0.000000000 0.000000000 1.464986000 H 0.000000000 1.484789000 -2.297664000 H 0.000000000 -1.484789000 -2.297664000	E=-561.7055032 ZPE=22.18 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-561.7757394 C 0.000000000 0.682454000 -1.573449000 B 0.000000000 0.000000000 -0.270977000 Cl 0.000000000 0.000000000 1.460970000 C 0.000000000 -0.682454000 -1.573449000 H 0.000000000 1.478905000 -2.300106000 H 0.000000000 -1.478905000 -2.300106000
Br	E=-2676.4158206 ZPE=21.63 C 0.000000000 0.677968000 -2.168353000 C 0.000000000 -0.677968000 -2.168353000 B 0.000000000 0.000000000 -0.869366000 Br 0.000000000 0.000000000 1.032478000 H 0.000000000 1.488010000 -2.884825000 H 0.000000000 -1.488010000 -2.884825000	E=-2674.6818091 ZPE=21.89 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2674.7502418 C 0.000000000 0.681728000 -2.154493000 C 0.000000000 -0.681728000 -2.154493000 B 0.000000000 0.000000000 -0.852019000 Br 0.000000000 0.000000000 1.024732000 H 0.000000000 1.482757000 -2.875809000 H 0.000000000 -1.482757000 -2.875809000
CH_3	E=-142.1715377 ZPE=43.91 C -0.001498000 -1.721540000 0.000000000 B -0.014087000 -0.166100000 0.000000000 C -0.001498000 1.148444000 0.675471000 C -0.001498000 1.148444000 -0.675471000 H 0.003396000 1.871900000 -1.480799000	E=-141.7786359 ZPE=44.47 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-141.8466509 C -0.001370000 -1.724784000 0.000000000 B -0.015048000 -0.167061000 0.000000000 C -0.001370000 1.148777000 0.679299000 C -0.001370000 1.148777000 -0.679299000 H 0.003353000 1.874427000 -1.477461000

	H 0.003396000 1.871900000 1.480799000 H -0.474365000 -2.148290000 0.888662000 H -0.474365000 -2.148290000 -0.888662000 H 1.039340000 -2.068812000 0.000000000	H 0.003353000 1.874427000 1.477461000 H -0.472180000 -2.144568000 0.886257000 H -0.472180000 -2.144568000 -0.886257000 H 1.037554000 -2.061031000 0.000000000
Ph	E=-333.9547687 ZPE=78.12 C 0.000000000 1.204497000 0.533900000 C 0.000000000 0.000000000 -0.192231000 C 0.000000000 -1.204497000 0.533900000 C 0.000000000 -1.207764000 1.926116000 C 0.000000000 0.000000000 2.623660000 C 0.000000000 1.207764000 1.926116000 B 0.000000000 0.000000000 -1.731332000 C 0.000000000 -0.675199000 -3.046057000 C 0.000000000 0.675199000 -3.046057000 H 0.000000000 1.481513000 -3.767708000 H 0.000000000 -1.481513000 -3.767708000 H 0.000000000 -2.146481000 -0.004229000 H 0.000000000 -2.147038000 2.468087000 H 0.000000000 0.000000000 3.708292000 H 0.000000000 2.147038000 2.468087000 H 0.000000000 2.146481000 -0.004229000	E=-333.106505 ZPE=78.59 CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-333.2143353 C 0.000000000 1.205192000 0.532465000 C 0.000000000 0.000000000 -0.188571000 C 0.000000000 -1.205192000 0.532465000 C 0.000000000 -1.207725000 1.924434000 C 0.000000000 0.000000000 2.621490000 C 0.000000000 1.207725000 1.924434000 B 0.000000000 0.000000000 -1.728198000 C 0.000000000 -0.679260000 -3.043607000 C 0.000000000 0.679260000 -3.043607000 H 0.000000000 1.479178000 -3.767303000 H 0.000000000 -1.479178000 -3.767303000 H 0.000000000 -2.143116000 -0.008278000 H 0.000000000 -2.144116000 2.465911000 H 0.000000000 0.000000000 3.703308000 H 0.000000000 2.144116000 2.465911000 H 0.000000000 2.143116000 -0.008278000
NH_2	E=-158.2536362 ZPE=38.00 C 0.000000000 0.673507000 -1.098113000 C 0.000000000 -0.673507000 -1.098113000 B 0.000000000 0.000000000 0.225358000 N 0.000000000 0.000000000 1.622768000 H 0.000000000 1.475632000 -1.824758000 H 0.000000000 -1.475632000 -1.824758000 H 0.000000000 -0.844770000 2.170353000 H 0.000000000 0.844770000 2.170353000	E=-157.8527456 ZPE=38.30 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-157.9165336 C 0.000000000 0.677707000 -1.098071000 C 0.000000000 -0.677707000 -1.098071000 B 0.000000000 0.000000000 0.226491000 N 0.000000000 0.000000000 1.624091000 H 0.000000000 1.471206000 -1.828709000 H 0.000000000 -1.471206000 -1.828709000 H 0.000000000 -0.842705000 2.166589000 H 0.000000000 0.842705000 2.166589000
NHMe	E=-197.5661712 ZPE=55.72 C -0.365095000 1.900901000 0.000000000 C -1.379973000 1.016207000 0.000000000 B 0.000000000 0.459493000 0.000000000 N 0.911938000 -0.595247000 0.000000000 C 0.576740000 -2.014158000 0.000000000 H -0.239397000 2.975987000 0.000000000 H -2.462166000 1.039761000 0.000000000 H 1.900530000 -0.393714000 0.000000000 H 0.967890000 -2.523884000 0.887709000 H -0.508346000 -2.122710000 0.000000000 H 0.967890000 -2.523884000 -0.887709000	E=-197.0610543 ZPE=56.46 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-197.1458185 C -0.395630000 1.895134000 0.000000000 C -1.396246000 0.981430000 0.000000000 B 0.000000000 0.458883000 0.000000000 N 0.929160000 -0.581415000 0.000000000 C 0.601559000 -1.995192000 0.000000000 H -0.302422000 2.969951000 0.000000000 H -2.475110000 0.988286000 0.000000000 H 1.911574000 -0.368910000 0.000000000 H 0.991705000 -2.500530000 0.883984000 H -0.479670000 -2.101012000 0.000000000 H 0.991705000 -2.500530000 -0.883984000
NMe_2	E=-236.8815899 ZPE=73.07 C 0.000000000 0.673395000 -2.014374000 C 0.000000000 -0.673395000 -2.014374000 B 0.000000000 0.000000000 -0.687184000 N 0.000000000 0.000000000 0.707362000 C 0.000000000 1.224545000 1.493621000 C 0.000000000 -1.224545000 1.493621000 H 0.000000000 1.472284000 -2.744585000 H 0.000000000 -1.472284000 -2.744585000 H -0.886330000 -1.281983000 2.139749000 H 0.000000000 -2.090293000 0.831801000 H 0.886330000 -1.281983000 2.139749000 H -0.886330000 1.281983000 2.139749000	E=-236.2748487 ZPE=74.14 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-236.3799471 C 0.000000000 0.677746000 -2.014939000 C 0.000000000 -0.677746000 -2.014939000 B 0.000000000 0.000000000 -0.686679000 N 0.000000000 0.000000000 0.707526000 C 0.000000000 1.215175000 1.494696000 C 0.000000000 -1.215175000 1.494696000 H 0.000000000 1.469074000 -2.748585000 H 0.000000000 -1.469074000 -2.748585000 H -0.883404000 -1.264566000 2.137190000 H 0.000000000 -2.078904000 0.836021000 H 0.883404000 -1.264566000 2.137190000 H -0.883404000 1.264566000 2.137190000

	H 0.886330000 1.281983000 2.139749000 H 0.000000000 2.090293000 0.831801000	H 0.883404000 1.264566000 2.137190000 H 0.000000000 2.078904000 0.836021000

Boriranes

R	B3LYP/6-311+G**	MP2/cc-pVTZ
H	E=-104.0393617 ZPE=36.36 C 0.000000000 0.776576000 -0.351702000 B 0.000000000 0.000000000 0.963766000 C 0.000000000 -0.776576000 -0.351702000 H 0.903278000 1.281915000 -0.685539000 H -0.903278000 1.281915000 -0.685539000 H 0.903278000 -1.281915000 -0.685539000 H -0.903278000 -1.281915000 -0.685539000 H 0.000000000 0.000000000 2.143749000	E=-103.7361205 ZPE=40.00 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-103.7931794 C 0.000000000 0.774712000 -0.353265000 B 0.000000000 0.000000000 0.966930000 C 0.000000000 -0.774712000 -0.353265000 H 0.903394000 1.269963000 -0.685164000 H -0.903394000 1.269963000 -0.685164000 H 0.903394000 -1.269963000 -0.685164000 H -0.903395000 -1.269963000 -0.685164000 H 0.000000000 0.000000000 2.145188000
F	E=-203.3789556 ZPE=36.20 C 0.000000000 0.801502000 -0.944725000 B 0.000000000 0.000000000 0.336598000 F 0.000000000 0.000000000 1.654973000 C 0.000000000 -0.801502000 -0.944725000 H 0.904159000 1.281538000 -1.310262000 H -0.904159000 1.281538000 -1.310262000 H 0.904159000 -1.281538000 -1.310262000 H -0.904159000 -1.281538000 -1.310262000	E=-202.9438004 ZPE=36.82 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-203.0087192 C 0.000000000 0.799121000 -0.946874000 B 0.000000000 0.000000000 0.342749000 F 0.000000000 0.000000000 1.655788000 C 0.000000000 -0.799121000 -0.946874000 H 0.903712000 1.268426000 -1.313339000 H -0.903712000 1.268426000 -1.313339000 H 0.903712000 -1.268426000 -1.313339000 H -0.903712000 -1.268426000 -1.313339000
Cl	E=-563.7180458 ZPE=35.41 C 0.000000000 0.790238000 -1.487706000 B 0.000000000 0.000000000 -0.194140000 Cl 0.000000000 0.000000000 1.539173000 C 0.000000000 -0.790238000 -1.487706000 H 0.905142000 1.281488000 -1.835694000 H -0.905142000 1.281488000 -1.835694000 H 0.905142000 -1.281488000 -1.835694000 H -0.905142000 -1.281488000 -1.835694000	E=-562.90967 ZPE=35.97 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-562.9890191 C 0.000000000 0.787409000 -1.485678000 B 0.000000000 0.000000000 -0.185527000 Cl 0.000000000 0.000000000 1.534468000 C 0.000000000 -0.787409000 -1.485678000 H 0.905032000 1.269192000 -1.832546000 H -0.905032000 1.269192000 -1.832546000 H 0.905032000 -1.269192000 -1.832546000 H -0.905032000 -1.269192000 -1.832546000
Br	E=-2677.6335151 ZPE=35.11 C 0.000000000 0.788264000 -2.083459000 B 0.000000000 0.000000000 -0.787686000 Br 0.000000000 0.000000000 1.104355000 C 0.000000000 -0.788264000 -2.083459000 H 0.905123000 1.281856000 -2.428120000 H -0.905123000 1.281856000 -2.428120000 H 0.905123000 -1.281856000 -2.428120000 H -0.905123000 -1.281856000 -2.428120000	E=-2675.8854196 ZPE=35.67 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2675.9633491 C 0.000000000 0.784977000 -2.070347000 B 0.000000000 0.000000000 -0.768298000 Br 0.000000000 0.000000000 1.095327000 C 0.000000000 -0.784977000 -2.070347000 H 0.905221000 1.269666000 -2.412701000 H -0.905221000 1.269666000 -2.412701000 H 0.905221000 -1.269666000 -2.412701000 H -0.905221000 -1.269666000 -2.412701000
CH_3	E=-143.3860266 ZPE=57.19 C -0.002914000 -1.791414000 0.000000000 B -0.027730000 -0.245859000 0.000000000 C -0.002914000 1.072438000 0.780128000 C -0.002914000 1.072438000 -0.780128000 H 0.905253000 1.404395000 1.278078000 H -0.900403000 1.433445000 1.277496000	E=-142.9789614 ZPE=58.06 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-143.0560677 C -0.002340000 -1.794838000 0.000000000 B -0.035327000 -0.247800000 0.000000000 C -0.002340000 1.073894000 0.778167000 C -0.002340000 1.073894000 -0.778167000 H 0.907908000 1.394913000 1.268732000 H -0.897799000 1.439253000 1.264987000

	H 0.905253000 1.404395000 -1.278078000 H -0.900403000 1.433445000 -1.277496000 H -0.439603000 -2.244005000 0.894531000 H -0.439603000 -2.244005000 -0.894531000 H 1.060604000 -2.079151000 0.000000000	H 0.907908000 1.394913000 -1.268732000 H -0.897799000 1.439253000 -1.264987000 H -0.431857000 -2.244111000 0.892483000 H -0.431857000 -2.244111000 -0.892483000 H 1.062251000 -2.058808000 0.000000000
Ph	E=-335.1722102 ZPE=91.65 C 0.000000000 1.207515000 0.629949000 C 0.000000000 0.000000000 -0.097678000 C 0.000000000 -1.207515000 0.629949000 C 0.000000000 -1.210430000 2.021122000 C 0.000000000 0.000000000 2.716109000 C 0.000000000 1.210430000 2.021122000 B 0.000000000 0.000000000 -1.626000000 C 0.000000000 -0.780509000 -2.943610000 C 0.000000000 0.780509000 -2.943610000 H -0.903072000 -1.274467000 -3.294355000 H 0.903072000 -1.274467000 -3.294355000 H -0.903072000 1.274467000 -3.294355000 H 0.903072000 1.274467000 -3.294355000 H 0.000000000 -2.146752000 0.087407000 H 0.000000000 -2.147999000 2.565826000 H 0.000000000 0.000000000 3.800841000 H 0.000000000 2.147999000 2.565826000 H 0.000000000 2.146752000 0.087407000	E=-334.3098659 ZPE=92.46 CCSD(T)/cc-pVTZ//MP2/cc-pVTZ E=-334.4258627 C 0.000000000 1.208336000 0.627781000 C 0.000000000 0.000000000 -0.092967000 C 0.000000000 -1.208336000 0.627781000 C 0.000000000 -1.210018000 2.018629000 C 0.000000000 0.000000000 2.713226000 C 0.000000000 1.210018000 2.018629000 B 0.000000000 0.000000000 -1.621495000 C 0.000000000 -0.779108000 -2.942104000 C 0.000000000 0.779108000 -2.942104000 H -0.903991000 -1.264575000 -3.287581000 H 0.903991000 -1.264575000 -3.287581000 H -0.903991000 1.264575000 -3.287581000 H 0.903991000 1.264575000 -3.287581000 H 0.000000000 -2.143079000 0.081725000 H 0.000000000 -2.144572000 2.562974000 H 0.000000000 0.000000000 3.795164000 H 0.000000000 2.144572000 2.562974000 H 0.000000000 2.143079000 0.081725000
NH_2	E=-159.4828497 ZPE=52.19 C 0.000000000 0.787522000 -1.015505000 C 0.000000000 -0.787522000 -1.015505000 B 0.000000000 0.000000000 0.296540000 N 0.000000000 0.000000000 1.678856000 H -0.904244000 -1.270442000 -1.376845000 H -0.904244000 1.270442000 -1.376845000 H 0.904244000 1.270442000 -1.376845000 H 0.904244000 -1.270442000 -1.376845000 H 0.000000000 -0.845600000 2.229372000 H 0.000000000 0.845600000 2.229372000	E=-159.069199 ZPE=52.90 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-159.1412486 C 0.000000000 0.785576000 -1.016908000 C 0.000000000 -0.785576000 -1.016908000 B 0.000000000 0.000000000 0.298490000 N 0.000000000 0.000000000 1.680717000 H -0.903980000 -1.259450000 -1.376381000 H -0.903980000 1.259450000 -1.376381000 H 0.903980000 1.259450000 -1.376381000 H 0.903980000 -1.259450000 -1.376381000 H 0.000000000 -0.843986000 2.225472000 H 0.000000000 0.843986000 2.225472000
NHMe	E=-198.7969169 ZPE=69.92 C -0.430230000 1.853677000 0.000000000 C -1.499943000 0.697934000 0.000000000 B 0.000000000 0.384065000 0.000000000 N 1.010534000 -0.554664000 0.000000000 C 0.846483000 -2.006115000 0.000000000 H -2.094287000 0.591705000 0.904022000 H -0.369745000 2.453968000 0.904226000 H -0.369745000 2.453968000 -0.904226000 H -2.094287000 0.591705000 -0.904022000 H 1.972929000 -0.244315000 0.000000000 H 1.300736000 -2.458756000 0.887476000 H -0.217931000 -2.240168000 0.000000000 H 1.300736000 -2.458756000 -0.887476000	E=-198.2792133 ZPE=71.00 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-198.3722818 C -0.477794000 1.841271000 0.000000000 C -1.510027000 0.656182000 0.000000000 B 0.000000000 0.384743000 0.000000000 N 1.031252000 -0.531651000 0.000000000 C 0.882106000 -1.978104000 0.000000000 H -2.093294000 0.537573000 0.903945000 H -0.439629000 2.434868000 0.904032000 H -0.439629000 2.434868000 -0.904032000 H -2.093294000 0.537573000 -0.903945000 H 1.984057000 -0.204015000 0.000000000 H 1.337562000 -2.422832000 0.884180000 H -0.177812000 -2.213463000 0.000000000 H 1.337562000 -2.422832000 -0.884180000
NMe_2	E=-238.1130152 ZPE=87.25 C 0.000000000 0.788151000 -1.912293000 C 0.000000000 -0.788151000 -1.912293000 B 0.000000000 0.000000000 -0.598813000 N 0.000000000 0.000000000 0.780976000 C 0.000000000 1.225633000 1.574625000	E=-237.4940324 ZPE=88.67 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-237.6075023 C 0.000000000 0.786704000 -1.913697000 C 0.000000000 -0.786704000 -1.913697000 B 0.000000000 0.000000000 -0.597353000 N 0.000000000 0.000000000 0.782130000 C 0.000000000 1.216615000 1.574937000

	C 0.000000000 -1.225633000 1.574625000 H -0.903938000 -1.268182000 -2.279228000 H -0.903938000 1.268182000 -2.279228000 H 0.903938000 1.268182000 -2.279228000 H 0.903938000 -1.268182000 -2.279228000 H -0.886626000 -1.273531000 2.218595000 H 0.000000000 -2.089153000 0.910887000 H 0.886626000 -1.273531000 2.218595000 H -0.886626000 1.273531000 2.218595000 H 0.886626000 1.273531000 2.218595000 H 0.000000000 2.089153000 0.910887000	C 0.000000000 -1.216615000 1.574937000 H -0.903847000 -1.257442000 -2.278432000 H -0.903847000 1.257442000 -2.278432000 H 0.903847000 1.257442000 -2.278432000 H 0.903847000 -1.257442000 -2.278432000 H -0.883503000 -1.256444000 2.215610000 H 0.000000000 -2.077753000 0.914134000 H 0.883503000 -1.256444000 2.215610000 H -0.883503000 1.256444000 2.215610000 H 0.883503000 1.256444000 2.215610000 H 0.000000000 2.077753000 0.914134000

Boranes (rotamers B)

R	B3LYP/6-311+G**	MP2/cc-pVTZ
H	E=-65.9681113 ZPE=34.79 C -0.018210000 -0.682047000 0.000000000 H 1.054256000 -0.952363000 0.000000000 H -0.439811000 -1.144362000 0.896158000 H 0.012838000 1.486259000 1.024376000 H -0.439811000 -1.144362000 -0.896158000 B -0.018210000 0.872170000 0.000000000 H 0.012838000 1.486259000 -1.024376000	E=-65.7546838 ZPE=35.46352 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-65.8005818 C -0.018839000 -0.684471000 0.000000000 H 1.050946000 -0.941151000 0.000000000 H -0.436884000 -1.141952000 0.892905000 H 0.015026000 1.483576000 1.022837000 H -0.436884000 -1.141952000 -0.892905000 B -0.018839000 0.872946000 0.000000000 H 0.015026000 1.483576000 -1.022837000
F	E=-165.3189997 ZPE=31.92 C -1.152063000 -0.521278000 0.000000000 B 0.000000000 0.522497000 0.000000000 F 1.277321000 0.121027000 0.000000000 H -1.799511000 -0.360215000 0.871416000 H -1.799511000 -0.360215000 -0.871416000 H -0.173241000 1.705140000 0.000000000 H -0.811251000 -1.558776000 0.000000000	E=-164.9742683 ZPE=32.57 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-165.0280898 C -1.147735000 -0.536089000 0.000000000 B 0.000000000 0.520339000 0.000000000 F 1.273244000 0.137435000 0.000000000 H -1.789347000 -0.377488000 0.868815000 H -1.789347000 -0.377488000 -0.868815000 H -0.195861000 1.697830000 0.000000000 H -0.798228000 -1.564936000 0.000000000
Cl	E=-525.6537274 ZPE=31.09 C -1.549546000 0.849480000 0.000000000 B 0.000000000 0.764856000 0.000000000 Cl 0.848588000 -0.788050000 0.000000000 H -1.881776000 1.431070000 0.870474000 H -1.881776000 1.431070000 -0.870474000 H 0.699788000 1.725563000 0.000000000 H -2.064963000 -0.112006000 0.000000000	E=-524.9345146 ZPE=31.64 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-525.003001 C -1.553650000 0.828484000 0.000000000 B 0.000000000 0.758889000 0.000000000 Cl 0.850622000 -0.774447000 0.000000000 H -1.885285000 1.403149000 0.868277000 H -1.885285000 1.403149000 -0.868277000 H 0.682261000 1.730987000 0.000000000 H -2.050356000 -0.137041000 0.000000000
Br	E=-2639.5685264 ZPE=30.78 C 0.439148000 -2.231994000 0.000000000 B -0.573659000 -1.058141000 0.000000000 Br 0.000000000 0.788101000 0.000000000 H -1.750762000 -1.211275000 0.000000000 H 0.246863000 -2.873730000 0.870771000 H 0.246863000 -2.873730000 -0.870771000 H 1.490443000 -1.942140000 0.000000000	E=-2637.9084571 ZPE=31.31 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-2637.9755911 C 0.439308000 -2.215000000 0.000000000 B -0.572044000 -1.035858000 0.000000000 Br 0.000000000 0.779801000 0.000000000 H -1.746721000 -1.202242000 0.000000000 H 0.243175000 -2.849335000 0.868281000 H 0.243175000 -2.849335000 -0.868281000 H 1.484741000 -1.922821000 0.000000000
CH_3	E=-105.3137799 ZPE=52.76 C 1.379219000 -0.192422000 0.011629000	E=-104.9961041 ZPE=53.64 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-105.0623291 C 1.372232000 -0.193681000 0.013286000

	B -0.000017000 0.544006000 -0.000094000 H 1.772579000 -0.123593000 -1.016712000 H 2.130898000 0.301885000 0.635442000 H 0.000038000 1.744434000 0.000019000 H 1.335890000 -1.255933000 0.263499000 C -1.379258000 -0.192420000 -0.011652000 H -1.771797000 -0.124024000 1.017051000 H -2.131420000 0.302059000 -0.634716000 H -1.335870000 -1.255811000 -0.263976000	B -0.000013000 0.557502000 -0.000045000 H 1.708447000 -0.187885000 -1.032315000 H 2.153005000 0.316039000 0.574543000 H -0.000006000 1.754437000 0.000013000 H 1.314642000 -1.236978000 0.317444000 C -1.372256000 -0.193692000 -0.013294000 H -1.707982000 -0.188213000 1.032472000 H -2.153236000 0.316209000 -0.574081000 H -1.314664000 -1.236879000 -0.317804000
Ph	E=-297.0999335 ZPE=87.44 C -1.994311000 2.457317000 0.000000000 B -0.498790000 1.995908000 0.000000000 H -2.177100000 3.104591000 0.868566000 H -2.177100000 3.104591000 -0.868566000 H 0.343334000 2.850136000 0.000000000 H -2.749941000 1.668228000 0.000000000 C 0.000000000 0.527437000 0.000000000 C 1.384405000 0.258014000 0.000000000 C 1.874874000 -1.044470000 0.000000000 C 0.984035000 -2.117779000 0.000000000 C -0.392394000 -1.884775000 0.000000000 C -0.873368000 -0.579573000 0.000000000 H 2.078536000 1.091999000 0.000000000 H 2.943894000 -1.226426000 0.000000000 H 1.360818000 -3.134975000 0.000000000 H -1.082834000 -2.721055000 0.000000000 H -1.945109000 -0.413651000 0.000000000	E=-296.3266779 ZPE=88.11 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-296.4345805 C -2.012433000 2.425717000 0.000000000 B -0.507709000 1.993243000 0.000000000 H -2.201396000 3.065216000 0.866183000 H -2.201396000 3.065216000 -0.866183000 H 0.325231000 2.854392000 0.000000000 H -2.744112000 1.621990000 0.000000000 C 0.000000000 0.527650000 0.000000000 C 1.383784000 0.270577000 0.000000000 C 1.880258000 -1.029177000 0.000000000 C 0.995228000 -2.106593000 0.000000000 C -0.381588000 -1.880540000 0.000000000 C -0.869807000 -0.578268000 0.000000000 H 2.069221000 1.108904000 0.000000000 H 2.947225000 -1.206105000 0.000000000 H 1.376090000 -3.119223000 0.000000000 H -1.065479000 -2.718477000 0.000000000 H -1.939491000 -0.414314000 0.000000000
NH_2	E=-121.4166905 ZPE=47.93 C -1.280308000 -0.378058000 0.000000000 B 0.000000000 0.536730000 0.000000000 N 1.293195000 0.005358000 0.000000000 H -1.067442000 -1.452539000 0.000000000 H -1.907660000 -0.159952000 0.872845000 H -0.095776000 1.730589000 0.000000000 H -1.907660000 -0.159952000 -0.872845000 H 2.124724000 0.575138000 0.000000000 H 1.483298000 -0.986089000 0.000000000	E=-121.0928712 ZPE=48.60 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-121.1542737 C -1.277662000 -0.378300000 0.000000000 B 0.000000000 0.541490000 0.000000000 N 1.288966000 0.002883000 0.000000000 H -1.054100000 -1.444861000 0.000000000 H -1.899793000 -0.163143000 0.870324000 H -0.091316000 1.733445000 0.000000000 H -1.899793000 -0.163143000 -0.870324000 H 2.120173000 0.565954000 0.000000000 H 1.468036000 -0.986081000 0.000000000
NHMe	E=-160.7305464 ZPE=65.58 C 1.175474000 -1.673795000 0.000000000 B -0.097965000 -0.746489000 0.000000000 N 0.000000000 0.645544000 0.000000000 C -1.095184000 1.607030000 0.000000000 H 1.169394000 -2.337769000 0.872978000 H 1.169394000 -2.337769000 -0.872978000 H -1.201484000 -1.214554000 0.000000000 H 2.127764000 -1.132079000 0.000000000 H 0.917828000 1.071664000 0.000000000 H -1.066548000 2.249226000 -0.886784000 H -2.041711000 1.066286000 0.000000000 H -1.066548000 2.249226000 0.886784000	E=-160.3025395 ZPE=66.67 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-160.3848788 C 1.178718000 -1.665802000 0.000000000 B -0.100518000 -0.745558000 0.000000000 N 0.000000000 0.645899000 0.000000000 C -1.095595000 1.597583000 0.000000000 H 1.173581000 -2.323893000 0.870512000 H 1.173581000 -2.323893000 -0.870512000 H -1.204776000 -1.208257000 0.000000000 H 2.119758000 -1.115894000 0.000000000 H 0.915354000 1.068835000 0.000000000 H -1.070762000 2.235488000 -0.883217000 H -2.032120000 1.047944000 0.000000000 H -1.070762000 2.235488000 0.883217000
NMe_2	E=-200.0440358 ZPE=83.10 C -0.349323000 -2.172691000 0.000000000 B -0.829030000 -0.671188000 0.000000000 N 0.000000000 0.457927000 0.000000000 C 1.458224000 0.438055000 0.000000000	E=-199.5150838 ZPE=84.44 CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ E=-199.617798 C -0.355453000 -2.165501000 0.000000000 B -0.839597000 -0.664925000 0.000000000 N 0.000000000 0.455324000 0.000000000 C 1.450257000 0.429145000 0.000000000

	C -0.535378000 1.816127000 0.000000000 H -2.007722000 -0.451034000 0.000000000 H -0.767479000 -2.692041000 0.871593000 H -0.767479000 -2.692041000 -0.871593000 H 0.729762000 -2.345567000 0.000000000 H -0.198626000 2.369601000 -0.885645000 H -1.623593000 1.784134000 0.000000000 H -0.198626000 2.369601000 0.885645000 H 1.853663000 0.951300000 -0.885320000 H 1.853663000 0.951300000 0.885320000 H 1.830449000 -0.583748000 0.000000000	C -0.515688000 1.813056000 0.000000000 H -2.014178000 -0.429933000 0.000000000 H -0.770382000 -2.680208000 0.869057000 H -0.770382000 -2.680208000 -0.869057000 H 0.719774000 -2.328133000 0.000000000 H -0.169535000 2.356079000 -0.882519000 H -1.600558000 1.792457000 0.000000000 H -0.169535000 2.356079000 0.882519000 H 1.841210000 0.941092000 -0.882200000 H 1.841210000 0.941092000 0.882200000 H 1.815660000 -0.591162000 0.000000000

Boranes (rotamers A)

R		MP2/cc-pVTZ
H		E=-65.7543922 ZPE=35.32 U=160.7i C -0.012074000 -0.685049000 0.000000000 H 0.555210000 -1.042148000 0.863986000 H -0.988960000 -1.158036000 0.000000000 H -1.016464000 1.516247000 0.000000000 H 0.555210000 -1.042148000 -0.863986000 B -0.012074000 0.875495000 0.000000000 H 1.027820000 1.458904000 0.000000000
F		E=-164.973758 ZPE=32.48 U=107.5i C -1.153895000 -0.509029000 0.000000000 B 0.000000000 0.543440000 0.000000000 F 1.259080000 0.110857000 0.000000000 H -1.058400000 -1.159387000 0.871312000 H -2.146336000 -0.069237000 0.000000000 H -0.145219000 1.727276000 0.000000000 H -1.058400000 -1.159387000 -0.871312000
Cl		E=-524.933915 ZPE=31.57 U=125.0i C -1.557753000 0.796424000 0.000000000 B 0.000000000 0.785283000 0.000000000 Cl 0.853457000 -0.750394000 0.000000000 H -1.930081000 0.251351000 0.869523000 H -1.986483000 1.794327000 0.000000000 H 0.684400000 1.754707000 0.000000000 H -1.930081000 0.251351000 -0.869523000
Br		E=-2637.907866 ZPE=31.26 U=122.1i C -0.437202000 -2.197677000 0.000000000 B 0.602707000 -1.039561000 0.000000000 Br 0.000000000 0.770447000 0.000000000 H 1.779601000 -1.182832000 0.000000000 H 0.013485000 -3.186323000 0.000000000 H -1.091703000 -2.106303000 0.869164000 H -1.091703000 -2.106303000 -0.869164000
CH_3		E=-104.9955718 ZPE=53.46 U=129.7i C 1.377155000 -0.174123000 0.000000000

		B 0.000000000 0.572953000 0.000000000 H 2.260649000 0.457391000 0.000000000 H 1.421454000 -0.840883000 0.866016000 H -0.046519000 1.768726000 0.000000000 H 1.421454000 -0.840883000 -0.866016000 C -1.357813000 -0.209349000 0.000000000 H -1.953207000 0.092595000 -0.865746000 H -1.266674000 -1.293474000 0.000000000 H -1.953207000 0.092595000 0.865746000
Ph		E=-296.3258519 ZPE=88.01 U=123.6i C 2.076191000 2.326932000 0.000000000 B 0.539609000 2.002579000 0.000000000 H 2.557106000 1.871525000 0.869627000 H 2.557106000 1.871525000 -0.869627000 H -0.273248000 2.881238000 0.000000000 H 2.309320000 3.388017000 0.000000000 C 0.000000000 0.546897000 0.000000000 C -1.386863000 0.312220000 0.000000000 C -1.903871000 -0.980056000 0.000000000 C -1.036217000 -2.071077000 0.000000000 C 0.344432000 -1.866963000 0.000000000 C 0.852558000 -0.572694000 0.000000000 H -2.059253000 1.161166000 0.000000000 H -2.973533000 -1.140243000 0.000000000 H -1.433092000 -3.077584000 0.000000000 H 1.014879000 -2.715799000 0.000000000 H 1.925289000 -0.424287000 0.000000000
NH_2		E=-121.0910809 ZPE=48.42 U=168.5i C -1.280866000 -0.369106000 0.000000000 B 0.000000000 0.557215000 0.000000000 N 1.281014000 -0.003033000 0.000000000 H -1.287515000 -1.022635000 0.874260000 H -2.213213000 0.189406000 0.000000000 H -0.062630000 1.750426000 0.000000000 H -1.287515000 -1.022635000 -0.874260000 H 2.119176000 0.549162000 0.000000000 H 1.449798000 -0.993932000 0.000000000
NHMe rot 1		E=-160.3005829 ZPE=66.49 U=169.3i C 1.172075000 -1.671038000 0.000000000 B -0.117058000 -0.752668000 0.000000000 N 0.000000000 0.638424000 0.000000000 C -1.086572000 1.600338000 0.000000000 H 1.794718000 -1.473827000 0.874631000 H 0.935725000 -2.732194000 0.000000000 H -1.229907000 -1.193104000 0.000000000 H 1.794718000 -1.473827000 -0.874631000 H 0.918154000 1.055881000 0.000000000 H -1.056532000 2.238258000 -0.883199000 H -2.028075000 1.059120000 0.000000000 H -1.056532000 2.238258000 0.883199000
NHMe rot 2		E=-160.3012118 ZPE=66.72 C 0.748552000 -1.584652000 0.000000000 B 1.006052000 -0.029781000 0.000000000 N 0.000000000 0.941320000 0.000000000 C -1.440248000 0.766214000 0.000000000 H 1.232176000 -2.034448000 0.869249000

		H -0.293537000 -1.896316000 0.000000000 H 2.127384000 0.389190000 0.000000000 H 1.232176000 -2.034448000 -0.869249000 H 0.286813000 1.906810000 0.000000000 H -1.893680000 1.215786000 -0.883092000 H -1.677737000 -0.292061000 0.000000000 H -1.893680000 1.215786000 0.883092000
NHMe rot 3		E=-160.3006543 ZPE=66.54 U=63.7i C -0.743624000 -1.548028000 0.000000000 B -1.032549000 0.007808000 0.000000000 N 0.000000000 0.950096000 0.000000000 C 1.428588000 0.697268000 0.000000000 H -0.161420000 -1.846357000 0.874178000 H -1.657413000 -2.136957000 0.000000000 H -2.143070000 0.451653000 0.000000000 H -0.161420000 -1.846357000 -0.874178000 H -0.242915000 1.927151000 0.000000000 H 1.907626000 1.119817000 0.883103000 H 1.603941000 -0.373918000 0.000000000 H 1.907626000 1.119817000 -0.883103000
NMe_2		E=-199.51475 ZPE=84.27 U=26.4i C 0.429912000 -2.121844000 0.000000000 B 0.903842000 -0.611006000 0.000000000 N 0.000000000 0.457040000 0.000000000 C -1.443062000 0.310814000 0.000000000 C 0.415926000 1.847330000 0.000000000 H 2.063043000 -0.313430000 0.000000000 H 1.270872000 -2.811253000 0.000000000 H -0.181478000 -2.352762000 0.874649000 H -0.181478000 -2.352762000 -0.874649000 H 0.032668000 2.364563000 0.882585000 H 1.499671000 1.903842000 0.000000000 H 0.032668000 2.364563000 -0.882585000 H -1.876824000 0.786844000 0.882333000 H -1.876824000 0.786844000 -0.882333000 H -1.718179000 -0.738496000 0.000000000

Borane dimers

R	MP2/6-311+G**	
	H-bridged	Halo- or BN-bridged
H	E=-131.4749965 ZPE=76.85 C -1.857687000 -1.037564000 -0.548542000 B -0.852457000 0.144640000 -0.231314000 B 0.852457000 -0.144640000 0.231314000 C 1.857687000 1.037564000 0.548542000 H -1.185959000 1.290965000 -0.286127000 H 1.185959000 -1.290965000 0.286127000 H -2.251668000 -0.935523000 -1.565695000 H -1.404450000 -2.028427000 -0.455441000 H 0.258945000 0.030585000 -0.935042000 H -2.720223000 -0.990965000 0.125321000 H -0.258945000 -0.030585000 0.935042000 H 2.720223000 0.990965000 -0.125321000 H 1.404450000 2.028427000 0.455441000 H 2.251668000 0.935523000 1.565695000	
F	E=-329.7665921	E=-329.7436382

	ZPE=69.30 C 1.868272000 -1.027555000 -0.551040000 B -0.866059000 0.140626000 -0.234976000 F -1.254257000 1.446242000 -0.300161000 H -2.255026000 -0.924668000 -1.570231000 H -1.403807000 -2.012015000 -0.454901000 H 0.261202000 0.030395000 -0.943250000 H -2.725826000 -0.980789000 0.128127000 B 0.866059000 -0.140626000 0.234976000 H -0.261202000 -0.030395000 0.943250000 F 1.254257000 -1.446242000 0.300161000 C 1.868272000 1.027555000 0.551040000 H 2.725826000 0.980789000 -0.128127000 H 1.403807000 2.012015000 0.454901000 h 2.255026000 0.924668000 1.570231000	ZPE=67.81297 C -2.045654000 -1.001491000 -0.597239000 B -1.087514000 0.193489000 -0.286836000 B 1.087514000 -0.193489000 0.286836000 C 2.045654000 1.001491000 0.597239000 H -1.406048000 1.337398000 -0.325014000 H 1.406048000 -1.337398000 0.325014000 H -2.440585000 -0.912954000 -1.614841000 H -1.548011000 -1.971106000 -0.503121000 F 0.283332000 0.044062000 -1.044325000 H -2.901911000 -0.984697000 0.085304000 F -0.283332000 -0.044062000 1.044325000 H 2.901911000 0.984697000 -0.085304000 H 1.548011000 1.971106000 0.503121000 H 2.440585000 0.912954000 1.614841000
Cl	E=-1049.6925954 ZPE=67.67 C -1.875354000 -1.008269000 -0.552504000 B -0.857174000 0.147383000 -0.232637000 B 0.857174000 -0.147383000 0.232637000 C 1.875354000 1.008269000 0.552504000 Cl -1.386830000 1.853352000 -0.323555000 Cl 1.386830000 -1.853352000 0.323555000 H -2.262671000 -0.888338000 -1.569676000 H -1.431650000 -2.002326000 -0.462077000 H 0.259808000 0.030683000 -0.937855000 H -2.732437000 -0.943772000 0.125940000 H -0.259808000 -0.030683000 0.937855000 H 2.732437000 0.943772000 -0.125940000 H 1.431650000 2.002326000 0.462077000 H 2.262671000 0.888338000 1.569676000	E=-1049.670514 ZPE=66.28 C -2.092915000 -1.109705000 -0.614642000 B -1.378408000 0.269193000 -0.362561000 B 1.133293000 -0.065253000 0.304680000 C 2.283352000 0.945467000 0.659365000 H -1.936860000 1.311420000 -0.470032000 H 1.291577000 -1.242767000 0.297877000 H -2.482199000 -1.147722000 -1.638507000 H -1.427632000 -1.966568000 -0.470353000 Cl 0.286223000 0.395036000 -1.410464000 H -2.944686000 -1.219732000 0.066289000 Cl -0.472992000 0.276808000 1.388177000 H 3.122631000 0.818430000 -0.034204000 H 1.958095000 1.988904000 0.615196000 H 2.660519000 0.746489000 1.669177000
Br	E=-5275.3765466 ZPE=66.76 C -1.881646000 -1.004702000 -0.554128000 B -0.856557000 0.144877000 -0.232552000 B 0.856557000 -0.144877000 0.232552000 C 1.881646000 1.004702000 0.554128000 Br -1.450442000 2.006724000 -0.336180000 Br 1.450442000 -2.006724000 0.336180000 H -2.268856000 -0.880700000 -1.570873000 H -1.442549000 -2.001140000 -0.465025000 H 0.260002000 0.030699000 -0.938550000 H -2.738514000 -0.936078000 0.124213000 H -0.260002000 -0.030699000 0.938550000 H 2.738514000 0.936078000 -0.124213000 H 1.442549000 2.001140000 0.465025000 H 2.268856000 0.880700000 1.570873000	E=-5275.3522932 ZPE=65.17 C -2.111621000 -1.146942000 -0.621267000 B -1.503145000 0.287378000 -0.395641000 B 1.170770000 -0.024730000 0.316564000 C 2.370167000 0.924494000 0.682013000 H -2.128484000 1.288829000 -0.523003000 H 1.261764000 -1.209433000 0.291230000 H -2.493101000 -1.229992000 -1.645918000 H -1.390712000 -1.953825000 -0.459764000 Br 0.285180000 0.530311000 -1.546753000 H -2.956088000 -1.302047000 0.060754000 Br -0.545536000 0.401025000 1.515445000 H 3.199758000 0.761157000 -0.016476000 H 2.103767000 1.984594000 0.654501000 H 2.737281000 0.689181000 1.688315000
CH_3	E=-209.8926739 ZPE=112.63 C -1.718900000 -1.369504000 -0.000044000 B -0.908252000 -0.000036000 0.000059000 C -1.718732000 1.369649000 0.000032000 B 0.908253000 0.000037000 0.000060000 C 1.718732000 -1.369650000 0.000031000 C 1.718900000 1.369505000 -0.000043000 H -2.375091000 -1.409359000 -0.877771000 H -1.103082000 -2.271849000 -0.000536000 H 0.000000000 0.000003000 -0.967454000 H -2.374634000 -1.410030000 0.877969000 H 0.000000000 -0.000003000 0.967556000 H 2.375062000 1.409375000 -0.877791000 H 1.103081000 2.271848000 -0.000501000 H 2.374664000 1.410016000 0.877949000 H -2.374497000 1.409813000 0.878078000 H -1.103169000 2.272134000 -0.000358000	

	H -2.375012000 1.409512000 -0.877659000 H 2.374475000 -1.409826000 0.878093000 H 1.103167000 -2.272133000 -0.000386000 H 2.375033000 -1.409501000 -0.877644000	
Ph	E=-592.3221504 ZPE=178.52 C -0.135506000 1.894773000 1.104095000 B -0.601949000 0.578402000 0.349892000 B 0.601923000 -0.578321000 -0.349890000 C 0.135578000 -1.894750000 -1.104072000 C -2.140411000 0.255233000 0.180301000 C 2.140389000 -0.255189000 -0.180300000 H -0.586882000 1.916681000 2.103020000 H 0.949412000 1.984800000 1.208676000 H 0.003929000 -0.486851000 0.840464000 H -0.504059000 2.784431000 0.578045000 H -0.003945000 0.486893000 -0.840485000 H 0.503912000 -2.784335000 -0.577728000 H -0.949310000 -1.984748000 -1.208960000 H 0.587274000 -1.916887000 -2.102842000 C 2.989389000 -1.187300000 0.451081000 C 4.359198000 -0.940552000 0.600268000 C 4.914882000 0.244063000 0.100857000 C 4.094062000 1.177663000 -0.543014000 C 2.721782000 0.930407000 -0.672034000 H 2.575505000 -2.119029000 0.834465000 H 4.991812000 -1.670777000 1.099064000 H 5.979405000 0.435579000 0.208709000 H 4.520173000 2.096739000 -0.937924000 H 2.095904000 1.669071000 -1.171292000 C -2.989540000 1.187566000 -0.450575000 C -4.359339000 0.940771000 -0.599782000 C -4.914886000 -0.244121000 -0.100876000 C -4.093945000 -1.177957000 0.542499000 C -2.721673000 -0.930647000 0.671529000 H -2.575764000 2.119509000 -0.833555000 H -4.992051000 1.671172000 -1.098194000 H -5.979400000 -0.435678000 -0.208742000 H -4.519957000 -2.097248000 0.937017000 H -2.095699000 -1.669493000 1.170393000	
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NHMe	E=-320.3645064 ZPE=135.31 C 0.138304000 -2.218053000 0.259600000 B -0.517010000 -0.766418000 0.133273000 N -1.955243000 -0.734734000 -0.036090000 B 0.516988000 0.766437000 0.133229000	E=-320.4271382 ZPE=136.99 C 0.000986000 2.107198000 1.169424000 B 0.000469000 1.115886000 -0.089924000 N -1.157831000 0.000595000 -0.025575000 B -0.000449000 -1.115732000 -0.089694000

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NMe_2	E=-398.7310336 ZPE=170.89 C -0.613330000 -2.112172000 0.321727000 B -0.761060000 -0.537995000 0.089169000 B 0.761059000 0.538060000 0.089128000 C 0.613424000 2.112255000 0.321627000 N -2.079259000 0.020899000 -0.169610000 C -2.335982000 1.307510000 -0.785935000 N 2.079232000 -0.020932000 -0.169576000 C 2.335931000 -1.307433000 -0.786138000 H -1.004822000 -2.684507000 -0.527112000 H 0.414208000 -2.427343000 0.508090000 H -0.000005000 0.000047000 -0.874302000 H -1.189732000 -2.410195000 1.205266000 H -0.000024000 0.000083000 1.074362000 H 1.004818000 2.684520000 -0.527304000 H -0.414072000 2.427484000 0.508126000 H 1.189977000 2.410308000 1.205059000 C 3.254936000 0.493784000 0.511393000 C -3.254962000 -0.493967000 0.511255000 H 3.229418000 -1.233622000 -1.420804000 H 2.519157000 -2.110736000 -0.054141000 H 1.493839000 -1.604766000 -1.415313000 H -3.229510000 1.233815000 -1.420555000 H -2.519146000 2.110692000 -0.053790000 H -1.493925000 1.604930000 -1.415115000 H 4.113413000 0.499441000 -0.173419000 H 3.089789000 1.515237000 0.854290000 H 3.530049000 -0.123201000 1.382769000 H -4.113436000 -0.499468000 -0.173560000 H -3.089824000 -1.515496000 0.853922000 H -3.530078000 0.122824000 1.382768000	E=-398.8016014 ZPE=172.60 C 0.000003000 2.368677000 -0.569179000 B 0.000001000 1.106150000 0.419680000 N -1.160186000 0.000053000 0.202752000 C -2.216505000 -0.000121000 1.230268000 N 1.160186000 0.000051000 0.202752000 C 2.216505000 -0.000126000 1.230268000 B -0.000002000 -1.106165000 0.419556000 C -0.000003000 -2.368610000 -0.569373000 H 0.877734000 3.000065000 -0.378196000 H 0.000004000 2.127779000 -1.638763000 H -0.877727000 3.000065000 -0.378198000 H 0.000002000 1.401284000 1.591601000 C -1.802263000 0.000072000 -1.125159000 C 1.802263000 0.000069000 -1.125159000 H -0.877726000 -3.000003000 -0.378364000 H -0.000004000 -2.127713000 -1.638949000 H 0.877720000 -3.000004000 -0.378365000 H -0.000002000 -1.401354000 1.591462000 H 2.843057000 -0.893277000 1.121573000 H 2.843638000 0.892587000 1.121302000 H 1.753521000 0.000175000 2.216124000 H -2.843060000 -0.893271000 1.121573000 H -1.753521000 0.000179000 2.216124000 H -2.843636000 0.892594000 1.121302000 H -2.425487000 -0.893749000 -1.235946000 H -2.425675000 0.893780000 -1.235828000 H -1.052679000 0.000208000 -1.915694000 H 2.425485000 -0.893752000 -1.235947000 H 1.052679000 0.000208000 -1.915694000 H 2.425677000 0.893776000 -1.235827000

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Intermolecular Interactions

Computational Study of van der Waals Complexes between Borylenes and Hydrocarbons

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Abstract: The addition of borylenes (RB) to prototypical carbon–carbon multiple bonds (ethyne, ethene) and the insertion into a C–H bond of methane involves weakly bound van der Waals complexes of the reaction partners according to computational chemistry methods. Geometries of all complexes were optimized using spin-component scaled second-order Møller–Plesset perturbation theory (SCS-MP2) in combination with a quadruple-ζ (def2-QZVP) basis set. Energies were further refined using the coupled-cluster (CCSD(T)) method in combination with basis sets up to quadruple-ζ quality (def2-QZVP and aug-cc-pVTZ). All of the complexes of borylenes studied correspond to shallow minima on their potential-energy surfaces. Borylene complexes with ethyne are the most stable and those with methane are the least stable ones. Aminoborylene complexes BNHR with ethyne and ethene are stabilized mainly by NH···π interactions. Symmetry-adapted perturbation theory (SAPT) was performed to analyze the nature of the interaction between borylene molecules and hydrocarbons. Most of the ethyne complexes are dominated by electrostatic interactions, whereas for most of the ethene and all of the methane complexes the interaction is mainly dispersive.

Introduction

Monovalent boron species, called borylenes, are intriguing reactive intermediates. Owing to the vacant p orbitals on the boron atom, they are capable of accepting lone pairs of electrons and can behave like a typical Lewis acid. The first generation of subvalent boron monohalides was reported by Timms in 1967 by reduction of boron trihalide with boron under high temperature and low pressure, followed by trapping reactions.[1] This procedure produced haloborylenes (BF, BCl, BBr, BI) that were all studied by microwave spectroscopy.[2] Parent BH was also studied by rotational spectroscopy.[3] Further experiments on borylenes involve the photogeneration of triphenylsilylborylene Ph_3SiB from $(Ph_3Si)_3B$ in a glass matrix and its addition to bis(trimethylsilyl)ethyne and insertion into a C–O bond of THF.[4] Arylborylene was invoked as an intermediate in the reduction of arylboron dihalides that yield borafluorenyls by intramolecular insertion into a C–C σ bond.[5] Another arylborylene, TbtB (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), was concluded to be an intermediate in the photolysis of TbtB-$(SeMe)_2$ based on trapping with phenanthrenequinone to give dioxaborolene.[6] In the experiments discussed above, the existence of borylenes was inferred indirectly from the products that were formed. Borylenes could be directly observed by infrared (IR) spectroscopy under cryogenic matrix isolation conditions. In their experiment reported in 1993, Andrews et al. co-deposited atomic boron with ethyne in an argon matrix. This resulted in production of several organoboron species.[7] One of the newly formed compounds was recognized as ethynylborylene, HCCB, on the basis of IR spectroscopy. Another organoborylene, phenylborylene, was also detected by means of IR spectroscopy after irradiation of diazidophenylborane in an N_2 matrix at 10 K.[8] Free borylenes could not be isolated, although they can be stabilized either by cyclic alkyl amino carbenes (CAAC)[9] or by transition-metal centers.[10] Borylene ligands can also be transferred photochemically from transition-metal complexes to unsaturated hydrocarbons, which can result in borirene formation[11] or C–H insertion in the case of olefins.[12]

Borylenes are subvalent boron counterparts of carbenes. A hallmark of carbenes is their facile addition to alkenes, a reaction that has received intense scrutiny. The involvement of carbene–alkene van der Waals complexes has been discussed ever since negative activation energies for the addition of carbenes to various alkenes were observed.[13] To explain this, the reversible formation of a 'loose' van der Waals complex between the singlet carbene and the alkene was invoked.[14] Houk and co-workers offered an alternative explanation based on theoretical computations: as enthalpy barriers are low or completely absent, the reaction barrier $\Delta G^{\neq}$ (activation free energy) is dominated by entropy (S). As $-T\Delta S^{\neq} > 0$ the reaction becomes faster at lower temperature.[15] Subsequent theoretical studies were able to identify complexes between carbenes and some alkenes[16] or H_2,[17] but could not locate them for reactive carbenes (like $ClCCF_3$) and alkenes (e.g., tetramethylethene, TME).[18] Although the participation of alkene–carbene complexes in cyclopropanation reactions is still not fully

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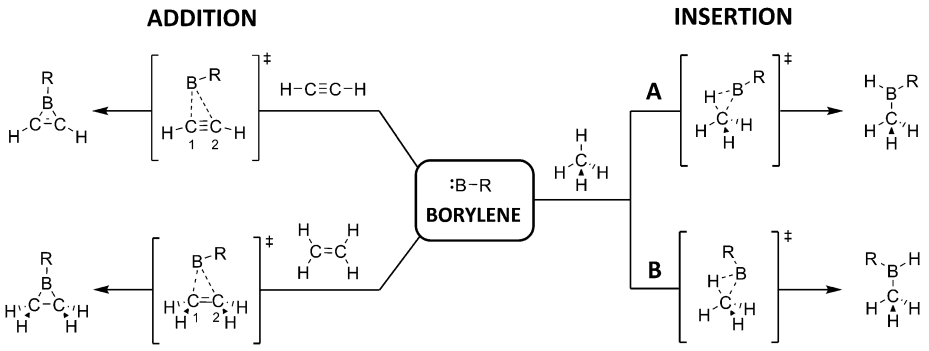
resolved, the complexation of carbenes to solvents is well established.[19]

Clearly, the understanding of the reactivity of borylenes lags far behind that of carbenes. We have thus embarked on a theoretical investigation of the reaction of borylenes towards prototypical C≡C, C=C, and C–H bonds in ethyne, ethene, and methane, respectively. In a previous paper[20] we identified transition states and barrier heights depending on the substituents of RB (R = H, F, Cl, Br, NH_2, NHMe, NMe_2). We here report a detailed high-level computational investigation that focuses on the existence, stability, and origin of the interaction of complexes between RB and the organic substrates ethyne, ethene, and methane.



Scheme 1. Reactions considered in the present work.

Results and Discussion

We consider two possible fundamental reactions of borylenes: addition to C–C multiple bonds (ethyne, ethene) and insertion into the C–H single bond of methane (Scheme 1). These reactions involve transition states on the potential-energy surface for most borylenes (not for BH) that were identified in our previous work.[20] In addition to transition structures and products, van der Waals complexes that correspond to shallow minima on the potential-energy surface can be found for the addition as well as for the insertion reaction. In this study we focus on those borylene complexes that are involved in the reactions described above as stationary points (see Table 1). These species were obtained by computation of intrinsic reaction coordinates (IRC) starting at the transition states identified earlier and moving in the direction of reactants.[20]

Table 1. Interaction energies (E_{rel} with respect to separated reactants in kcal mol^{-1}) of van der Waals complexes calculated at the CCSD(T)/def2-QZVP//SCS-MP2/def2-QZVP (I) and CCSD(T)/aug-cc-pVTZ//SCS-MP2/def2-QZVP (II) level of theory.

Borylene	Method	Hydrocarbon			
		Ethyne	Ethene	Methane A	Methane B
BH	I			−0.9	−0.8
	II			−1.0	−1.0
BPh	I[a]	−1.8	−1.9	−1.5	−1.5
	II	−2.2	−2.4	−2.1	−2.0
BCH_3	I	−2.0	−1.5	−0.9	−0.8
	II	−2.1	−1.7	−1.0	−1.0
BBr	I	−1.2	−1.1	−0.7	−0.7
	II	−1.4	−1.3	−0.9	−0.9
BCl	I	−1.2	−1.0	−0.7	−0.6
	II	−1.4	−1.2	−0.9	−0.8
BF	I	−1.0	−0.9	−0.5	−0.5
	II	−1.2	−1.0	−0.7	−0.7
BNH_2	I	−2.7	−2.7	−1.1	−1.1
	II	−2.9	−3.0	−1.4	−1.3
BNH_2 (rot)	I	−2.8	−2.8	–	–
	II	−3.1	−3.1	–	–
BNHMe	I	−2.8	−2.8	−1.3	−1.3
	II	−3.1	−3.2	−1.6	−1.6
BNHMe (rot)	I	−2.8	−2.8	–	–
	II	−3.2	−3.2	–	–
$BNMe_2$	I	−2.8	−1.7	−0.9	−0.8
	II	−3.0	−2.0	−1.1	−1.0
$BNMe_2$ (rot)	I	−0.9	−2.1	–	–
	II	−1.2	−2.4	–	–

[a] Energy calculated at the CCSD(T)/def2-TZVP//SCF-MP2/def2-QZVP level of theory.

Van der Waals complexes in the addition reactions

Most of the complexes computed for the addition reactions are of C_s symmetry (see Figures 1 and 2). The complexes for the addition of borylene to ethyne are in most cases more favorable than the RB–ethene complexes. Borylene molecules do not significantly affect the geometry of the hydrocarbon: the angle H-C1-C2 of ethyne is close to 180°. The distances between the boron and carbon C1 atom are longer than 3.3 Å. The longest distance was found for the ethyne complex with BNH_2 (3.695 Å), whereas the shortest B–C1 distance was obtained for the complex with BCH_3 (3.347 Å). In ethyne complexes one can notice the shift of the borylene molecule towards one of the hydrogen atoms to possibly form B···H in-

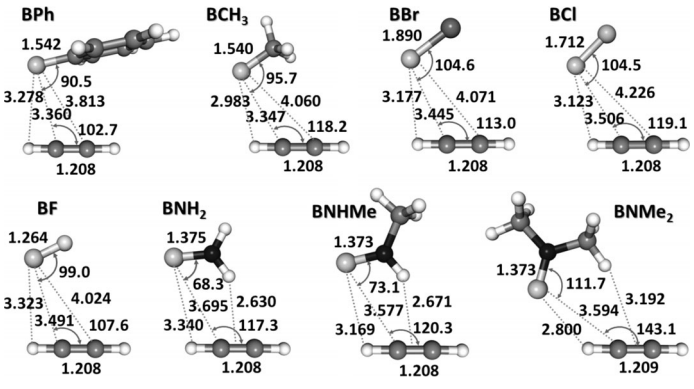


Figure 1. Geometries of borylene–ethyne complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths [Å] and bond angles [°] are given.

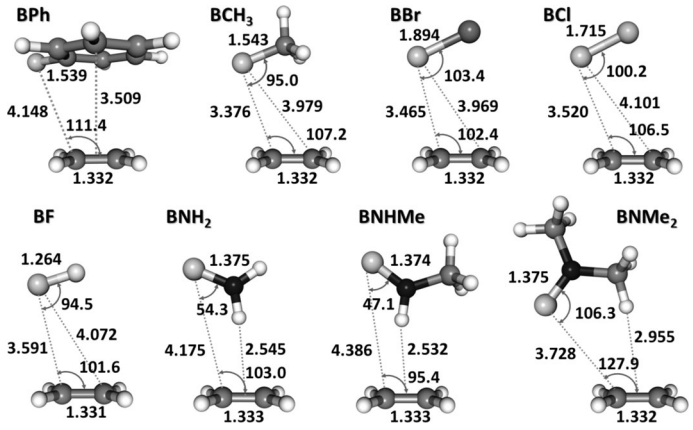


Figure 2. Geometries of borylene–ethene complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths [Å] and bond angles [°] are given. The depicted ethene–BNRR′ complexes are saddle points.

teractions as judged by the short distances in the range of 3.3–2.8 Å.

The binding energies of methylborylene and haloborylene complexes are lower with ethyne than with ethene by 0.5–0.1 kcal mol^{-1}. That might indicate stabilization by B···H interactions in ethyne complexes that is absent in the ethene complexes owing to the trigonal coordination of the olefinic carbon atoms. On the other hand, the phenylborylene complex with ethene is stronger than its ethyne counterpart. Comparison of the geometries of the two complexes reveals that ethene is shifted away from the boron atom and interacts with the π system of the phenyl ring. The two units are twisted at about 42° with respect to each other, thereby resulting in C_1 symmetry. The increased π···π stacking interaction between the phenyl ring and the C1=C2 double bond probably causes the somewhat stronger bonding. The least stable complexes formed involve fluoroborylene, while aminoborylene complexes are most strongly bound among all of the studied complexes. This might be caused by the presence of an NH···π interaction between the hydrogen atom attached to the nitrogen and the π system of the hydrocarbon. The importance of the NH···π interaction in aminoborylene (BNH_2 and BNHMe) complexes is demonstrated by the formation of unusual complexes with ethene in which the borylene molecule is rotated by 90° and is perpendicular to the organic substrate (Figure 3). The "regular" ethene complexes (Figure 2) are saddle points that are about 0.1 kcal mol^{-1} higher in energy. In turn, the rotated BNHR–ethyne complexes (Figure 3) are minima and about 0.1–0.2 kcal mol^{-1} lower in energy than the product-forming complexes. The rotated dimethylaminoborylene complex with ethyne is a saddle point with the energy higher than a normal $BNMe_2$ complex by 1.8 kcal mol^{-1}. In the case of ethene, its rotated complex with $BNMe_2$ is a minimum and is lower in energy by 0.4 kcal mol^{-1} than the 'regular' complex, which is a saddle point. The distance between hydrogen and the π system (2.5 Å for BNHMe and BNH_2, and 2.9 Å for $BNMe_2$) is shorter in aminoborylene–ethene complexes, but the interaction energies are very similar, except for $BNMe_2$ complexes. The interaction of $BNMe_2$ with ethene is weaker than with ethyne, probably due to reduced H···π hydrogen bonding and the lack of B···H interaction that appears in the complex with ethyne.

Complexes of the insertion reaction

In our previous work we identified two different orientations of methane and borylenes in the transition state (TS) for C–H insertion (approaches A and B in Scheme 1). These two approaches differ by the orientation of the substituent at boron and the migrating hydrogen atom. With the exception of BNH_2 and BNHMe complexes, the product-forming complexes along approach B with C_s symmetry (see Figure 4) are saddle points. Reduction of symmetry lowers the energy by at most 0.05 kcal mol^{-1} and produces the complexes of approach A. Van der Waals complexes

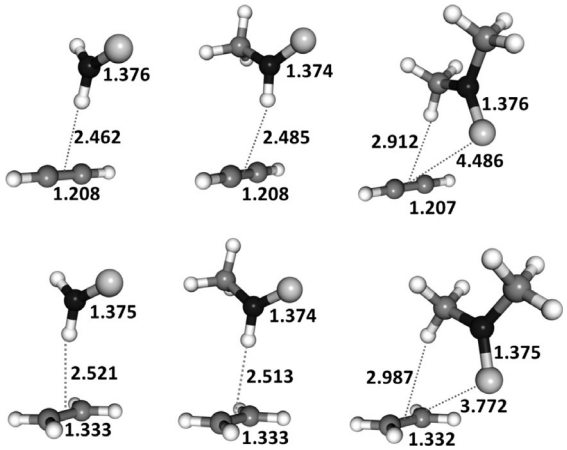


Figure 3. Geometries of other aminoborylene complexes (denoted in Tables 1 and 2 as BNRR′ (rot)) computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths are given in Å. All complexes except for ethyne–$BNMe_2$ are minima.

with methane are weaker than the ones involved in the addition reactions. In the case of aminoborylene complexes, C-(methane)···H(borylene) interactions occur. Also in the phenylborylene complexes H···π interaction appears, which leads to a lowering of their energies relative to BH and BCH_3 complexes. The weakest complexes of methane are those with haloborylenes.

Symmetry-adapted perturbation theory (SAPT) analysis

Symmetry-adapted perturbation theory is a powerful tool for partitioning the interaction energy into particular contributions. The SAPT interaction energy components are the attractive electrostatic interaction energy (E_{elst}), induction energy (E_{ind}), and dispersion energy (E_{disp}), and the repulsive exchange interaction (E_{exch}). A more detailed description of the particular interaction energy terms can be found in the comprehensive reviews by Szalewicz et al.[21]

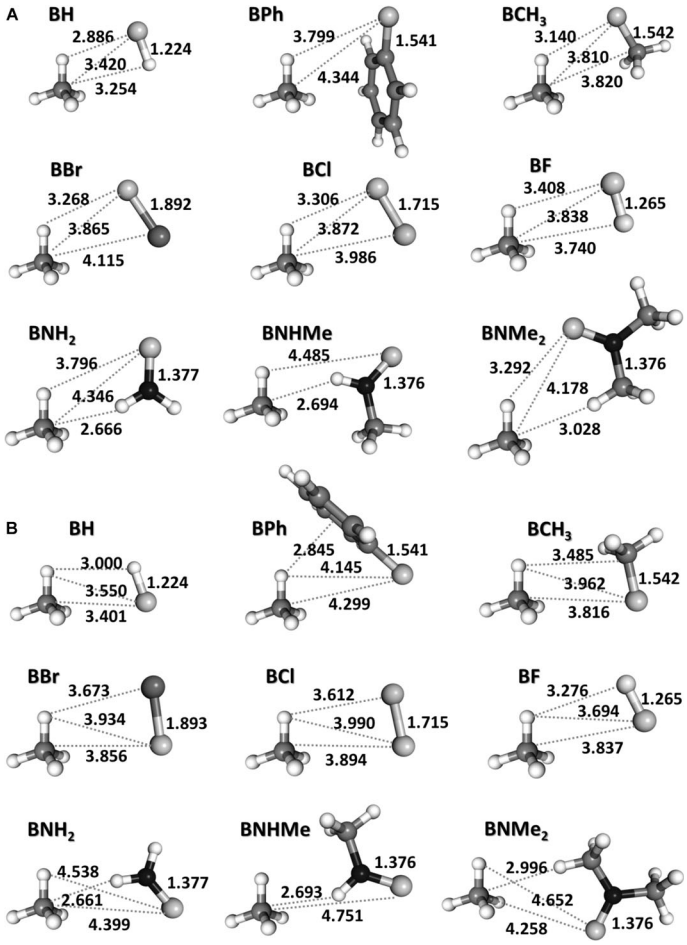


Figure 4. Geometries of borylene–methane complexes computed at the SCS-MP2/def2-QZVP level of theory. Important bond lengths are given in Å.

The computed SAPT interaction energies (Table 2) agree well with the values obtained at the CCSD(T) level of theory, slightly better so when CCSD(T) is combined with the aug-cc-pVTZ rather than with the def2-QZVP basis set (see Table 1). However, for phenylborylene complexes with ethyne and ethene, qualitative differences are observed: whereas the SAPT interaction is stronger for ethyne by 0.2 kcal mol^{-1}, it is stronger for ethene by 0.2 kcal mol^{-1} at CCSD(T)/aug-cc-pVTZ.

The dominant component of the attractive interaction varies with the borylene and the organic substrate. With the exception of the $BNMe_2$–ethene complex in which dispersion dominates, the electrostatic term is the largest in all complexes of aminoborylenes with ethyne and ethene. It contributes 48–53% of the attractive interaction in the aminoborylene–ethyne complexes and it is largest (53%) in the $BNMe_2$–ethyne complex. The electrostatic term in aminoborylene–ethene complexes amounts to 40–49% of overall attraction energy and is the largest for the BNH_2–ethene complex (49%). The electrostatic and dispersive terms are almost of equal size in ethyne complexes of the haloborylenes and methylborylene, whereas dispersion dominates in the phenylborylene complex (53%). In comparison with ethyne complexes, ethene complexes have a greater contribution of dispersion interaction. This is the largest contribution to the attraction for complexes that involve the organo- and haloborylenes and prevails in the ethene complex with phenylborylene (73%). Induction is the smallest component of attraction energy both in ethyne and ethene complexes and varies from 7 to 18%.

The main component of the attraction energy in both types of methane complexes is dispersion, and it is in the range of 53–80% of total attraction. Phenylborylene complexes reveal the largest contribution of the dispersion term (80% for approach A and 77% for approach B). Contribution of electrostatic energy is smaller than 30% for methane A and B complexes. For all types of complexes the smallest contribution to the attractive part of interaction energy is due to the induction term. For various complexes it varies in the range 4–18%.

Conclusion

Van der Waals complexes of borylenes with ethyne, ethene, and methane studied at the CCSD(T)/def2-QZVP//SCS-MP2/def2-QZVP and CCSD(T)/aug-cc-pVTZ//SCS-MP2/def2-QZVP levels of theory are represented by shallow minima on the potential-energy surface of the C–C addition or C–H insertion reactions. The strongest complexes are formed between borylenes and ethyne. The most stable ethyne and ethene complexes are formed with aminoborylenes in which H···π interactions play a crucial role in stabilization of the systems. The weakest addition complexes are those that involve haloborylenes. For the borylene C–H insertion reaction two types of complexes were found depending on the borylene arrangement, but these have very similar binding energies. These complexes are much weaker than the ones with unsaturated hydrocarbons. Most stable are aminoborylenes and phenylborylene complexes, which are stabilized by H···C and H···π interactions, respectively. SAPT analysis showed that for most borylene complexes with ethyne the main contribution to the interaction is electrostatic energy. In the case of all methane complexes, the main contribution to the interaction is due to dispersion. Induction is the smallest contribution to the overall attraction for all types of van der Waals complexes.

Computational Methods

Geometries of van der Waals complexes discussed in the main article have been optimized using spin-component scaled[22] second-order Møller–Plesset perturbation theory[23] (SCS-MP2) with the resolution of the identity approximation[24] (RI) in conjunction with Ahlrichs' polarized quadruple-ζ def2-QZVP[25] basis set and the complementary fitting basis set,[26] followed by numerical frequency analysis performed at the same level of theory. The energies have been refined with coupled-cluster theory[27] of single, double, and a perturbative estimate of triple excitations (CCSD(T)) in combination with def2-QZVP (the smaller def2-TZVP[25] basis set was used in the case of phenylborylene complexes owing to computational limitations) and aug-cc-pVTZ[28] basis sets using SCS-MP2 geometries. The RI approximation was applied in coupled-cluster calculations[29] using suitable fitting basis sets.[26]

For more extensive analysis of van der Waals complexes, additional computations were carried out at various levels of theory (included

Table 2. Computed SAPT2+3 interaction energies [kcal mol^{-1}] and their components. Computations were performed on the SCS-MP2/def2-QZVP geometries using the aug-cc-pVTZ basis set.

Borylene	Ethyne					Ethene				
	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}(SAPT)	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}(SAPT)
BCH_3	−2.9	3.5	−0.7	−2.2	−2.3	−1.9	3.4	−0.7	−2.5	−1.7
BPh	−2.3	4.2	−0.6	−3.3	−2.1	−1.3	4.4	−0.4	−4.6	−1.9
BBr	−1.6	2.4	−0.5	−1.9	−1.6	−1.3	2.8	−0.5	−2.3	−1.3
BCl	−1.6	2.1	−0.4	−1.6	−1.5	−1.1	2.2	−0.4	−1.9	−1.2
BF	−1.4	1.8	−0.3	−1.3	−1.2	−1.0	1.6	−0.3	−1.3	−1.0
BNH_2	−3.3	3.5	−0.9	−2.2	−2.9	−3.2	3.9	−1.2	−2.2	−2.7
BNH_2 (rot)	−3.6	4.0	−1.3	−2.1	−3.0	−3.4	4.1	−1.3	−2.3	−2.8
BNHMe	−3.4	3.8	−0.9	−2.5	−3.1	−3.2	4.1	−1.2	−2.6	−2.8
BNHMe (rot)	−3.4	4.0	−1.1	−2.5	−3.0	−3.3	4.3	−1.3	−2.5	−2.8
$BNMe_2$	−3.8	4.0	−1.0	−2.4	−3.2	−1.9	2.9	−0.6	−2.3	−1.9
$BNMe_2$ (rot)	−0.8	1.5	−0.3	−1.5	−1.1	−2.4	3.4	−0.6	−2.8	−2.4
Borylene	**Methane A**					**Methane B**				
	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}(SAPT)	E_{elst}	E_{exch}	E_{ind}	E_{disp}	E_{int}(SAPT)
BH	−0.8	1.5	−0.4	−1.5	−1.0	−0.6	1.4	−0.3	−1.5	−1.0
BCH_3	−0.6	1.2	−0.2	−1.4	−1.0	−0.5	1.3	−0.2	−1.5	−0.9
BPh	−0.7	2.1	−0.2	−2.9	−1.6	−0.7	2.1	−0.2	−2.9	−1.6
BBr	−0.4	1.0	−0.1	−1.3	−0.9	−0.3	0.9	−0.1	−1.3	−0.8
BCl	−0.4	0.9	−0.1	−1.2	−0.8	−0.3	0.8	−0.1	−1.1	−0.7
BF	−0.3	0.6	−0.1	−0.8	−0.6	−0.3	0.5	−0.1	−0.8	−0.6
BNH_2	−0.8	1.3	−0.4	−1.3	−1.2	−0.8	1.3	−0.4	−1.3	−1.2
BNHMe	−0.7	1.4	−0.4	−1.8	−1.4	−0.7	1.4	−0.4	−1.7	−1.4
$BNMe_2$	−0.7	1.2	−0.2	−1.4	−1.1	−0.4	0.9	−0.2	−1.3	−0.9

in the Supporting Information to this article). These include full geometry optimization at the MP2 level of theory with the RI approximation in combination with the def2-QZVP basis set. Density functional theory with London dispersion correction (DFT-D3) is a reasonable choice to study noncovalent interactions.[30] Thus, the dispersion-corrected[31] TPSS-D3 meta GGA[32] and the B3LYP-D3 hybrid[33] functionals in combination with the def2-QZVP basis set within the RI approximation[34] and suitable fitting basis set[35] were chosen to examine the geometries and energetics of the borylene complexes. Moreover, geometry optimization at the non-RI MP2 level of theory with the cc-pVTZ basis set[36] was performed.

In addition to the aforementioned methods, symmetry-adapted perturbation theory[21] of third order with density fitting (DF-SAPT2+3)[37] was used to analyze the interaction energies of the systems, which allowed us to investigate the nature of the interaction between hydrocarbons and borylenes. The SAPT analysis in combination with the aug-cc-pVTZ basis set was performed on the geometries calculated at the SCS-MP2/def2-QZVP level of theory.

The frozen-core approximation was applied in MP2, CCSD(T), and SAPT calculations. Computations were performed using the Turbomole 6.5 program,[38] except for the MP2/cc-pVTZ geometry optimization, which was done using Gaussian 09.[39] SAPT analysis was carried out using the PSI4 program.[40]

The energies given in the text refer to CCSD(T)/aug-cc-pVTZ//SCS-MP2/def2-QZVP (level II in Table 1) unless noted otherwise.

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Keywords: borylenes · carbenes · computer chemistry · hydrocarbons · insertion

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Supporting Information

Computational Study of van der Waals Complexes between Borylenes and Hydrocarbons

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Table of Contents

Table 1. Relative energies E_{rel} and zero-point corrected energies E_0 (in kcal/mol) of van der Waals complexes calculated at various levels of theory using def2-QZVP and cc-pVTZ[a] basis sets.

Borylene	Method	Hydrocarbon							
		Acetylene		Ethylene		Methane A		Methane B	
		E_{rel}	E_0	E_{rel}	E_0	E_{rel}	E_0	E_{rel}	E_0
BH	RI-B3LYP+D3					-1.32	-0.46	-1.28	-0.49
	RI-TPSS+D3					-2.06	-0.76	-1.44	-0.71
	RI-MP2					-1.00	-0.17	-0.95	-0.18
	SCS-RI-MP2					-0.66	0.04	-0.61	0.02
	MP2[a]					-0.89	-0.15	-0.78	-0.15
BPh	RI-B3LYP+D3	-	-	-1.52	-1.10	-1.37	-0.69	-1.55	-0.87
	RI-TPSS+D3	-	-	-	-	-1.56	-1.07	-1.72	-1.21
	RI-MP2	-2.98	-2.57	-3.14	-2.74	-2.01	-1.51	-2.00	-1.52
	SCS-RI-MP2	-1.85	-1.64	-1.91	-1.55	-1.31	-0.86	-1.30	-0.91
	MP2[a]	-2.72	-2.47	-3.06	-2.66	-1.95	-1.49	-1.94	-1.51
BCH_3	RI-B3LYP+D3	-2.36	-1.75	-1.80	-0.94	-1.13	-0.33	-0.99	-0.25
	RI-TPSS+D3	-	-	-	-	-1.34	-0.68	-1.20	-0.67
	RI-MP2	-2.37	-1.81	-1.84	-1.12	-0.92	0.16	-0.86	-0.35
	SCS-RI-MP2	-1.87	-1.36	-1.30	-0.73	-0.61	0.16	-0.57	-0.14
	MP2[a]	-2.31	-1.74	-1.82	-1.14	-0.86	-0.31	-0.78	-0.34
BBr	RI-B3LYP+D3	-1.59	-1.22	-1.46	-0.97	-1.00	-0.42	-0.90	-0.43
	RI-TPSS+D3	-2.03	-1.63	-2.23	-1.55	-1.15	-0.66	-1.07	-0.66
	RI-MP2	-1.65	-1.32	-1.48	-1.10	-0.84	-0.46	-0.78	-0.45
	SCS-RI-MP2	-1.21	-0.91	-0.98	-0.68	-0.55	-0.22	-0.50	-0.21
	MP2[a]	-1.58	-1.26	-1.45	-1.07	-0.81	-0.40	-0.75	-0.40
BCl	RI-B3LYP+D3	-1.56	-1.17	-1.30	-0.82	-0.90	-0.34	-0.81	-0.33
	RI-TPSS+D3	-1.88	-1.50	-1.89	-1.29	-1.06	-0.60	-0.99	-0.61
	RI-MP2	-1.56	-1.22	-1.32	-0.95	-0.76	-0.38	-0.71	-0.37
	SCS-RI-MP2	-1.19	-0.86	-0.90	-0.60	-0.50	-0.17	-0.46	-0.17
	MP2[a]	-1.47	-1.13	-1.25	-0.90	-0.68	-0.29	-0.62	-0.31
BF	RI-B3LYP+D3	-1.29	-0.88	-1.09	-0.62	-0.69	-0.16	-0.66	-0.15
	RI-TPSS+D3	-1.58	-1.20	-1.44	-0.93	-0.85	-0.37	-0.83	-0.45
	RI-MP2	-1.22	-0.85	-0.99	-0.62	-0.51	-0.13	-0.49	-0.17
	SCS-RI-MP2	-0.96	-0.62	-0.73	-0.41	-0.35	-0.03	-0.33	-0.05
	MP2[a]	-1.22	-0.85	-1.05	-0.67	-0.51	-0.17	-0.50	-0.19
BNH_2	RI-B3LYP+D3	-3.08	-2.29	-3.11	-2.16	-1.43	-0.55	-1.38	-0.64

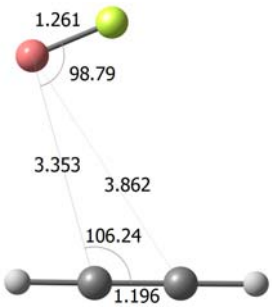
	RI-TPSS+D3	-3.18	-2.52	-3.28	-2.38	-1.51	-0.78	-1.42	-0.80
	RI-MP2	-3.02	-2.29	-3.05	-2.19	-1.18	-0.52	-1.16	-0.52
	SCS-RI-MP2	-2.52	-1.83	-2.53	-1.69	-0.87	-0.27	-0.86	-0.27
	MP2[a]	-2.94	-2.25	-3.05	-2.23	-1.12	-0.53	-1.10	-0.54
BNH_2 R	RI-B3LYP+D3	-3.14	-2.30	-3.22	-2.23				
	RI-TPSS+D3	-3.31	-2.47	-3.41	-2.44				
	RI-MP2	-3.16	-2.37	-3.17	-2.24				
	SCS-RI-MP2	-2.66	-1.89	-2.62	-1.72				
BNHMe	RI-B3LYP+D3	-3.20	-2.56	-3.19	-2.44	-1.46	-0.74	-1.58	-0.82
	RI-TPSS+D3	-3.30	-2.77	-3.36	-2.66	-1.53	-0.89	-1.44	-0.93
	RI-MP2	-3.16	-2.59	-3.22	-2.63	-1.38	-0.81	-1.36	-0.83
	SCS-RI-MP2	-2.61	-2.06	-2.59	-1.99	-0.98	-0.48	-0.98	-0.48
	MP2[a]	-3.11	-2.56	-3.24	-2.65	-1.28	-0.79	-1.30	-0.78
BNHMe R	RI-B3LYP+D3	-3.13	-2.59	-3.23	-2.44				
	RI-TPSS+D3	-3.28	-2.68	-3.42	-2.66				
	RI-MP2	-3.26	-2.72	-3.25	-2.56				
	SCS-RI-MP2	-2.67	-2.12	-2.64	-1.97				
BNHMe 1	RI-B3LYP+D3	-3.23	-2.58	-2.16	-1.51	-1.24	-0.51		
	RI-TPSS+D3	-3.54	-2.94	-2.54	-1.89	-1.42	-0.79		
	RI-MP2	-3.09	-2.51	-2.07	-1.59	-0.98	-0.48		
	SCS-RI-MP2	-2.55	-2.00	-1.55	-1.11	-0.68	-0.24		
	MP2[a]	-3.06	-2.49	-2.07	-1.59	-0.92	-0.47		
$BNMe_2$	RI-B3LYP+D3	-3.25	-2.66	-2.00	-1.43	-1.20	-0.54	-0.94	-0.42
	RI-TPSS+D3	-3.57	-3.02	-2.35	-1.77	-1.39	-0.81	-1.13	-0.71
	RI-MP2	-3.15	-2.63	-2.02	-1.59	-0.98	-0.53	-0.83	-0.47
	SCS-RI-MP2	-2.62	-2.12	-1.51	-1.13	-0.68	-0.29	-0.56	-0.25
	MP2[a]	-3.14	-2.60	-2.04	-1.60	-0.93	-0.50	-0.78	-0.45
$BNMe_2$ R	RI-B3LYP+D3	-1.05	-0.73	-2.76	-2.13				
	RI-TPSS+D3	-1.20	-0.97	-2.50	-1.79				
	RI-MP2	-1.13	-0.90	-2.47	-1.88				
	SCS-RI-MP2	-0.81	-0.58	-1.84	-1.31				
	MP2[a]	-1.11	-0.89	-2.47	-1.89				

Geometries and Cartesian coordinates of van der Waals complexes of borylenes and hydrocarbons.

1. Geometries of van der Waals complexes with acetylene

Fluoroborylene (BF)

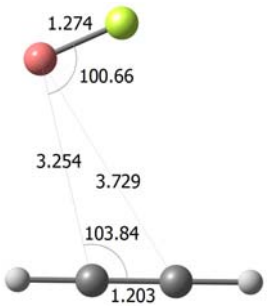
RI-B3LYP+D3/def2-QZVP



E=-201.9983670
ZPE=0.0308452

```
C    1.287817263  -0.735001878   0.000000000
C    1.108603032   0.447879002   0.000000000
B   -2.214995489   0.892543141   0.000000000
H    1.447704560  -1.784752377   0.000000000
H    0.942199235   1.496746209   0.000000000
F   -2.571328600  -0.317414098   0.000000000
```

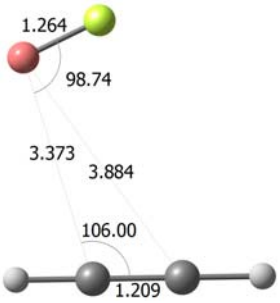
RI-TPSS+D3/def2-QZVP



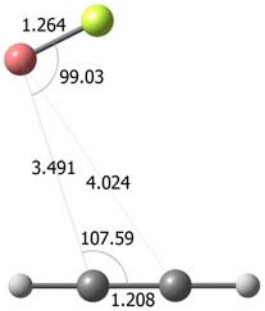
E=-202.1145512
ZPE=0.0302213

```
C    1.237710845  -0.724516082   0.000000000
C    1.093047962   0.469558791   0.000000000
B   -2.137175916   0.862152153   0.000000000
H    1.363265556  -1.782086869   0.000000000
H    0.965182953   1.527006305   0.000000000
F   -2.522031400  -0.352114298   0.000000000
```

RI-MP2/def2-QZVP



SCS-RI-MP2/def2-QZVP



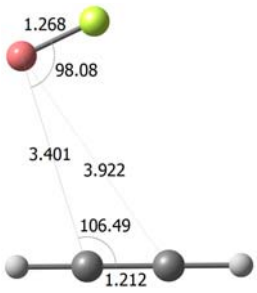
E=-201.70242678401596
ZPE=0.0304641

```
C    1.292599771  -0.742653813   0.000000000
C    1.114692962   0.453508591   0.000000000
B   -2.229304600   0.895857987   0.000000000
H    1.449428577  -1.792261487   0.000000000
H    0.956118173   1.503179989   0.000000000
F   -2.583534883  -0.317631272   0.000000000
```

E=-201.7014311631
ZPE=0.0304333

```
C    1.350612605  -0.750120916   0.000000000
C    1.145794551   0.439946826   0.000000000
B   -2.312313519   0.914999968   0.000000000
H    1.533053373  -1.795903179   0.000000000
H    0.961704576   1.485764374   0.000000000
F   -2.678851585  -0.294687078   0.000000000
```

MP2/cc-pVTZ

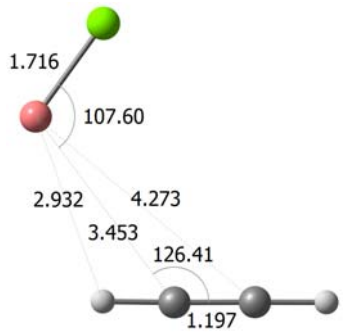


E=-201.639783
ZPE=030341

```
C    1.205283000   1.682442000   0.000000000
C    0.000000000   1.810258000   0.000000000
B   -1.303946000  -1.331185000   0.000000000
F   -0.212990000  -1.976962000   0.000000000
H    2.261151000   1.571486000   0.000000000
H   -1.056207000   1.920900000   0.000000000
```

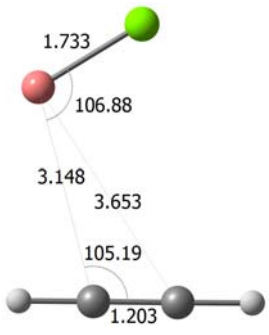
Chloroborylene (BCl)

RI-B3LYP+D3/def2-QZVP



E=-562.27621792196
ZPE=0.0294778

RI-TPSS+D3/def2-QZVP

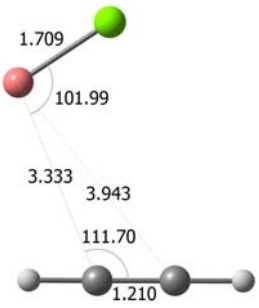


E=-562.4262326
ZPE=0.0289649

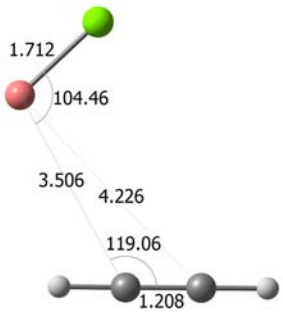
```
C   1.428698725  -1.013762287   0.000000000
C   1.155732997   0.151240133   0.000000000
B  -2.017386781   1.512745772   0.000000000
Cl -3.139266516   0.214197568   0.000000000
H   1.676068959  -2.046310991   0.000000000
H   0.896152617   1.181889800   0.000000000
```

```
C   1.124748505  -0.887928001   0.000000000
C   1.183070976   0.313882454   0.000000000
B  -1.811393573   1.284993181   0.000000000
Cl -2.801641371  -0.137143798   0.000000000
H   1.066744138  -1.951252172   0.000000000
H   1.238471320   1.377448332   0.000000000
```

RI-MP2/def2-QZVP



SCS-RI-MP2/def2-QZVP



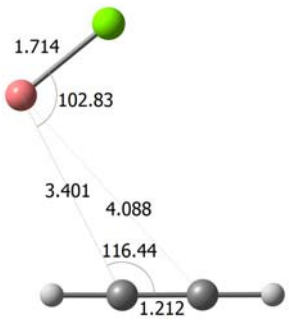
E=-561.63208574341786
ZPE=0.0291630

```
C   1.219415718  -0.944210887   0.000000000
C   1.183366098   0.264848038   0.000000000
B  -1.948546951   1.404056458   0.000000000
Cl -2.853565433  -0.045765676   0.000000000
H   1.253135592  -2.004896084   0.000000000
H   1.146194976   1.325968151   0.000000000
```

E=-561.6349764193
ZPE=0.0291297

```
C   1.364205324  -0.991827482   0.000000000
C   1.201956726   0.204975789   0.000000000
B  -2.063334713   1.480876327   0.000000000
Cl -3.064768052   0.092719864   0.000000000
H   1.510527897  -2.043207826   0.000000000
H   1.051412819   1.256463328   0.000000000
```

MP2/cc-pVTZ

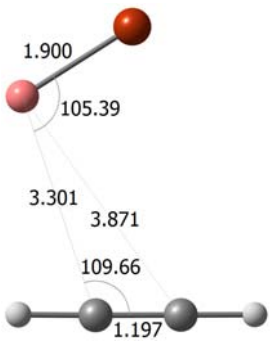


E=-561.5770271
ZPE=0.029023

```
C   1.617956000  -2.154620000   0.000000000
C   2.127385000  -1.054578000   0.000000000
B   0.000000000   1.599336000   0.000000000
Cl -1.542034000   0.850924000   0.000000000
H   1.173903000  -3.118921000   0.000000000
H   2.568626000  -0.088273000   0.000000000
```

Bromoborylene (BBr)

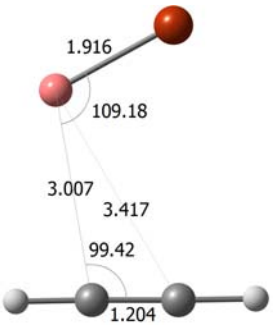
RI-B3LYP+D3/def2-QZVP



E=-2676.1874218
ZPE=0.0291035

```
C    1.182544450  -0.956709158   0.000000000
C    1.230512420   0.238829318   0.000000000
B   -1.830931633   1.472893831   0.000000000
H    1.140171397  -2.017613767   0.000000000
H    1.261290205   1.300340459   0.000000000
Br  -2.983586840  -0.037740683   0.000000000
```

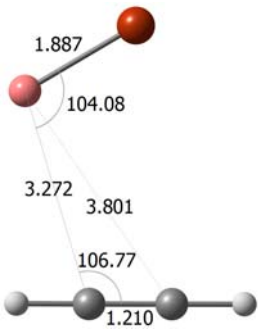
RI-TPSS+D3/def2-QZVP



E=-2676.2876378
ZPE=0.0286646

```
C    1.013030848  -0.864810237   0.000000000
C    1.211225423   0.322499915   0.000000000
B   -1.633784342   1.296566404   0.000000000
H    0.818235781  -1.911710275   0.000000000
H    1.406992472   1.369125543   0.000000000
Br  -2.815700187  -0.211671355   0.000000000
```

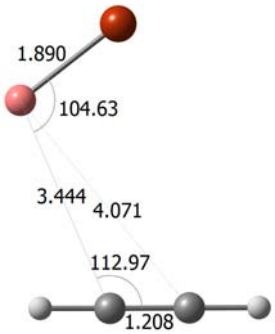
RI-MP2/def2-QZVP



E=-2674.53273889029924
ZPE=0.0287782

```
C    1.135197628  -0.943569238   0.000000000
C    1.230447394   0.262359346   0.000000000
B   -1.817817624   1.450195324   0.000000000
H    1.051021281  -2.001488983   0.000000000
H    1.311260479   1.320888679   0.000000000
Br  -2.910109156  -0.088385128   0.000000000
```

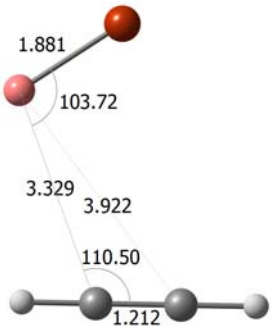
SCS-RI-MP2/def2-QZVP



E=-2674.5366025606
ZPE=0.0287395

```
C    1.257192694  -0.994746401   0.000000000
C    1.248392587   0.212996678   0.000000000
B   -1.932446287   1.534264348   0.000000000
H    1.267198432  -2.056240119   0.000000000
H    1.234460774   1.274918814   0.000000000
Br  -3.074798200   0.028806681   0.000000000
```

MP2/cc-pVTZ

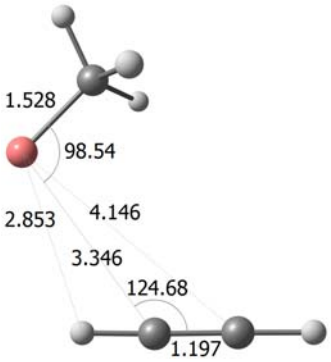


E=-2674.5469051
ZPE=0.028651

```
C   1.130425000  -2.919551000   0.000000000
C  -0.078591000  -3.009358000   0.000000000
B  -1.472445000   0.013847000   0.000000000
Br  0.000000000   1.183726000   0.000000000
H   2.189195000  -2.841181000   0.000000000
H  -1.137973000  -3.085012000   0.000000000
```

Methylborylene (BCH_3)

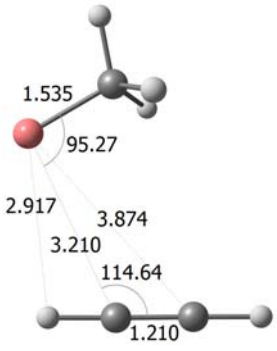
RI-B3LYP+D3/def2-QZVP



E=-141.9470626
ZPE=0.0626997

```
C   2.437693167  -0.592014550   0.000000000
C   2.022378399   0.530577653   0.000000000
B  -1.219313188   1.361350701   0.000000000
H   2.816169282  -1.584047586   0.000000000
H   1.629153972   1.519373178   0.000000000
C  -1.814321045  -0.046275571   0.000000000
H  -2.909354887  -0.000232277   0.000000000
H  -1.481202850  -0.594365774  -0.888876366
H  -1.481202850  -0.594365774   0.888876366
```

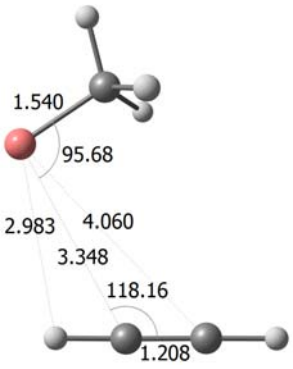
RI-MP2/def2-QZVP



E=-141.6666978782882
ZPE=0.0628769

```
C   2.173253756  -0.582214643   0.000000000
C   1.942277875   0.605636573   0.000000000
B  -1.176798622   1.362591082   0.000000000
H   2.384479922  -1.622290985   0.000000000
H   1.726046905   1.646153205   0.000000000
C  -1.674261628  -0.089596637   0.000000000
H  -2.765836094  -0.106424314   0.000000000
H  -1.304581057  -0.606927140  -0.887267237
H  -1.304581057  -0.606927140   0.887267237
```

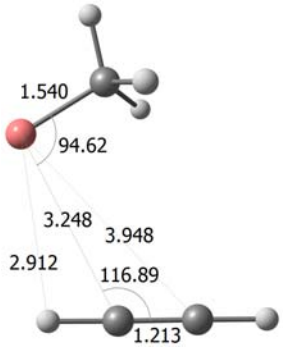
SCS-RI-MP2/def2-QZVP



E=-141.6785788493
ZPE=0.0629273

```
C    2.309011963  -0.589084039   0.000000000
C    2.008300677   0.581055988   0.000000000
B   -1.243266697   1.376804169   0.000000000
H    2.582635482  -1.614811601   0.000000000
H    1.730600902   1.607163245   0.000000000
C   -1.755764783  -0.075906205   0.000000000
H   -2.848435505  -0.087942683   0.000000000
H   -1.391541019  -0.598639437  -0.887681741
H   -1.391541019  -0.598639437   0.887681741
```

MP2/cc-PVTZ

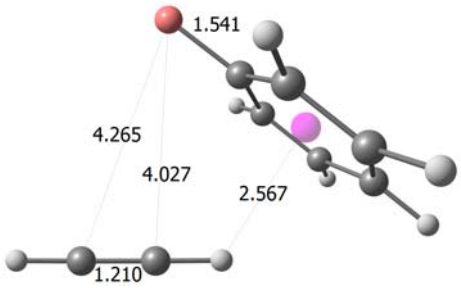


E=-141.6226195
ZPE=0.062755

```
C    0.208811000  -1.971455000   0.000000000
B    1.510187000  -1.147953000   0.000000000
C    0.000000000   1.728122000   0.000000000
C   -1.212686000   1.710801000   0.000000000
H   -2.274434000   1.705334000   0.000000000
H    1.063260000   1.729470000   0.000000000
H    0.444293000  -3.038505000   0.000000000
H   -0.380401000  -1.730670000   0.888096000
H   -0.380401000  -1.730670000  -0.888096000
```

Phenylborylene (BPh)

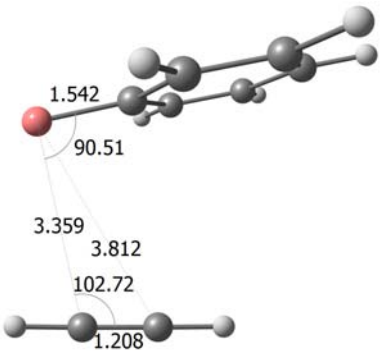
RI-MP2/def2-QZVP



E=-333.04892772060867
ZPE=0.1188389

```
C   -2.111545538  -1.015227145   0.000000000
C   -3.259762689  -0.633935109   0.000000000
```

SCS-RI-MP2/def2-QZVP



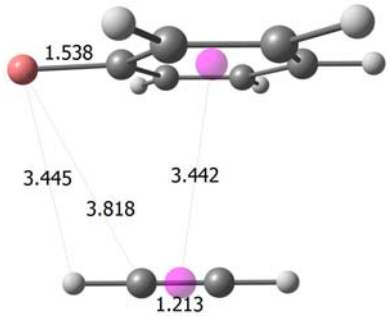
E=-333.0392757964
ZPE=0.1185007

```
C    0.617605156   0.634494089   1.212164836
C    0.159418067   1.174693184   0.000000000
```

```
B  -0.641892421   2.733649873   0.000000000
H  -1.100522345  -1.343348032   0.000000000
H  -4.264768987  -0.292860988   0.000000000
C   0.185388931   1.433796384   0.000000000
C   0.555536907   0.833706296  -1.212270299
C   1.282220987  -0.349884846  -1.210662377
C   1.642737606  -0.939398116   0.000000000
C   1.282220987  -0.349884846   1.210662377
C   0.555536907   0.833706296   1.212270299
H   0.266834714   1.291394532  -2.150002683
H   1.566468412  -0.816063267  -2.143387532
H   2.208243405  -1.860982297   0.000000000
H   1.566468412  -0.816063267   2.143387532
H   0.266834714   1.291394532   2.150002683
```

```
C   0.617605156   0.634494089  -1.212164836
C   1.514170476  -0.427440837  -1.211052584
C   1.959557622  -0.956575389   0.000000000
C   1.514170476  -0.427440837   1.211052584
B  -0.859214906   2.332103712   0.000000000
C  -3.400528156   0.134985084   0.000000000
C  -2.831093058  -0.930528891   0.000000000
H  -2.324242193  -1.863388864   0.000000000
H  -3.887700629   1.078848344   0.000000000
H   0.265475053   1.043532372  -2.150851752
H   1.866166022  -0.844116935  -2.144346277
H   2.656969838  -1.783074554   0.000000000
H   1.866166022  -0.844116935   2.144346277
H   0.265475053   1.043532372   2.150851752
```

MP2/cc-pVTZ

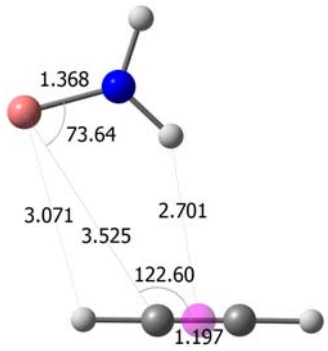


E=-332.9461744
ZPE=0.118322

```
C   0.802977000  -1.013910000   1.212650000
C   0.802977000   0.375847000   1.214743000
C   0.800360000   1.081875000   0.000000000
C   0.802977000   0.375847000  -1.214743000
C   0.802977000  -1.013910000  -1.212650000
C   0.799875000  -1.704956000   0.000000000
B   0.728413000   2.618214000   0.000000000
C  -2.615908000   0.776069000   0.000000000
C  -2.600369000  -0.436606000   0.000000000
H  -2.588564000  -1.497940000   0.000000000
H  -2.626822000   1.838438000   0.000000000
H   0.795964000   0.917505000  -2.152848000
H   0.802707000  -1.560531000  -2.145726000
H   0.800795000  -2.787049000   0.000000000
H   0.802707000  -1.560531000   2.145726000
H   0.795964000   0.917505000   2.152848000
```

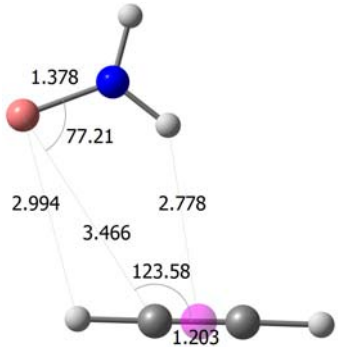
Aminoborylene (BNH_2)

RI-B3LYP+D3/def2-QZVP **RI-TPSS+D3/def2-QZVP**



E=-158.0577617
ZPE=0.0533733

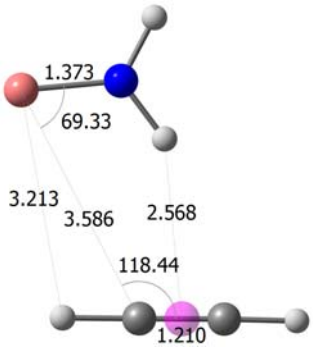
C	2.023127000	0.407853882	0.000000000
C	1.518186503	-0.677124137	0.000000000
B	-1.975234422	-1.145729372	0.000000000
H	2.488699731	1.362532005	0.000000000
H	1.056349773	-1.635532648	0.000000000
N	-1.767906892	0.206198778	0.000000000
H	-2.512388123	0.889523968	0.000000000
H	-0.830833576	0.592277519	0.000000000



E=-158.1705204
ZPE=0.0522400

C	2.047576756	0.396705218	0.000000000
C	1.524059762	-0.686476911	0.000000000
B	-1.910310279	-1.155777003	0.000000000
H	2.530736847	1.346069846	0.000000000
H	1.043931666	-1.639824360	0.000000000
N	-1.789997201	0.216524228	0.000000000
H	-2.572475628	0.863053575	0.000000000
H	-0.873521918	0.659725403	0.000000000

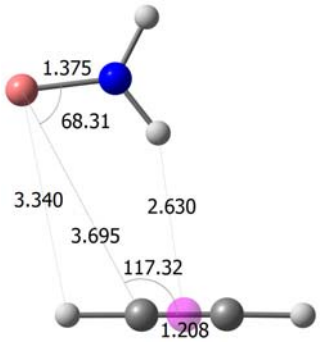
RI-MP2/def2-QZVP



E=-157.77567072796779
ZPE=0.0531389

C	1.953203042	0.430830032	0.000000000
C	1.509186147	-0.694684081	0.000000000
B	-2.050488224	-1.126053306	0.000000000
H	2.361297751	1.410950288	0.000000000
H	1.113909374	-1.681666793	0.000000000
N	-1.723900576	0.207423629	0.000000000
H	-2.406766208	0.949047737	0.000000000
H	-0.756441306	0.504152493	0.000000000

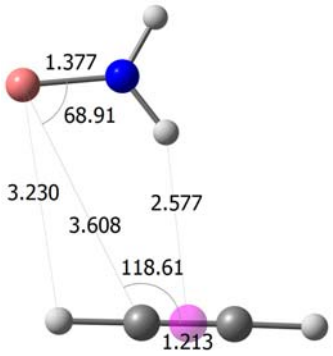
SCS-RI-MP2/def2-QZVP



E=-157.7808558853
ZPE=0.0532189

C	2.021620654	0.171204553	0.000000000
C	1.450419824	-0.893341332	0.000000000
B	-2.244283695	-0.835821254	0.000000000
H	2.540927646	1.097559630	0.000000000
H	0.944812222	-1.828647906	0.000000000
N	-1.716232620	0.433621747	0.000000000
H	-2.280334987	1.268854131	0.000000000
H	-0.716929045	0.586570432	0.000000000

MP2/cc-pVTZ

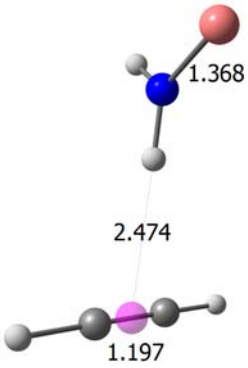


E=-157.7252692
ZPE=0.052954

```
C    1.800878000  -1.069812000   0.000000000
C    0.669056000  -1.505265000   0.000000000
B   -2.081025000   0.830434000   0.000000000
N   -0.872034000   1.488673000   0.000000000
H    2.800018000  -0.709306000   0.000000000
H   -0.325845000  -1.881325000   0.000000000
H   -0.784416000   2.493670000   0.000000000
H    0.000000000   0.974540000   0.000000000
```

Rotated aminoborylene (BNH_2 R)

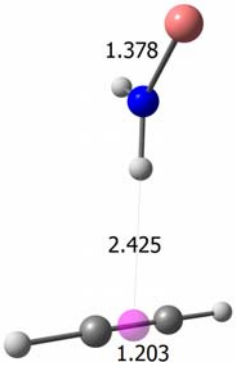
RI-B3LYP+D3/def2-QZVP



E=-158.0578627
ZPE=0.0534592

```
C    1.758880631   0.549640539  -0.261217961
C    1.486851553  -0.275186447  -1.084405952
B   -1.982285936  -0.959824774   1.614494280
H    2.009484985   1.278899219   0.469795799
H    1.254408589  -1.012043255  -1.813890072
N   -1.608249296  -0.093244947   0.624025624
H   -2.256504528   0.551676463   0.192266404
H   -0.662585998  -0.039916792   0.258931873
```

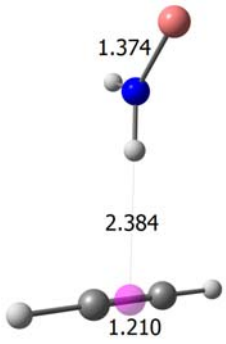
RI-TPSS+D3/def2-QZVP



E=-158.1707290
ZPE=0.0525397

```
C    1.738635538   0.550006994  -0.250707882
C    1.465743529  -0.278859905  -1.078768013
B   -1.965761128  -0.964578537   1.613853373
H    1.989621301   1.281611310   0.482507626
H    1.233290797  -1.018168762  -1.810424258
N   -1.588339467  -0.091914580   0.616612280
H   -2.235431859   0.557779226   0.179501828
H   -0.637758705  -0.035875757   0.247425046
```

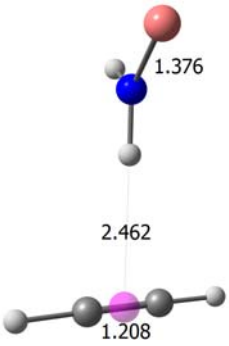
RI-MP2/def2-QZVP



E=-157.77589663662425
ZPE=0.0532406

```
C    1.719285191    0.550096907   -0.239105503
C    1.444258105   -0.284105538   -1.071011440
B   -1.939618783   -0.957618141    1.598011692
H    1.969714457    1.279367057    0.491293020
H    1.211780338   -1.019895449   -1.800806583
N   -1.565522841   -0.086969352    0.603670558
H   -2.218588384    0.553369392    0.177946623
H   -0.621308083   -0.034244876    0.240001634
```

SCS-RI-MP2/def2-QZVP

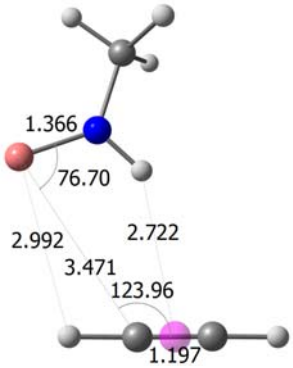


E=-157.7810712256
ZPE=0.0533361

```
C    1.754382698    0.551608629   -0.253459000
C    1.479788690   -0.280763216   -1.084891690
B   -1.972147205   -0.962656932    1.613851911
H    2.006087757    1.281586910    0.476337521
H    1.248564904   -1.017219458   -1.814938922
N   -1.601831411   -0.089119434    0.617881290
H   -2.254934943    0.550871486    0.192496264
H   -0.659910491   -0.034307985    0.252722626
```

Methylaminoborylene (BNHMe)

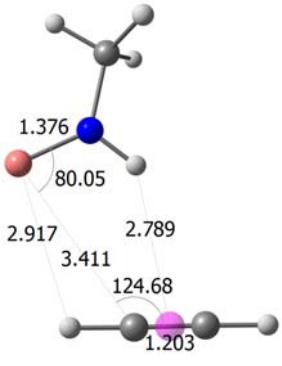
RI-B3LYP+D3/def2-QZVP



E=-197.3524449
ZPE=0.0828323

```
C   -2.878178494   -0.562008877    0.000000000
C   -2.575876291    0.596009414    0.000000000
B    0.699874642    1.744784112    0.000000000
N    0.843188520    0.386312372    0.000000000
H   -3.164810801   -1.584652049    0.000000000
```

RI-TPSS+D3/def2-QZVP



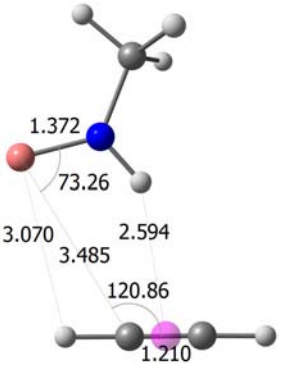
E=-197.5013867
ZPE=0.0814448

```
C   -2.928484062   -0.539625526    0.000000000
C   -2.594803527    0.616402281    0.000000000
B    0.638854160    1.703350062    0.000000000
N    0.845387321    0.342874578    0.000000000
H   -3.244713301   -1.556758005    0.000000000
```

H	-2.289343432	1.620904379	0.000000000
C	2.098534731	-0.369615878	0.000000000
H	-0.011327351	-0.161232672	0.000000000
H	2.170380719	-0.996691865	-0.887746239
H	2.937177032	0.322882917	0.000000000
H	2.170380719	-0.996691865	0.887746239

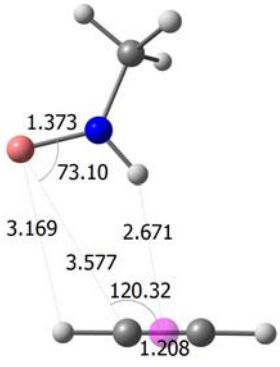
H	-2.277587336	1.636036277	0.000000000
C	2.138317811	-0.361424764	0.000000000
H	0.012949676	-0.246338651	0.000000000
H	2.234008812	-0.985285217	-0.892030522
H	2.942061634	0.376054176	0.000000000
H	2.234008812	-0.985285217	0.892030522

RI-MP2/def2-QZVP



E=-196.99826347045513
ZPE=0.0832453

SCS-RI-MP2/def2-QZVP

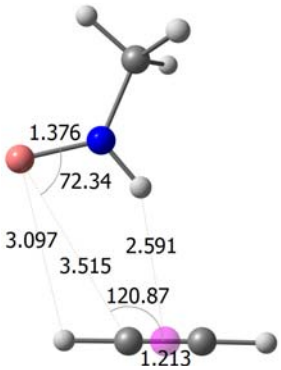


E=-197.0062397629
ZPE=0.0833200

C	-2.771430238	-0.582869233	0.000000000
C	-2.536034322	0.604116960	0.000000000
B	0.746359609	1.775511454	0.000000000
N	0.815677634	0.405197366	0.000000000
H	-2.997088114	-1.620216081	0.000000000
H	-2.320478921	1.645570342	0.000000000
C	2.041225807	-0.386459632	0.000000000
H	-0.061939192	-0.101849783	0.000000000
H	2.094650182	-1.011611360	-0.886241032
H	2.894407373	0.284221328	0.000000000
H	2.094650182	-1.011611360	0.886241032

C	-2.798722568	-0.665104785	0.000000000
C	-2.603374136	0.527237751	0.000000000
B	0.735879154	1.809804123	0.000000000
N	0.834280298	0.439921422	0.000000000
C	2.077084908	-0.331598551	0.000000000
H	-2.989495028	-1.709720184	0.000000000
H	-2.424800890	1.575626448	0.000000000
H	-0.029751341	-0.088094797	0.000000000
H	2.140132795	-0.956368533	-0.886986699
H	2.918634012	0.354665641	0.000000000
H	2.140132795	-0.956368533	0.886986699

MP2/cc-pVTZ

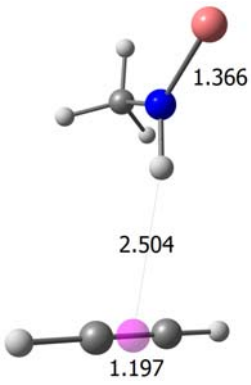


E=-196.935147
ZPE=0.083065

```
C  -2.565915000  -0.707941000   0.000763000
C  -2.288634000   0.472790000  -0.001235000
B   1.060410000   1.538842000   0.001398000
N   1.060271000   0.162483000   0.000431000
C   2.242480000  -0.695433000  -0.000638000
H  -2.828928000  -1.736931000   0.002593000
H  -2.036659000   1.506392000  -0.003005000
H   0.156897000  -0.298952000  -0.000218000
H   2.262659000  -1.322940000  -0.888124000
H   3.131411000  -0.071092000  -0.000279000
H   2.263084000  -1.324563000   0.885690000
```

Rotated methylaminoborylene (BNHMe R)

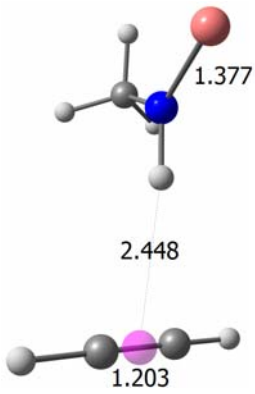
RI-B3LYP+D3/def2-QZVP



E=-197.35233219113
ZPE=0.0826809

```
C  -2.362030316  -0.719025613  -0.167964755
C  -2.415393068   0.475621264  -0.127020502
B   1.554042854   0.068101177   2.027688197
N   0.959623952   0.042585938   0.797577434
H  -2.322997580  -1.780291525  -0.201995407
H  -2.470538835   1.536008964  -0.088192765
C   1.641479179   0.088902333  -0.499606757
H  -0.053314729  -0.014807653   0.750255802
H   1.331684736   0.966222841  -1.065933673
H   2.716450125   0.141454673  -0.342916539
H   1.420993683  -0.804772398  -1.081891036
```

RI-TPSS+D3/def2-QZVP

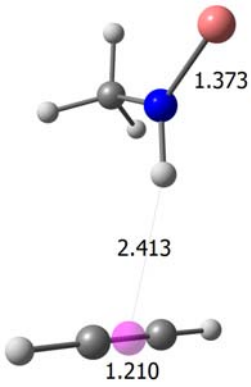


E=-197.5013404
ZPE=0.0815511

```
C  -2.382412750  -0.726907683  -0.148512023
C  -2.438884673   0.473196699  -0.090093681
B   1.457145516   0.116268169   2.024810958
N   0.925893749   0.054897017   0.756414802
H  -2.341616005  -1.790678818  -0.197073720
H  -2.496673168   1.535879264  -0.034624268
C   1.690710642   0.082651988  -0.502607603
H  -0.087526409  -0.015248777   0.643961880
H   1.399201723   0.944642711  -1.107722888
H   2.754098272   0.158607408  -0.270905514
H   1.520063103  -0.833307977  -1.073647943
```

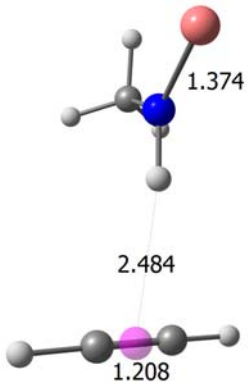
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-196.99842833413402
ZPE=0.0832091

C	-2.264098983	-0.717898532	-0.200414044
C	-2.336441823	0.489024467	-0.155354174
B	1.563646854	0.101184269	2.027189999
N	0.917343284	0.050554302	0.817309807
H	-2.209396487	-1.777955821	-0.238458018
H	-2.408284909	1.547985310	-0.114494349
C	1.575293438	0.073815682	-0.485663022
H	-0.094900087	-0.007163820	0.795489532
H	1.251890179	0.934889080	-1.063001200
H	2.648902372	0.137992395	-0.340106870
H	1.356046163	-0.832427333	-1.042497661

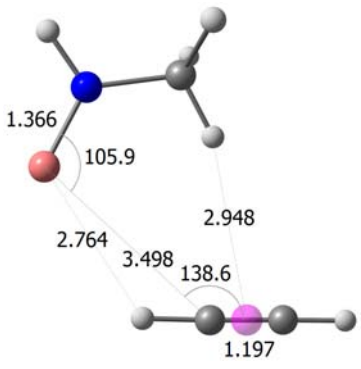


E=-197.0063347820
ZPE=0.0833197

C	-2.349859551	-0.724502830	-0.170880787
C	-2.412145670	0.481075825	-0.124577164
B	1.557392427	0.074062728	2.020778577
N	0.945981152	0.045138102	0.790590529
H	-2.305745476	-1.785276409	-0.209531303
H	-2.476945508	1.540638370	-0.082276588
C	1.637965635	0.086508916	-0.498342628
H	-0.064426975	-0.009168429	0.743030549
H	1.338423041	0.963491090	-1.066181325
H	2.708918383	0.134923645	-0.324874247
H	1.420442541	-0.806891008	-1.077735613

Methylaminoborylene in other conformation (BNHMe 1)

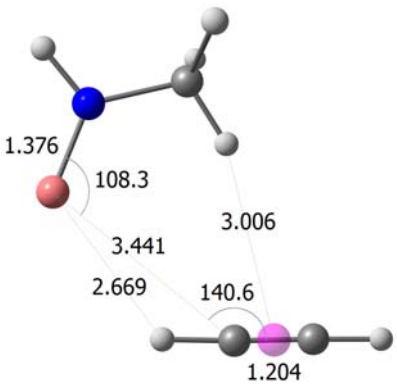
RI-B3LYP+D3/def2-QZVP



E=-197.3524964
ZPE=0.0828602

C	2.818013946	0.778595193	-0.005672013
C	2.378222429	-0.334913561	-0.000423019

RI-TPSS+D3/def2-QZVP



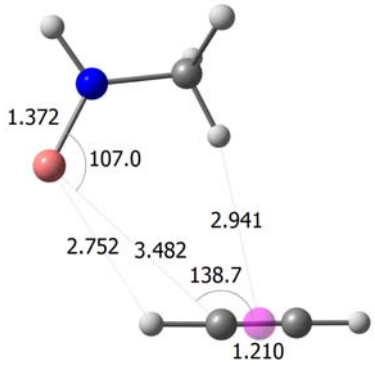
E=-197.5017681
ZPE=0.0815567

C	2.860447966	0.773237098	-0.005519208
C	2.381558092	-0.331098563	0.000866999

B	-0.735994239	-1.927959509	0.016034404
N	-1.667119921	-0.928727059	0.005097723
H	3.221361942	1.760735313	-0.010431422
H	1.958839293	-1.315007416	0.004611393
H	-2.646004558	-1.190326689	0.000832660
C	-1.390282229	0.515381434	-0.001309296
H	-0.314840190	0.674006707	0.003846193
H	-1.806066621	0.979174728	-0.894570880
H	-1.816129847	0.989040862	0.881984261

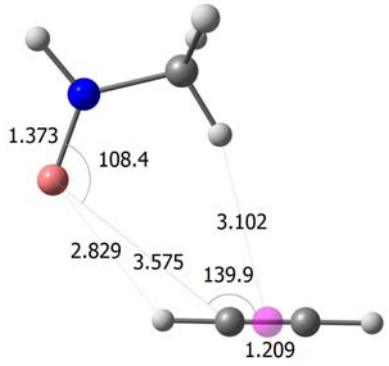
B	-0.680147756	-1.902018114	0.012047747
N	-1.660271843	-0.936891089	0.004424186
H	3.301911456	1.742325972	-0.011146039
H	1.918939741	-1.296843926	0.006603328
H	-2.636841844	-1.223828658	0.002121265
C	-1.422430118	0.521920223	-0.001289483
H	-0.346616527	0.700924519	0.002129706
H	-1.854686659	0.972057431	-0.897931462
H	-1.861862509	0.980215095	0.887692957

RI-MP2/def2-QZVP



E=-196.99815437390586
ZPE=0.0832614

SCS-RI-MP2/def2-QZVP

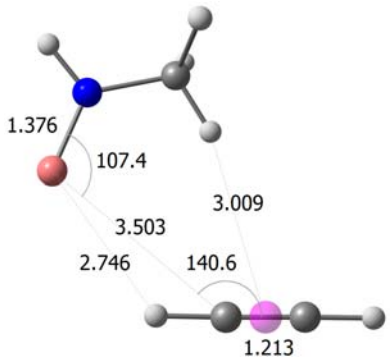


E=-197.0061411302
ZPE=0.0833173

C	2.821434749	0.789701475	-0.003525310
C	2.373009292	-0.334612808	0.001195750
B	-0.730498468	-1.913628183	0.007891149
N	-1.682137918	-0.925419109	0.004854529
H	3.227891158	1.769986839	-0.007655015
H	1.955622039	-1.314805392	0.005314416
H	-2.658347295	-1.188320176	0.007740048
C	-1.390165932	0.508672700	-0.002566092
H	-0.313599127	0.646864724	-0.004923021
H	-1.803072107	0.976492407	-0.890983767
H	-1.800136390	0.985067518	0.882657311

C	2.934490113	0.777291850	0.000000000
C	2.448738414	-0.329307473	0.000000000
B	-0.759631433	-1.907618592	0.000000000
N	-1.723521484	-0.929363649	0.000000000
H	3.373427004	1.743800768	0.000000000
H	2.002106143	-1.296196546	0.000000000
H	-2.696349535	-1.202727673	0.000000000
C	-1.452881718	0.512291695	0.000000000
H	-0.378162064	0.667598116	0.000000000
H	-1.872694137	0.977750590	-0.887516296
H	-1.872694137	0.977750590	0.887516296

MP2/cc-pVTZ



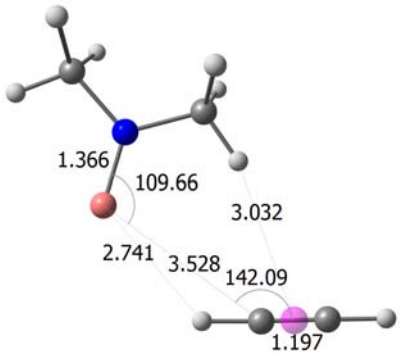
E=-196.935071

ZPE=0.083115

```
C   2.865671000  -0.384733000  -0.007217000
C   2.142424000   0.589301000   0.002877000
B  -1.257459000   1.434575000   0.015487000
N  -1.973727000   0.259909000  -0.015647000
H   3.509883000  -1.228500000  -0.016137000
H   1.488796000   1.431200000   0.011559000
H  -2.983513000   0.306277000  -0.062250000
C  -1.382256000  -1.080329000   0.011501000
H  -0.301314000  -0.984797000   0.059824000
H  -1.722844000  -1.630694000   0.884641000
H  -1.642654000  -1.631159000  -0.888503000
```

Dimethylaminoborylene ($BNMe_2$)

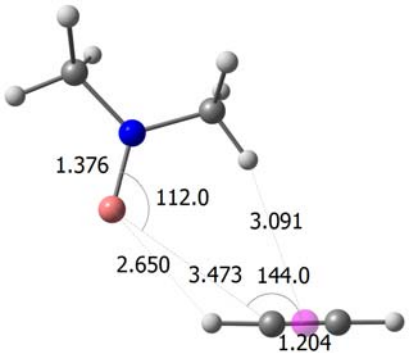
RI-B3LYP+D3/def2-QZVP



E=-236.6512551
ZPE=0.1113614

```
C  -3.812340463   0.151231439   0.591885007
C  -2.889928325   0.583768989   1.220816131
B   0.632825181   0.774753403   1.221825489
N   1.128127217   0.134657898   0.121226501
H  -4.638690563  -0.227330810   0.043210222
H  -2.048420683   0.957061945   1.759552194
C   2.560529050   0.053616017  -0.152857135
C   0.240121892  -0.508390421  -0.848185562
H   2.789248813   0.525975758  -1.109789320
H   3.120081687   0.563086906   0.629688382
H   2.879907983  -0.989416133  -0.187971173
H   0.373128144  -0.059348737  -1.833949690
H   0.463081121  -1.574872668  -0.911095720
H  -0.797671048  -0.384793586  -0.544355328
```

RI-TPSS+D3/def2-QZVP

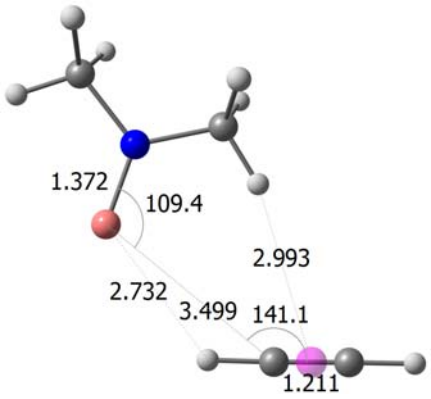


E=-236.8364388
ZPE=0.1096944

```
C  -3.843813391   0.185458861   0.621635363
C  -2.885551314   0.605239980   1.217083849
B   0.583204442   0.773461755   1.193595640
N   1.122274278   0.125309337   0.106599079
H  -4.702664229  -0.178383624   0.107874476
H  -2.007815103   0.962210972   1.717555439
C   2.567937484   0.068075182  -0.140161215
C   0.255394445  -0.549793794  -0.871943313
H   2.803805489   0.534590632  -1.102045684
H   3.094087961   0.603424251   0.652992432
H   2.906293131  -0.973007013  -0.152456796
H   0.397552140  -0.108235348  -1.863471975
H   0.498261661  -1.616412675  -0.912344838
H  -0.788966993  -0.431938516  -0.574912462
```

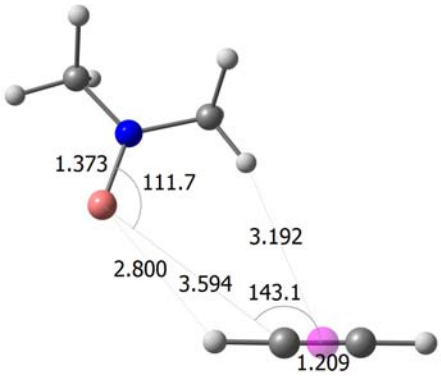
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-236.22642760230818
ZPE=0.1122595

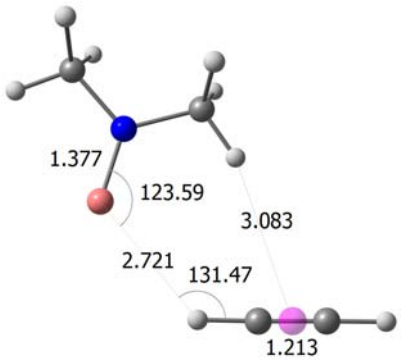
C	-3.783493307	0.141072961	0.569673413
C	-2.865611799	0.584069840	1.222789414
B	0.628184715	0.775615271	1.230580977
N	1.121725307	0.133905527	0.122538247
H	-4.596942867	-0.242242878	0.006251116
H	-2.040776328	0.964463538	1.780354742
C	2.546224358	0.044593106	-0.152595711
C	0.234190903	-0.496976196	-0.844315986
H	2.773222192	0.518263228	-1.106109804
H	3.104692287	0.547803708	0.631726691
H	2.854864596	-0.998644392	-0.191034014
H	0.370857253	-0.044003254	-1.824808895
H	0.452514740	-1.561548563	-0.909539086
H	-0.799652050	-0.366371897	-0.535511104



E=-236.2363785358
ZPE=0.1123569

C	-3.965479191	0.187125585	0.000000000
C	-3.098950381	1.029653053	0.000000000
B	0.466733735	1.482886138	0.000000000
N	1.131095545	0.281031119	0.000000000
H	-4.735194217	-0.543756845	0.000000000
H	-2.320041945	1.756634299	0.000000000
C	2.586360134	0.193584800	0.000000000
C	0.404780675	-0.985874166	0.000000000
H	2.929629110	-0.336713573	-0.887354118
H	3.013889849	1.192919477	0.000000000
H	2.929629110	-0.336713573	0.887354118
H	0.661621728	-1.562543580	-0.887671855
H	0.661621728	-1.562543580	0.887671855
H	-0.665695882	-0.795689154	0.000000000

MP2/cc-pVTZ



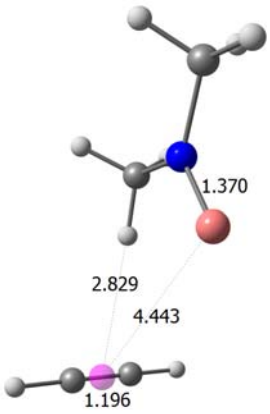
E=-236.1506499
ZPE=0.112097

C	-3.622071000	0.300642000	0.001413000
C	-2.817186000	-0.607125000	0.000154000
B	0.627732000	-1.324505000	-0.002643000
N	1.362109000	-0.159661000	-0.000758000
C	0.712297000	1.145786000	-0.001803000
C	2.817823000	-0.158089000	0.002454000
H	-4.336047000	1.086232000	0.002520000

```
H  -2.092196000  -1.389107000  -0.000960000
H   3.190418000   0.351307000   0.890844000
H   3.186658000  -1.181066000   0.002990000
H   3.194335000   0.351788000  -0.884006000
H   1.001226000   1.706804000   0.886677000
H   1.005107000   1.707320000  -0.888684000
H  -0.368099000   1.019586000  -0.004173000
```

Rotated dimethylaminoborylene ($BNMe_2$)

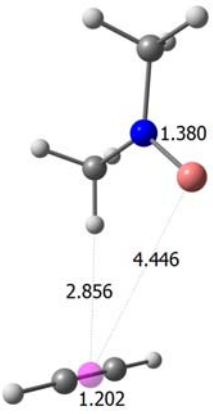
RI-B3LYP+D3/def2-QZVP



E=-236.6477442243
ZPE=0.1109128

```
C   3.425213129   0.735410270  -0.597925495
C   3.425213129   0.735410270   0.597925495
B  -0.928955091   1.620167726   0.000000000
N  -1.230374167   0.284136404   0.000000000
C  -2.615777161  -0.178365348   0.000000000
C  -0.198220859  -0.750007455   0.000000000
H   3.421848541   0.746730800  -1.659769906
H   3.421848541   0.746730800   1.659769906
H  -2.814240178  -0.781323331   0.888055113
H  -3.293056744   0.674206228   0.000000000
H  -2.814240178  -0.781323331  -0.888055113
H  -0.294509726  -1.378848180   0.887399928
H  -0.294509726  -1.378848180  -0.887399928
H   0.789760490  -0.294076675   0.000000000
```

RI-TPSS+D3/def2-QZVP



E=-236.83266602305
ZPE=

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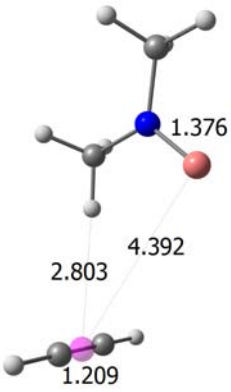
C   3.438823835   0.751512402  -0.601010182
C   3.438823835   0.751512402   0.601010182
B  -0.921331393   1.618520789   0.000000000
N  -1.229866607   0.273685319   0.000000000
C  -2.627708648  -0.175290432   0.000000000
C  -0.200902105  -0.773377129   0.000000000
H   3.435698621   0.762627148  -1.665980633
H   3.435698621   0.762627148   1.665980633
H  -2.831193864  -0.776050328   0.892522596
H  -3.288049478   0.695081226   0.000000000
H  -2.831193864  -0.776050328  -0.892522596
H  -0.303841084  -1.400955223   0.891714581
H  -0.303841084  -1.400955223  -0.891714581
H   0.788883217  -0.312887771   0.000000000
```

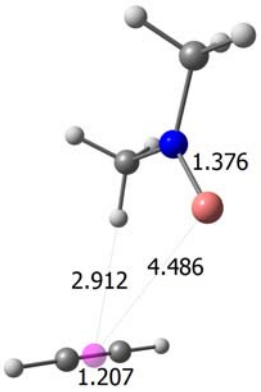
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-236.2232170228
ZPE=0.1117956

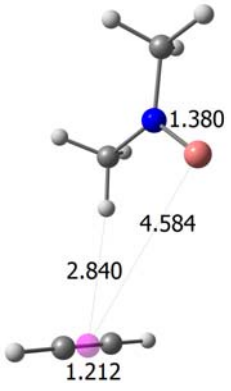
C	3.395211617	0.735864619	-0.604558477
C	3.395211617	0.735864619	0.604558477
B	-0.906906734	1.619220121	0.000000000
N	-1.217266659	0.279120845	0.000000000
C	-2.597729933	-0.175745511	0.000000000
C	-0.196028439	-0.755643176	0.000000000
H	3.394237135	0.747351330	-1.665885586
H	3.394237135	0.747351330	1.665885586
H	-2.794898838	-0.776089038	0.886662134
H	-3.266607964	0.680655558	0.000000000
H	-2.794898838	-0.776089038	-0.886662134
H	-0.297591897	-1.380618421	0.886113733
H	-0.297591897	-1.380618421	-0.886113733
H	0.790623692	-0.300624819	0.000000000



E=-236.2334925143
ZPE=0.1119213

C	3.471514612	0.755717189	-0.603692954
C	3.471514612	0.755717189	0.603692954
B	-0.931784846	1.613089665	0.000000000
N	-1.245883995	0.273056399	0.000000000
C	-2.631437087	-0.180462436	0.000000000
C	-0.224676500	-0.767984007	0.000000000
H	3.470879956	0.766884741	-1.665307585
H	3.470879956	0.766884741	1.665307585
H	-2.830470615	-0.780386680	0.887322311
H	-3.297856860	0.678489859	0.000000000
H	-2.830470615	-0.780386680	-0.887322311
H	-0.327716194	-1.392834471	0.886776441
H	-0.327716194	-1.392834471	-0.886776441
H	0.763223771	-0.314951035	0.000000000

MP2/cc-pVTZ



E=-236.1474062
ZPE=0.111579

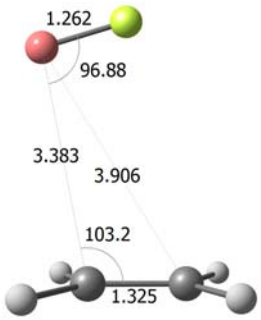
C	-0.039753000	3.294286000	0.605940000
C	-0.039753000	3.294286000	-0.605940000
B	1.576169816	-0.995079085	0.000000000
N	0.271476816	-1.446172085	0.000000000
C	-0.039753184	-2.867910085	0.000000000
C	-0.864438184	-0.535492085	0.000000000

```
H  -0.029643000   3.296580000   1.667745000
H  -0.029643000   3.296580000  -1.667745000
H  -0.617249184  -3.127056085  -0.887348000
H   0.881952816  -3.445395085   0.000000000
H  -0.617249184  -3.127056085   0.887348000
H  -1.476921184  -0.699869085  -0.886783000
H  -1.476921184  -0.699869085   0.886783000
H  -0.513325184   0.493633915   0.000000000
```

2. Geometries of van der Waals complexes with ethylene

Fluoroborylene (BF)

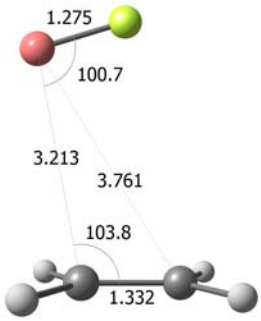
RI-B3LYP+D3/def2-QZVP



E=-203.2515946
ZPE=0.0548344

```
C  -0.904705031  -0.394123394   0.000000000
B   2.332089301  -1.377448554   0.000000000
F   2.841011005  -0.222659583   0.000000000
C  -0.819977229   0.928565792   0.000000000
H  -0.941218452  -0.964050387   0.919007428
H  -0.941218452  -0.964050387  -0.919007428
H  -0.782990576   1.496883256   0.920324566
H  -0.782990576   1.496883256  -0.920324566
```

RI-TPSS+D3/def2-QZVP

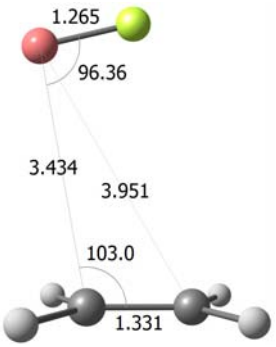


E=-203.3746372
ZPE=0.0542503

```
C  -0.869375068  -0.405172477   0.000000000
B   2.204399725  -1.341940247   0.000000000
F   2.796552602  -0.213336120   0.000000000
C  -0.796343803   0.924791483   0.000000000
H  -0.903865613  -0.977768238   0.921533503
H  -0.903865613  -0.977768238  -0.921533503
H  -0.763751109   1.495596916   0.923150965
H  -0.763751109   1.495596916  -0.923150965
```

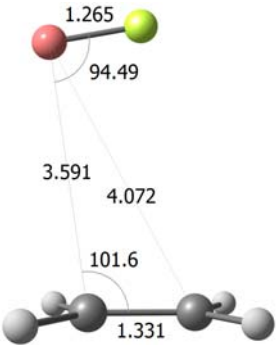
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-202.94397112638705
ZPE=0.0552802

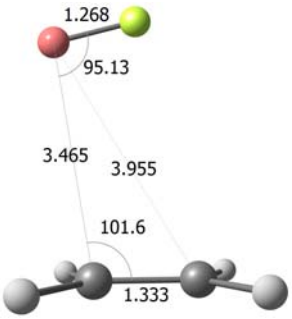
C	-0.917081157	-0.394686027	0.000000000
B	2.370159304	-1.387253453	0.000000000
F	2.867560796	-0.224538547	0.000000000
C	-0.827786956	0.932868793	0.000000000
H	-0.956149815	-0.956467267	0.921110672
H	-0.956149815	-0.956467267	-0.921110672
H	-0.790276179	1.493271885	0.922062588
H	-0.790276179	1.493271885	-0.922062588



E=-202.9490044488
ZPE=0.0551880

C	-0.959767506	-0.390794768	0.000000000
B	2.484437293	-1.407135154	0.000000000
F	2.936378387	-0.226163789	0.000000000
C	-0.846152035	0.935810462	0.000000000
H	-1.008746798	-0.952806497	0.921271756
H	-1.008746798	-0.952806497	-0.921271756
H	-0.798701272	1.496948122	0.921964587
H	-0.798701272	1.496948122	-0.921964587

MP2/cc-pVTZ

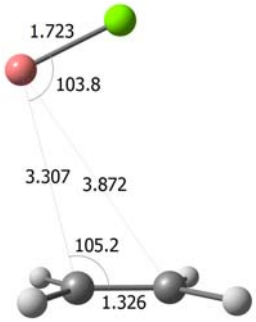


E=-202.8796131
ZPE=0.055279

C	0.000000131	1.738526284	0.000000000
C	1.298167131	1.436315284	0.000000000
B	-1.448874131	-1.408625284	0.000000000
F	-0.348773131	-2.039867284	0.000000000
H	-0.548462869	1.867575284	0.921986000
H	-0.548462869	1.867575284	-0.921986000
H	1.845629131	1.308868284	0.922879000
H	1.845629131	1.308868284	-0.922879000

Chloroborylene (BCl)

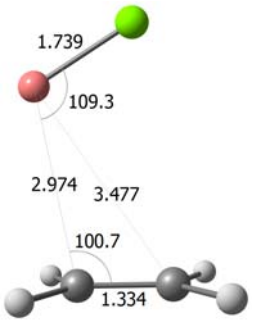
RI-B3LYP+D3/def2-QZVP



E=-563.5293511
ZPE=0.0535170

C	0.952643987	0.356819949	0.000000000
C	0.793694366	-0.959196619	0.000000000
B	-2.112294128	1.599011925	0.000000000
H	1.019961614	0.924474490	0.918415818
H	1.019961614	0.924474490	-0.918415818
H	0.723802191	-1.524364340	0.920370350
H	0.723802191	-1.524364340	-0.920370350
Cl	-3.121571829	0.203144447	0.000000000

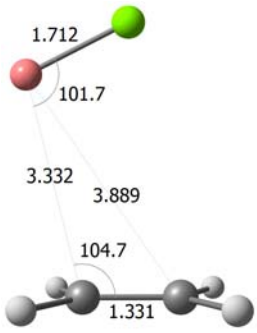
RI-TPSS+D3/def2-QZVP



E=-563.6865444
ZPE=0.0531430

C	0.919274805	0.400833409	0.000000000
C	0.693855029	-0.913735902	0.000000000
B	-1.868020238	1.436626853	0.000000000
H	1.025681925	0.964986300	0.920743240
H	1.025681925	0.964986300	-0.920743240
H	0.590407063	-1.475485767	0.923307739
H	0.590407063	-1.475485767	-0.923307739
Cl	-2.977287567	0.097274574	0.000000000

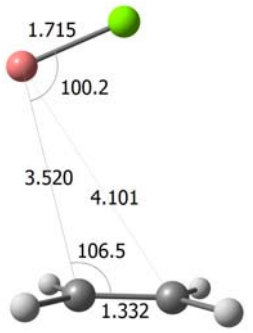
RI-MP2/def2-QZVP



E=-562.87360516309457
ZPE=0.0540111

C	0.954817344	0.359572966	0.000000000
C	0.784213469	-0.960314446	0.000000000
B	-2.133636556	1.610769291	0.000000000
H	1.027949191	0.918532256	0.920685620
H	1.027949191	0.918532256	-0.920685620
H	0.712082925	-1.517333092	0.922174707
H	0.712082925	-1.517333092	-0.922174707
Cl	-3.085458491	0.187573861	0.000000000

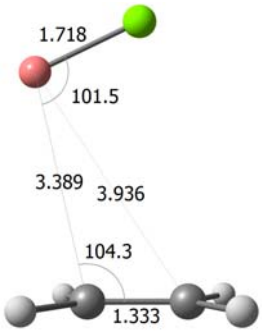
SCS-RI-MP2/def2-QZVP



E=-562.8824609375
ZPE=0.0538738

C	0.981159283	0.338433853	0.000000000
C	0.839806352	-0.985655673	0.000000000
B	-2.268286055	1.690487630	0.000000000
H	1.041367532	0.899861193	0.920899663
H	1.041367532	0.899861193	-0.920899663
H	0.780537522	-1.545644775	0.922060880
H	0.780537522	-1.545644775	-0.922060880
Cl	-3.196489687	0.248301353	0.000000000

MP2/cc-pVTZ

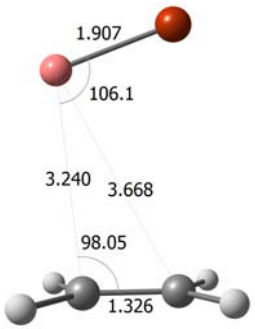


E=-562.8167876
ZPE=0.053978

```
C   2.056226000  -1.004489000   0.000000000
C   1.229619000  -2.050402000   0.000000000
B   0.000000000   1.688955000   0.000000000
Cl -1.546474000   0.940714000   0.000000000
H   2.406754000  -0.562625000   0.921568000
H   2.406754000  -0.562625000  -0.921568000
H   0.880735000  -2.491159000   0.922965000
H   0.880735000  -2.491159000  -0.922965000
```

Bromoborylene (BBr)

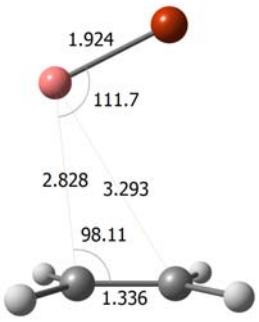
RI-B3LYP+D3/def2-QZVP



E=-2677.4407771
ZPE=0.0531872

```
C   1.021960978  -0.357608439   0.000000000
C   0.691897983   0.926423514   0.000000000
B  -1.971601186  -1.595796829   0.000000000
H   1.162623954  -0.911109807  -0.918684624
H   1.162623954  -0.911109807   0.918684624
H   0.546568834   1.476982471  -0.920299112
H   0.546568834   1.476982471   0.920299112
Br -3.160643361  -0.104763575   0.000000000
```

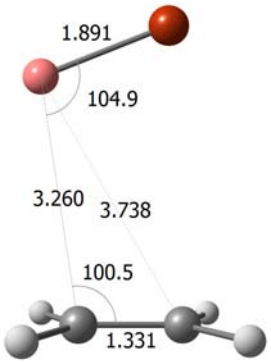
RI-TPSS+D3/def2-QZVP



E=-2677.5482623
ZPE=0.0529404

```
C   0.939369057  -0.396962229   0.000000000
C   0.621858988   0.900269166   0.000000000
B  -1.685007890  -1.449858353   0.000000000
H   1.093133535  -0.950074133  -0.920583270
H   1.093133535  -0.950074133   0.920583270
H   0.474584927   1.451841969  -0.923210857
H   0.474584927   1.451841969   0.923210857
Br -3.011657084  -0.056984256   0.000000000
```

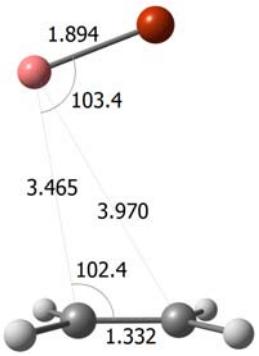
RI-MP2/def2-QZVP



E=-2675.77438104824978
ZPE=0.0536772

```
C   1.004453625  -0.352342802   0.000000000
C   0.712542246   0.946346206   0.000000000
B  -1.992800836  -1.633359724   0.000000000
H   1.129034491  -0.901999348  -0.920754067
H   1.129034491  -0.901999348   0.920754067
H   0.588521546   1.494112372  -0.922243177
H   0.588521546   1.494112372   0.922243177
Br -3.159307104  -0.144869723   0.000000000
```

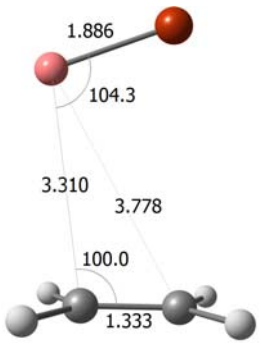
SCS-RI-MP2/def2-QZVP



E=-2675.7841771046
ZPE=0.0535237

```
C   1.033929248  -0.329360078   0.000000000
C   0.771724847   0.976265493   0.000000000
B  -2.137564029  -1.724350710   0.000000000
H   1.145148877  -0.882827183  -0.920960190
H   1.145148877  -0.882827183   0.920960190
H   0.660950311   1.528374330  -0.922083990
H   0.660950311   1.528374330   0.922083990
Br -3.280288441  -0.213648999   0.000000000
```

MP2/cc-pVTZ

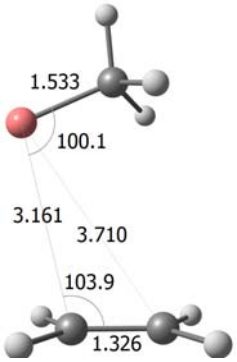


E=-2675.7868004
ZPE=0.053669

```
C   0.181596000  -2.933388000   0.000000000
C  -1.115798000  -2.626168000   0.000000000
B   1.493965000   0.104985000   0.000000000
Br  0.000000000   1.255750000   0.000000000
H   0.730080000  -3.064163000   0.921666000
H   0.730080000  -3.064163000  -0.921666000
H  -1.662388000  -2.495264000   0.923054000
H  -1.662388000  -2.495264000  -0.923054000
```

Methylborylene (BCH_3)

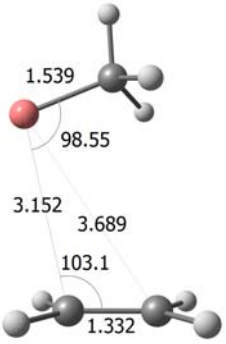
RI-B3LYP+D3/def2-QZVP



E=-143.1997275
ZPE=0.0869869

```
C    1.605180845    0.760183650    0.000000000
C    1.719369808   -0.561279623    0.000000000
B   -1.517415841    1.252779019    0.000000000
H    1.554888247    1.331124732    0.917085250
H    1.554888247    1.331124732   -0.917085250
H    1.768069863   -1.129039381    0.920305584
H    1.768069863   -1.129039381   -0.920305584
C   -2.018242286   -0.196243229    0.000000000
H   -3.114447828   -0.203860836    0.000000000
H   -1.660180459   -0.727874850   -0.888220954
H   -1.660180459   -0.727874850    0.888220954
```

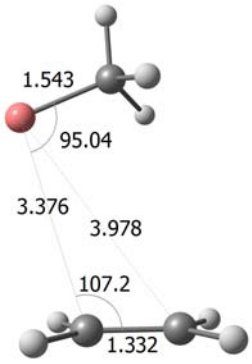
RI-MP2/def2-QZVP



E=-142.90777645851728
ZPE=0.0879473

```
C    1.591034161    0.762820551    0.000000000
C    1.682580967   -0.565657172    0.000000000
B   -1.521083383    1.264221546    0.000000000
H    1.554054385    1.326847436    0.919582486
H    1.554054385    1.326847436   -0.919582486
H    1.722594016   -1.126417770    0.922116458
H    1.722594016   -1.126417770   -0.922116458
C   -1.988907294   -0.201485331    0.000000000
H   -3.080729498   -0.225630915    0.000000000
H   -1.618095877   -0.717564006   -0.887062505
H   -1.618095877   -0.717564006    0.887062505
```

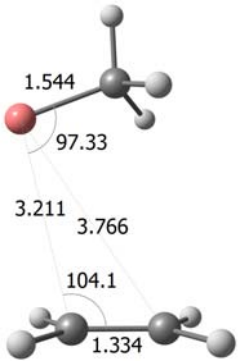
SCS-RI-MP2/def2-QZVP



E=-142.9256137812
ZPE=0.0878190

```
C    1.635483299    0.737716289    0.000000000
C    1.805712277   -0.583428813    0.000000000
B   -1.690389701    1.315431737    0.000000000
```

MP2/cc-pVTZ



E=-142.8619377
ZPE=0.087854

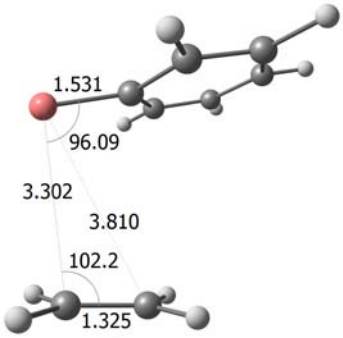
```
C   -0.357032000   -2.020542000    0.000000000
B   -1.589615000   -1.091488000    0.000000000
C    0.000000000    1.698021000    0.000000000
```

H	1.563968264	1.299039521	0.920054812
H	1.563968264	1.299039521	-0.920054812
H	1.880047096	-1.142047081	0.921992164
H	1.880047096	-1.142047081	-0.921992164
C	-2.086974739	-0.175530036	0.000000000
H	-3.176393743	-0.264233459	0.000000000
H	-1.687734056	-0.671970299	-0.887383025
H	-1.687734056	-0.671970299	0.887383025

C	1.285113000	1.340782000	0.000000000
H	-0.544304000	1.851359000	0.920551000
H	-0.544304000	1.851359000	-0.920551000
H	1.827626000	1.191793000	0.922928000
H	1.827626000	1.191793000	-0.922928000
H	-0.692430000	-3.060887000	0.000000000
H	0.252688000	-1.838770000	-0.887832000
H	0.252688000	-1.838770000	0.887832000

Phenylborylene (BPh)

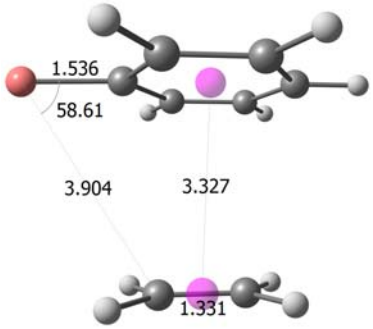
RI-B3LYP+D3/def2-QZVP



E=-334.9014901
ZPE=0.1426574

C	3.177315736	-0.003433090	0.000000000
C	2.515609881	1.144927351	0.000000000
B	0.731124437	-2.221093304	0.000000000
H	3.458508688	-0.502216266	-0.917636150
H	3.458508688	-0.502216266	0.917636150
H	2.225686573	1.635762618	-0.919947014
H	2.225686573	1.635762618	0.919947014
C	-0.411573199	-1.202438006	0.000000000
C	-0.940118372	-0.725858457	-1.210591580
C	-1.965759424	0.207291778	-1.209439535
C	-2.475686437	0.673279088	0.000000000
C	-1.965759424	0.207291778	1.209439535
C	-0.940118372	-0.725858457	1.210591580
H	-0.539982805	-1.085656245	-2.150332352
H	-2.369251874	0.574019745	-2.143263994
H	-3.274955982	1.402071605	0.000000000
H	-2.369251874	0.574019745	2.143263994
H	-0.539982805	-1.085656245	2.150332352

RI-MP2/def2-QZVP

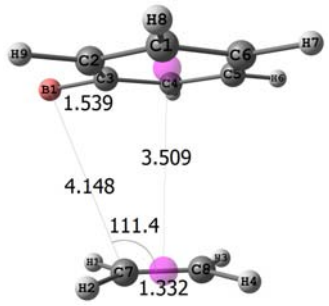


E=-334.29108211461983
ZPE=0.1436212

C	2.316683988	0.273184080	0.000000000
C	1.755325595	1.480037011	0.000000000
B	0.252027673	-3.039638080	0.000000000
H	2.554808775	-0.237001557	-0.921574440
H	2.554808775	-0.237001557	0.921574440
H	1.519381827	1.989715962	-0.922382469
H	1.519381827	1.989715962	0.922382469
C	-0.437447993	-1.667296526	0.000000000
C	-0.742801029	-1.031694163	-1.212838948
C	-1.336307703	0.222615879	-1.210329473
C	-1.627649477	0.848089423	0.000000000
C	-1.336307703	0.222615879	1.210329473
C	-0.742801029	-1.031694163	1.212838948
H	-0.509797632	-1.520680040	-2.150559442
H	-1.570859322	0.716552478	-2.142713654
H	-2.087789617	1.826606972	0.000000000
H	-1.570859322	0.716552478	2.142713654
H	-0.509797632	-1.520680040	2.150559442

SCS-RI-MP2/def2-QZVP

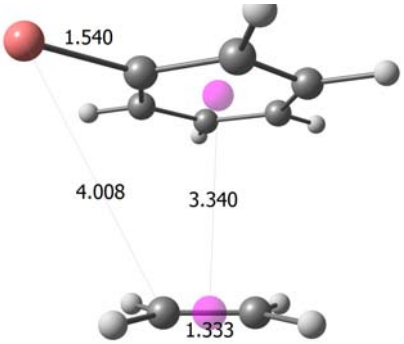
MP2/cc-pVTZ



dih C8C7B1C3=-42.702 degree

E=-334.2873181662
ZPE=0.1435403

C	-1.082038415	0.775317364	1.304953743
C	-1.251774548	-0.593745755	1.140195738
C	-1.321825222	-1.147984699	-0.148601616
C	-1.218635738	-0.306053557	-1.267641476
C	-1.044620539	1.062130467	-1.099904804
C	-0.977410283	1.599236113	0.185241926
B	-1.489116126	-2.667217105	-0.331974890
C	2.226837110	-0.946094657	0.327515063
C	2.380636687	0.167345759	-0.386341967
H	2.096956715	-1.907726668	-0.147868369
H	2.228045538	-0.926221724	1.407826270
H	2.380427047	0.147826619	-1.466638242
H	2.511561898	1.128328218	0.090054569
H	-1.270087212	-0.726362982	-2.264397583
H	-0.963729217	1.710900110	-1.960910290
H	-0.843549769	2.664646155	0.313913418
H	-1.029946363	1.202554818	2.296626405
H	-1.331731563	-1.236878476	2.007952104

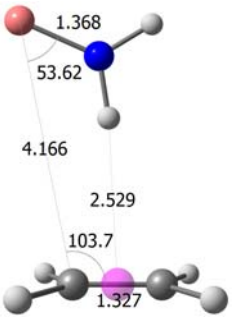


E=-334.1868321
ZPE=0.143499

C	0.906563000	0.234945000	1.249049000
C	0.982124000	1.057729000	0.113132000
C	0.910650000	0.482097000	-1.166974000
C	0.765904000	-0.893447000	-1.306185000
C	0.684390000	-1.699861000	-0.170727000
C	0.754659000	-1.139485000	1.105564000
B	1.112999000	2.583575000	0.271712000
C	-2.406651000	0.760473000	-0.320608000
C	-2.530475000	-0.394812000	0.333135000
H	-2.390521000	0.795303000	-1.400812000
H	-2.318954000	1.700166000	0.206406000
H	-2.618295000	-1.333269000	-0.195810000
H	-2.547509000	-0.430124000	1.413209000
H	0.970358000	1.113899000	-2.045237000
H	0.712886000	-1.339402000	-2.289994000
H	0.568884000	-2.770047000	-0.280353000
H	0.694080000	-1.775546000	1.978221000
H	0.961094000	0.675306000	2.237494000

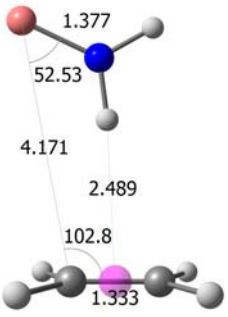
Aminoborylene (BNH_2)

RI-B3LYP+D3/def2-QZVP



E=-159.3113594
ZPE=0.0775199

RI-TPSS+D3/def2-QZVP

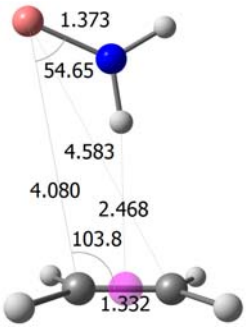


E=-159.4309898
ZPE=0.0764678

C	-1.402086290	-0.867638959	0.000000000
C	-1.425128408	0.458699925	0.000000000
H	-1.436556234	1.028105901	-0.920277580
H	-1.397617589	-1.436467751	-0.920895575
H	-1.397617589	-1.436467751	0.920895575
H	-1.436556234	1.028105901	0.920277580
B	2.604783598	1.514415173	0.000000000
N	2.099021077	0.243637201	0.000000000
H	2.688699209	-0.577781264	0.000000000
H	1.103058461	0.045391618	0.000000000

C	-1.380237514	-0.869114321	0.000000000
C	-1.421329132	0.462859820	0.000000000
H	-1.441035878	1.034163716	-0.923171338
H	-1.368177845	-1.439943911	-0.923773203
H	-1.368177845	-1.439943911	0.923773203
H	-1.441035878	1.034163716	0.923171338
B	2.615062713	1.512040448	0.000000000
N	2.079172342	0.243115125	0.000000000
H	2.651292161	-0.596313390	0.000000000
H	1.074466871	0.058972714	0.000000000

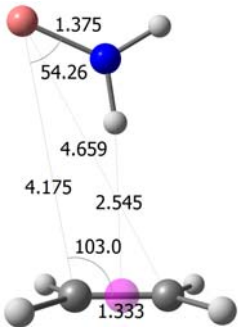
RI-MP2/def2-QZVP



E=-159.0176358171249
ZPE=0.0781722

C	-1.375201717	-0.863133115	0.000000000
C	-1.400892547	0.468676102	0.000000000
H	-1.414405780	1.030360591	-0.922185554
H	-1.370803351	-1.424150999	-0.922731475
H	-1.370803351	-1.424150999	0.922731475
H	-1.414405780	1.030360591	0.922185554
B	2.542774959	1.514390522	0.000000000
N	2.061954565	0.228092313	0.000000000
H	2.670835400	-0.576191904	0.000000000
H	1.070947601	0.015746898	0.000000000

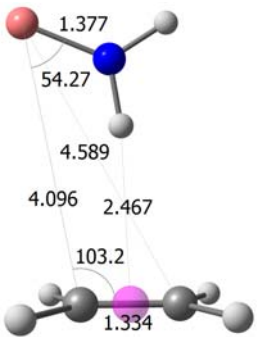
SCS-RI-MP2/def2-QZVP



E=-159.0288130501
ZPE=0.0782408

C	-1.407042357	-0.855368422	0.000000000
C	-1.433667100	0.477252077	0.000000000
B	2.615839832	1.495102001	0.000000000
N	2.108984493	0.216651258	0.000000000
H	-1.448272813	1.040217481	-0.922117513
H	-1.402434194	-1.417912515	-0.922575996
H	-1.402434194	-1.417912515	0.922575996
H	-1.448272813	1.040217481	0.922117513
H	2.701300851	-0.599461781	0.000000000
H	1.115998294	0.021214935	0.000000000

MP2/cc-pVTZ

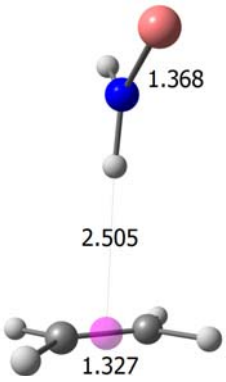


E=-158.9655576
ZPE=0.078095

```
C  -1.884321000   0.549252000   0.005063000
C  -1.552083000  -0.743163000  -0.003878000
B   2.543319000  -0.658513000   0.007255000
N   1.716357000   0.442414000  -0.004181000
H  -1.409177000  -1.293220000   0.915458000
H  -2.024758000   1.086373000   0.932463000
H  -2.036543000   1.096265000  -0.914670000
H  -1.420903000  -1.283693000  -0.930559000
H   2.073543000   1.386435000  -0.011691000
H   0.705168000   0.366972000  -0.005123000
```

Rotated aminoborylene (BNH_2 R)

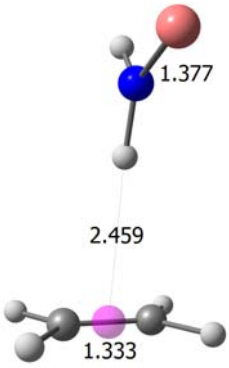
RI-B3LYP+D3/def2-QZVP



E=-159.3115475
ZPE=0.0775991

```
C   1.403472951  -0.663261239   0.173170937
C   1.403348573   0.663394644   0.172969749
B  -2.830241650   0.000122769   0.819782317
N  -2.071417324  -0.000109487  -0.318097382
H   1.082154806   1.232181641   1.035937888
H   1.082376542  -1.231827251   1.036341465
H   1.731258775  -1.233079417  -0.686632945
H   1.731035647   1.232997050  -0.687036146
H  -2.476021205  -0.000277098  -1.244735567
H  -1.055967115  -0.000141618  -0.301700317
```

RI-TPSS+D3/def2-QZVP

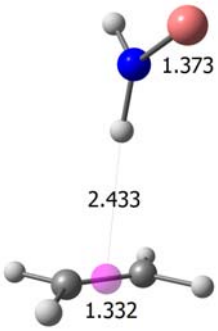


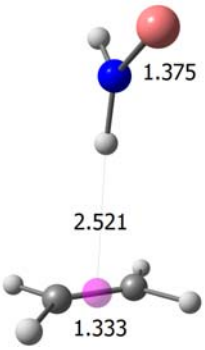
E=-159.4311973
ZPE=0.0765793

```
C   1.387482273  -0.666347506   0.170830201
C   1.387361012   0.666483579   0.170635453
B  -2.819681331   0.000194790   0.827218861
N  -2.048402432  -0.000118192  -0.313972070
H   1.070599067   1.237541778   1.038288716
H   1.070827084  -1.237203835   1.038658161
H   1.711182494  -1.238288553  -0.693641929
H   1.710953307   1.238228073  -0.694012374
H  -2.443416679  -0.000322094  -1.249747908
H  -1.026904790  -0.000168035  -0.294257111
```

RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP





E=-159.01781803544827
ZPE=0.0782770

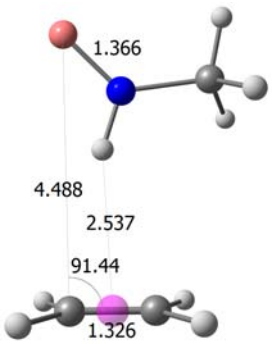
C	1.374444684	-0.666090996	0.171170189
C	1.374286469	0.666190565	0.170958421
B	-2.790231402	0.000160909	0.823175990
N	-2.027189903	-0.000113017	-0.318537863
H	1.063934181	1.228203733	1.039450893
H	1.064223550	-1.227900819	1.039840807
H	1.693578805	-1.228332132	-0.693832681
H	1.693282669	1.228231933	-0.694225121
H	-2.432564300	-0.000335774	-1.242203609
H	-1.013764753	-0.000014402	-0.295797027

E=-159.0289497738
ZPE=0.0783293

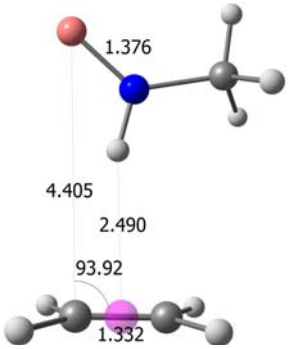
C	1.407653552	-0.666412510	0.176842072
C	1.407516258	0.666553808	0.176706368
B	-2.831757768	0.000180763	0.822076548
N	-2.076949319	-0.000105393	-0.327483661
H	1.096653086	1.229442362	1.045070925
H	1.096859448	-1.229106496	1.045462148
H	1.727673437	-1.229433768	-0.688022208
H	1.727466422	1.229385114	-0.688412092
H	-2.490211485	-0.000329205	-1.247277741
H	-1.064903632	-0.000174676	-0.314962359

Methylaminoborylene (BNHMe)

RI-B3LYP+D3/def2-QZVP



RI-TPSS+D3/def2-QZVP



E=-198.6059830
ZPE=0.1069060

C	1.822567542	0.717792991	0.000000000
C	2.222943562	-0.546700409	0.000000000
B	-2.020370807	-2.008492085	0.000000000
N	-1.367334648	-0.808743315	0.000000000
C	-1.979753733	0.522427297	0.000000000
H	2.397842331	-1.088256891	-0.920556610
H	1.654445538	1.261437031	-0.920716284
H	1.654445538	1.261437031	0.920716284

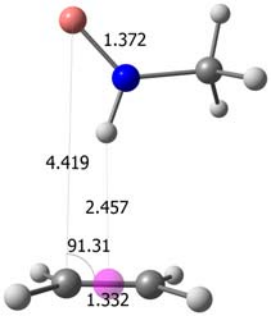
E=-198.7617776
ZPE=0.1055489

C	1.860910323	0.718672738	0.000000000
C	2.213093515	-0.566432470	0.000000000
B	-1.945468238	-2.018711243	0.000000000
N	-1.340527280	-0.782802898	0.000000000
C	-2.022838937	0.522179922	0.000000000
H	2.367579700	-1.116507104	-0.923355587
H	1.713449674	1.270556014	-0.923607613
H	1.713449674	1.270556014	0.923607613

H	2.397842331	-1.088256891	0.920556610
H	-0.351077433	-0.810133008	0.000000000
H	-1.684350069	1.081412015	-0.887197959
H	-3.062850098	0.424664224	0.000000000
H	-1.684350069	1.081412015	0.887197959

H	2.367579700	-1.116507104	0.923355587
H	-0.319443710	-0.729265665	0.000000000
H	-1.753102063	1.094020394	-0.891541753
H	-3.101580290	0.360221008	0.000000000
H	-1.753102063	1.094020394	0.891541753

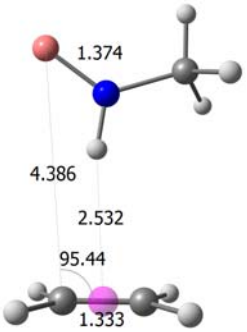
RI-MP2/def2-QZVP



E=-198.24026952760150
ZPE=0.1080977

C	1.792529478	0.712129285	0.000000000
C	2.195734331	-0.557575327	0.000000000
B	-1.984232685	-1.991223933	0.000000000
N	-1.323363329	-0.788528992	0.000000000
C	-1.962457016	0.523206747	0.000000000
H	2.369769354	-1.091212881	-0.922506547
H	1.628544566	1.248750924	-0.922835502
H	1.628544566	1.248750924	0.922835502
H	2.369769354	-1.091212881	0.922506547
H	-0.308557292	-0.778856780	0.000000000
H	-1.683129962	1.086048269	-0.886062274
H	-3.040021404	0.393676375	0.000000000
H	-1.683129962	1.086048269	0.886062274

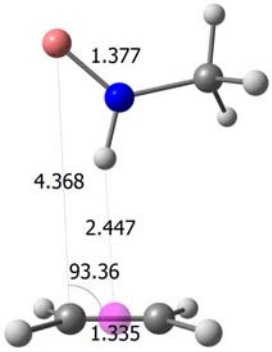
SCS-RI-MP2/def2-QZVP



E=-198.2541456427
ZPE=0.1081783

C	1.938466389	0.703898534	0.000000000
C	2.241182900	-0.594221047	0.000000000
B	-1.916145244	-1.990381746	0.000000000
N	-1.351124324	-0.738251738	0.000000000
C	-2.089955771	0.524585801	0.000000000
H	2.372876105	-1.141537011	-0.922243003
H	1.816979835	1.253210194	-0.922636422
H	1.816979835	1.253210194	0.922636422
H	2.372876105	-1.141537011	0.922243003
H	-0.340910055	-0.655439071	0.000000000
H	-1.853082169	1.106863288	-0.886810328
H	-3.155061439	0.312736328	0.000000000
H	-1.853082169	1.106863288	0.886810328

MP2/cc-pVTZ



E=-198.1754668
ZPE=0.108059

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C   2.087147000   0.685148000  -0.005464000
C   2.273764000  -0.636340000   0.004222000
B  -2.008410000  -1.499813000  -0.004109000
N  -1.230686000  -0.363926000   0.000447000
C  -1.735034000   1.007104000   0.002591000
H   2.351969000  -1.199396000  -0.915032000
H   2.010477000   1.234532000  -0.933232000
H   2.019983000   1.249496000   0.914017000
H   2.361357000  -1.184556000   0.931550000
H  -0.219226000  -0.456533000   0.002733000
H  -1.398472000   1.542927000  -0.881843000
H  -2.821222000   0.986195000  -0.000421000
H  -1.403277000   1.538413000   0.891547000
```
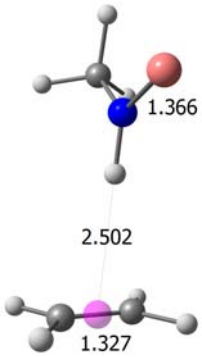

Rotated methylaminoborylene (BNHMe R)

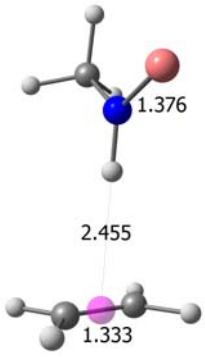
RI-B3LYP+D3/def2-QZVP



E=-198.6060461
ZPE=0.1069729

```
C  -2.128038014   0.159482100  -0.662681874
C  -2.126963276   0.151647748   0.663857595
N   1.368846444   0.549204184   0.000774350
C   2.140687330  -0.696917123  -0.001677206
B   1.871848078   1.819185930   0.004205668
H  -2.068973626   1.066874156   1.238702528
H  -2.070603656   1.081380810  -1.226782509
H  -2.192708909  -0.755703059  -1.236919259
H  -2.190392657  -0.770251909   1.227356545
H   0.358524201   0.436555122   0.000043451
H   1.917593292  -1.285783857  -0.890599711
H   3.203448757  -0.465885549  -0.000643157
H   1.916732030  -1.289788559   0.884363574
```

RI-TPSS+D3/def2-QZVP

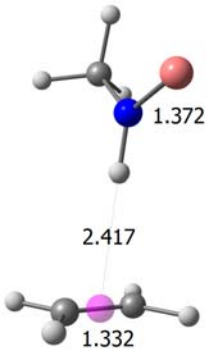


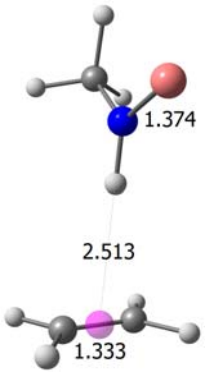
E=-198.7618717
ZPE=0.1056411

```
C  -2.110580017   0.162866247  -0.665739582
C  -2.109484160   0.155021380   0.666923833
N   1.346774376   0.544673543   0.000753734
C   2.131272319  -0.701952404  -0.001691277
B   1.853440314   1.824013503   0.004300518
H  -2.060519680   1.073728616   1.243721716
H  -2.062508493   1.088291161  -1.231757532
H  -2.166608410  -0.755597816  -1.242405642
H  -2.164480795  -0.770170310   1.232821999
H   0.331572770   0.419762058  -0.000045425
H   1.909178707  -1.291383944  -0.894813582
H   3.193609812  -0.453857112  -0.000630494
H   1.908333257  -1.295394928   0.888561733
```

RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP





E=-198.240315065217
ZPE=0.1082437

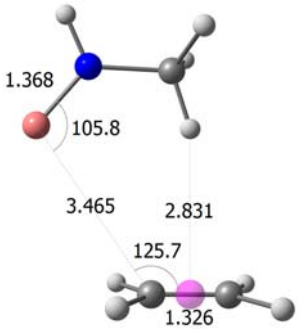
C	-2.092253569	0.166371118	-0.665566125
C	-2.090978828	0.158506835	0.666647583
N	1.321249244	0.527359417	0.000920334
C	2.116090014	-0.696815713	-0.001641909
B	1.829691547	1.801971159	0.003851303
H	-2.044218527	1.076685629	1.233262781
H	-2.046595475	1.091158346	-1.221403454
H	-2.147026784	-0.751244934	-1.232239452
H	-2.144707331	-0.765723056	1.222555465
H	0.313104479	0.406561701	0.000431429
H	1.908465313	-1.287132668	-0.889315959
H	3.169697950	-0.436255822	-0.000420320
H	1.907481968	-1.291442009	0.882918325

E=-198.2542199878
ZPE=0.1082802

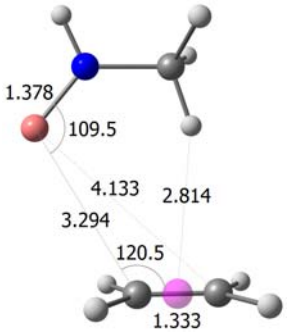
C	-2.136125917	0.161427176	-0.665914724
C	-2.135064890	0.153564878	0.667112210
N	1.369820326	0.541239299	0.000737731
C	2.146248099	-0.699037209	-0.001687499
B	1.896538885	1.809950120	0.004264989
H	-2.087364567	1.071159175	1.235742676
H	-2.089203257	1.085634231	-1.223771305
H	-2.193624417	-0.755868554	-1.234031830
H	-2.191525160	-0.770355464	1.224470507
H	0.361851810	0.433536801	-0.000054108
H	1.927437566	-1.286069496	-0.889850804
H	3.204378310	-0.455151956	-0.000665610
H	1.926633217	-1.290028996	0.883647767

Methylaminoborylene in other conformation (BNHMe 1)

RI-B3LYP+D3/def2-QZVP



RI-TPSS+D3/def2-QZVP



E=-198.6043428
ZPE=0.1067551

C	1.966850312	-1.373291422	0.000000000
C	2.072922579	-0.051362399	0.000000000
B	-0.569697838	2.189693376	0.000000000
N	-1.704813354	1.426406736	0.000000000
C	-1.800763122	-0.039254051	0.000000000

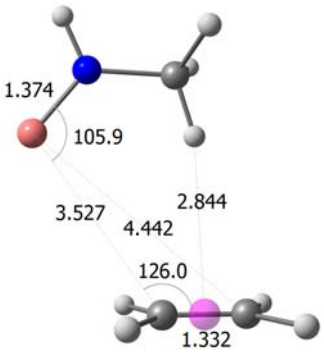
E=-198.7604696
ZPE=0.1054683

C	1.885827041	-1.315608128	0.000000000
C	2.090980557	0.001620939	0.000000000
B	-0.456083959	2.089839032	0.000000000
N	-1.635813927	1.377392503	0.000000000
C	-1.809291760	-0.088155088	0.000000000

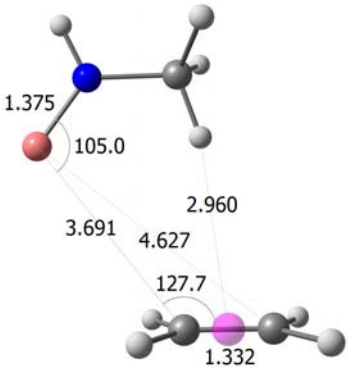
```
H    2.114939803    0.521971294    0.916185918
H    1.923590712   -1.941503912    0.920477551
H    1.923590712   -1.941503912   -0.920477551
H    2.114939803    0.521971294   -0.916185918
H   -2.588064941    1.924245823    0.000000000
H   -2.326989900   -0.388153957    0.887671477
H   -2.326989900   -0.388153957   -0.887671477
H   -0.799514850   -0.461064930    0.000000000
```

```
H    2.178594148    0.571640691    0.918985647
H    1.799664105   -1.881258823    0.923355434
H    1.799664105   -1.881258823   -0.923355434
H    2.178594148    0.571640691   -0.918985647
H   -2.499173414    1.918715307    0.000000000
H   -2.354899042   -0.406358845    0.891884326
H   -2.354899042   -0.406358845   -0.891884326
H   -0.823162966   -0.551850616    0.000000000
```

RI-MP2/def2-QZVP



SCS-RI-MP2/def2-QZVP



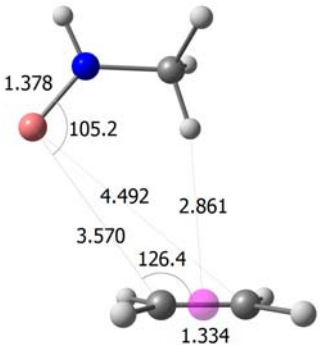
E=-198.23843735729812
ZPE=0.1079179

```
C    1.989311324   -1.393455306    0.000000000
C    2.084733999   -0.065314957    0.000000000
B   -0.612821054    2.207166100    0.000000000
N   -1.752170226    1.439242701    0.000000000
C   -1.803310696   -0.021894749    0.000000000
H    2.124540058    0.499765667    0.918907493
H    1.952104606   -1.954279975    0.922215232
H    1.952104606   -1.954279975   -0.922215232
H    2.124540058    0.499765667   -0.918907493
H   -2.641506272    1.921337938    0.000000000
H   -2.314475625   -0.385980697    0.886218543
H   -2.314475625   -0.385980697   -0.886218543
H   -0.788575154   -0.406091718    0.000000000
```

E=-198.2524915176
ZPE=0.1079299

```
C    2.077000203   -1.437457035    0.000000000
C    2.130447845   -0.106282106    0.000000000
B   -0.696997393    2.266391712    0.000000000
N   -1.824068589    1.478370681    0.000000000
C   -1.848471100    0.012979912    0.000000000
H    2.152673410    0.460353175    0.919304066
H    2.057580387   -2.000641899    0.922063067
H    2.057580387   -2.000641899   -0.922063067
H    2.152673410    0.460353175   -0.919304066
H   -2.723435616    1.940075478    0.000000000
H   -2.354002113   -0.359529554    0.887011711
H   -2.354002113   -0.359529554   -0.887011711
H   -0.826978717   -0.354442088    0.000000000
```

MP2/cc-pVTZ

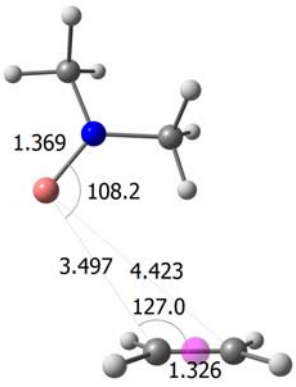


E=-198.1736092
ZPE=0.107905

```
C    2.609911000    0.429535000    0.000000000
C    1.670779000    1.376806000    0.000000000
B   -1.861720000    0.858739000    0.000000000
N   -2.026257000   -0.509641000    0.000000000
C   -0.956996000   -1.509162000    0.000000000
H    1.271467000    1.778960000    0.919797000
H    3.008219000    0.032226000    0.922986000
H    3.008219000    0.032226000   -0.922986000
H    1.271467000    1.778960000   -0.919797000
H   -2.974133000   -0.865668000    0.000000000
H   -1.017501000   -2.135039000    0.886848000
H   -1.017501000   -2.135039000   -0.886848000
H    0.000000000   -0.995905000    0.000000000
```

Dimethylaminoborylene ($BNMe_2$)

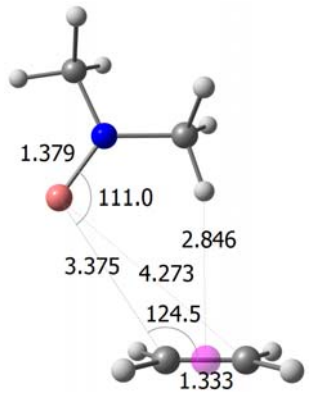
RI-B3LYP+D3/def2-QZVP



E=-237.9028123
ZPE=0.1352067

```
C   -3.057228172    1.046332062   -0.236678403
C   -2.040070123    1.890961796   -0.136115898
B    1.351112857    1.077562791    0.122838502
N    1.466226631   -0.286171648    0.114076735
C    2.777788770   -0.930281507    0.126747831
C    0.306098447   -1.175573249    0.095153901
H   -1.503348045    2.251798624   -1.002976670
H   -3.403599267    0.683017537   -1.195857438
H   -3.587072412    0.685976765    0.635897912
H   -1.687315203    2.254765657    0.819432023
H    2.901188259   -1.553918138   -0.760479587
H    3.563543937   -0.176734342    0.133704517
H    2.884333302   -1.554318403    1.015928030
H    0.334605934   -1.811036336   -0.792156947
H    0.304668673   -1.811489068    0.982633097
H   -0.610933589   -0.590892535    0.077852398
```

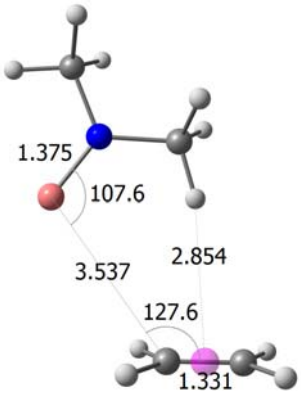
RI-TPSS+D3/def2-QZVP



E=-238.0948006
ZPE=0.1335725

```
C   -3.000550452    1.044121667   -0.232381659
C   -1.999299805    1.918008125   -0.133420973
B    1.258698406    1.069904839    0.109355251
N    1.413869384   -0.299896410    0.109241123
C    2.757010599   -0.894692665    0.125135311
C    0.280469472   -1.234030973    0.094900087
H   -1.472887348    2.294728609   -1.004253062
H   -3.341592743    0.670693380   -1.193804416
H   -3.521524073    0.669571492    0.644202677
H   -1.653949762    2.293056785    0.824563217
H    2.902301002   -1.518109164   -0.763024914
H    3.505881514   -0.099289046    0.126035505
H    2.887695419   -1.508284152    1.022568987
H    0.336532785   -1.875387062   -0.790980946
H    0.299883980   -1.861939446    0.992091415
H   -0.652538377   -0.668455976    0.069772385
```

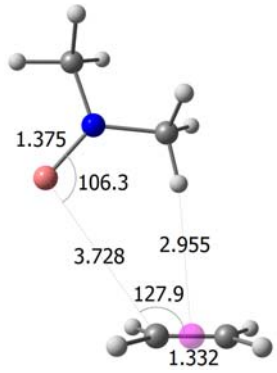
RI-MP2/def2-QZVP



E=-237.46653324050976
ZPE=0.1369141

```
C  -3.079955845   1.049100085  -0.238617600
C  -2.052701460   1.890065512  -0.136961279
B   1.379351113   1.078742731   0.127034194
N   1.484269001  -0.291818855   0.115852230
C   2.782715408  -0.946249290   0.127378572
C   0.321474980  -1.165374711   0.095464915
H  -1.520217708   2.243256176  -1.006944033
H  -3.421478116   0.692335261  -1.199049327
H  -3.608743453   0.699976523   0.635951122
H  -1.708544084   2.250275311   0.820696651
H   2.896681924  -1.567544580  -0.759364683
H   3.570754681  -0.198032849   0.135329729
H   2.880324190  -1.570389905   1.014224909
H   0.343852574  -1.794822402  -0.792918515
H   0.318179183  -1.801365194   0.979372495
H  -0.585962389  -0.568153814   0.082550621
```

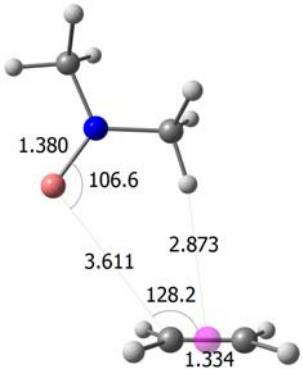
SCS-RI-MP2/def2-QZVP



E=-237.4825536256
ZPE=0.1372004

```
C  -3.171825539   1.080032395  -0.246936173
C  -2.140127657   1.916475790  -0.143965608
B   1.478097681   1.067841634   0.144008779
N   1.555883352  -0.305255136   0.124299429
C   2.838919131  -0.997834289   0.129761041
C   0.366172306  -1.149610653   0.100240993
H  -1.604172833   2.266143080  -1.014096823
H  -3.513780804   0.722988673  -1.207822951
H  -3.705789418   0.733427826   0.626309817
H  -1.795859786   2.276543810   0.814445992
H   2.934677328  -1.616656946  -0.761646283
H   3.647813338  -0.271730704   0.141993428
H   2.919994252  -1.630567618   1.012833312
H   0.368174498  -1.771157232  -0.794675696
H   0.347033365  -1.792826067   0.979498804
H  -0.525209216  -0.527814564   0.095751941
```

MP2/cc-pVTZ



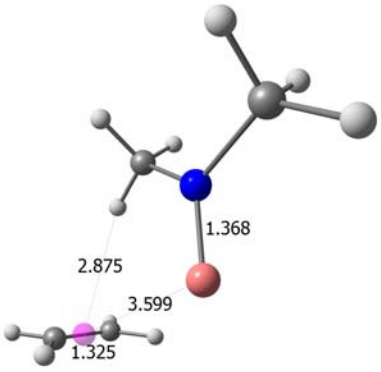
E=-237.3889937
ZPE=0.136859

```
C  -3.318139000  -0.464384000  -0.000017000
C  -2.704092000   0.719644000   0.000000000
```

```
B   0.843600000   1.394941000   0.000035000
N   1.476967000   0.169381000  -0.000007000
C   0.744082000  -1.089526000   0.000027000
C   2.929650000   0.069818000  -0.000026000
H  -2.442056000   1.222452000  -0.919654000
H  -3.579544000  -0.962562000  -0.922972000
H  -3.579549000  -0.962587000   0.922922000
H  -2.442063000   1.222431000   0.919668000
H   3.269793000  -0.463678000  -0.887475000
H   3.366403000   1.065900000  -0.000050000
H   3.269822000  -0.463648000   0.887430000
H   0.998361000  -1.670017000  -0.886962000
H   0.998290000  -1.669938000   0.887087000
H  -0.325231000  -0.892037000  -0.000029000
```

Rotated dimethylaminoborylene ($BNMe_2$)

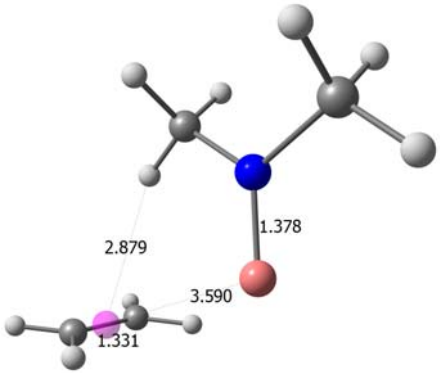
RI-B3LYP+D3/def2-QZVP



E=-237.90361858422
ZPE=0.1354470

```
C   2.742502028  -0.831015045  -0.662640768
C   2.742502028  -0.831015045   0.662640768
B  -0.827212325  -1.288153012   0.000000000
N  -1.390827513  -0.041283676   0.000000000
C  -2.841444927   0.135126454   0.000000000
C  -0.588167261   1.180794391   0.000000000
H   1.935782853  -1.292415881   1.218537967
H   1.935782853  -1.292415881  -1.218537967
H   3.543329223  -0.380358353  -1.235092997
H   3.543329223  -0.380358353   1.235092997
H  -3.155151540   0.686717446  -0.888101174
H  -3.335668110  -0.834940619   0.000000000
H  -3.155151540   0.686717446   0.888101174
H  -0.809984845   1.776114853  -0.887735385
H  -0.809984845   1.776114853   0.887735385
H   0.470364700   0.930370421   0.000000000
```

RI-TPSS+D3/def2-QZVP

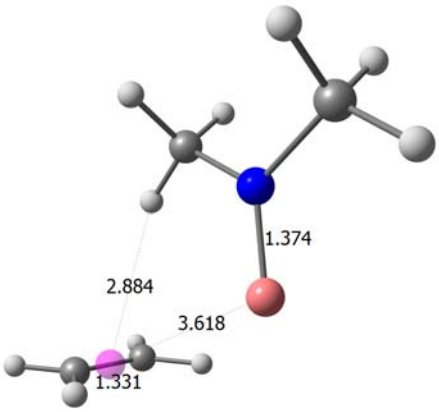


E=-238.09545432485
ZPE=0.1336399

```
C   2.742985823  -0.837935113  -0.665700020
C   2.742985823  -0.837935113   0.665700020
B  -0.818713068  -1.287355089   0.000000000
N  -1.389700414  -0.032971052   0.000000000
C  -2.848691377   0.134598143   0.000000000
C  -0.585347381   1.196588421   0.000000000
H   1.943323748  -1.318682291   1.222906654
H   1.943323748  -1.318682291  -1.222906654
H   3.535439471  -0.367796733  -1.241001926
H   3.535439471  -0.367796733   1.241001926
H  -3.164352293   0.684488253  -0.892551719
H  -3.327243859  -0.847298627   0.000000000
H  -3.164352293   0.684488253   0.892551719
H  -0.809769518   1.790547615  -0.892107687
H  -0.809769518   1.790547615   0.892107687
H   0.474441639   0.935194741   0.000000000
```

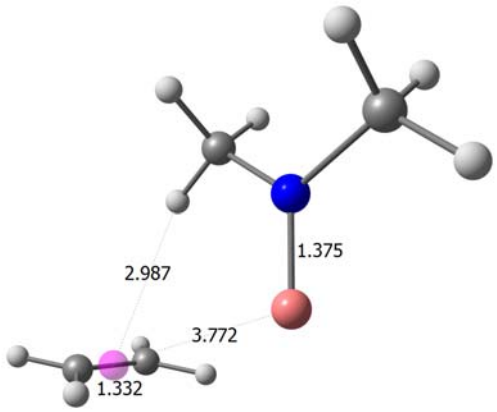
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-237.46725944917981
ZPE=0.1371814

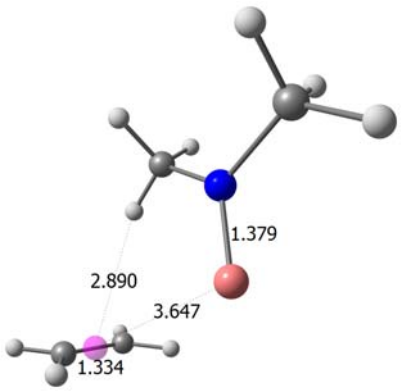
C	2.749901371	-0.834417538	-0.665568306
C	2.749901371	-0.834417538	0.665568306
B	-0.839396827	-1.290255479	0.000000000
N	-1.400977085	-0.035961721	0.000000000
C	-2.843486011	0.147048954	0.000000000
C	-0.596811872	1.176509916	0.000000000
H	1.965379049	-1.333051254	1.216385492
H	1.965379049	-1.333051254	-1.216385492
H	3.532313448	-0.347214623	-1.228823735
H	3.532313448	-0.347214623	1.228823735
H	-3.150739351	0.698894666	-0.886766134
H	-3.337060298	-0.820944633	0.000000000
H	-3.150739351	0.698894666	0.886766134
H	-0.817023021	1.769391384	-0.886449294
H	-0.817023021	1.769391384	0.886449294
H	0.458069102	0.916397692	0.000000000



E=-237.4830830679
ZPE=0.1372004

C	-2.436415464	1.616237113	-0.811507064
C	-1.998742105	2.268127847	0.264480044
B	1.238319773	0.534000167	-0.825767887
N	1.299917902	-0.652535345	-0.133458070
C	2.505635759	-1.472647823	-0.128420746
C	0.168666699	-1.161764357	0.634945062
H	-0.959965598	2.551888589	0.356584425
H	-1.762097796	1.357165106	-1.615396485
H	-3.474614767	1.334777532	-0.916803815
H	-2.666352876	2.538648174	1.070258148
H	2.291696035	-2.456366042	-0.544607926
H	3.275736781	-0.996332890	-0.729906109
H	2.875514713	-1.589235524	0.889558052
H	-0.136941410	-2.133846922	0.249300565
H	0.446714501	-1.266873412	1.683135971
H	-0.667072147	-0.471242214	0.557605836

MP2/cc-pVTZ



E=-237.3896876
ZPE=0.137093

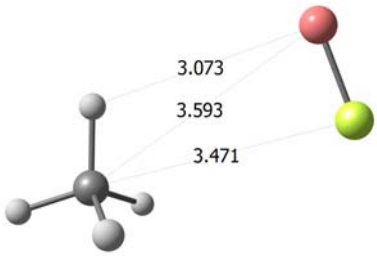
C	-2.874834000	-0.100270000	0.666961000
C	-2.875248000	-0.100428000	-0.666541000
B	0.573030000	-1.286905000	-0.000624000
N	1.372976000	-0.163474000	-0.000195000
C	2.825453000	-0.267367000	0.000453000

```
C   0.822611000   1.185627000  -0.000371000
H  -2.212291000  -0.752944000  -1.217817000
H  -2.211536000  -0.752658000   1.217980000
H  -3.538840000   0.539880000   1.230973000
H  -3.539606000   0.539590000  -1.230289000
H   3.235896000   0.213575000   0.888153000
H   3.119205000  -1.314550000   0.000530000
H   3.236697000   0.213669000  -0.886825000
H   1.154744000   1.724754000   0.886909000
H   1.155488000   1.724834000  -0.887322000
H  -0.263637000   1.137322000  -0.000818000
```

3. Geometries of van der Waals complexes with methane A

Fluoroborylene (BF)

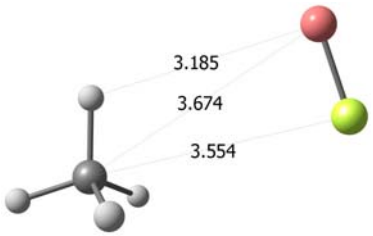
RI-B3LYP+D3/def2-QZVP



E=-165.1839621
ZPE=0.0485838

```
C  -0.961715022   0.247433577   0.000000000
B   2.307829604  -1.242015892   0.000000000
F   2.501146673   0.004586004   0.000000000
H  -0.535546945   0.709276640  -0.888242957
H  -2.040376501   0.388542040   0.000000000
H  -0.735790860  -0.817099002   0.000000000
H  -0.535546945   0.709276640   0.888242957
```

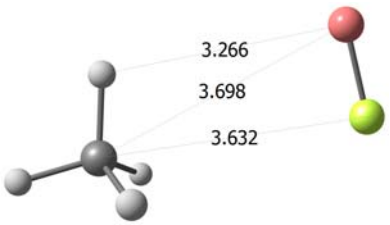
RI-TPSS+D3/def2-QZVP



E=-165.2788578
ZPE=0.0481622

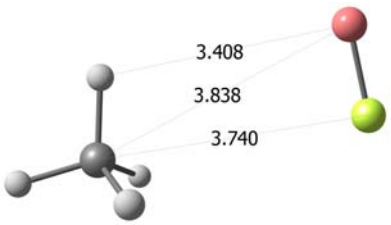
```
C  -0.985690212   0.248137800   0.000000000
B   2.369441701  -1.250037431   0.000000000
F   2.559888809   0.008989102   0.000000000
H  -0.546505592   0.700333354  -0.891269158
H  -2.063797081   0.417714153   0.000000000
H  -0.786832027  -0.825470332   0.000000000
H  -0.546505592   0.700333354   0.891269158
```

RI-MP2/def2-QZVP



E=-164.94404327492467

SCS-RI-MP2/def2-QZVP



E=-164.9511206491

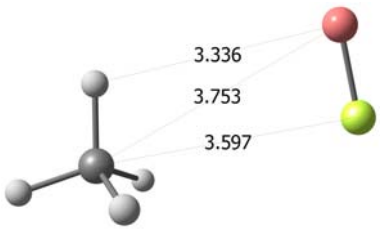
ZPE=0.0492659

```
C  -1.002132394   0.242327922   0.000000000
B   2.391093424  -1.228505429   0.000000000
F   2.622707149   0.014675003   0.000000000
H  -0.547969492   0.673028502  -0.885674288
H  -2.064882162   0.456992081   0.000000000
H  -0.850847033  -0.831546580   0.000000000
H  -0.547969492   0.673028502   0.885674288
```

ZPE=0.0491358

```
C  -1.036899089   0.251467028   0.000000000
B   2.493687628  -1.253971353   0.000000000
F   2.693916998  -0.005389510   0.000000000
H  -0.581378637   0.681903431  -0.886773106
H  -2.100650220   0.468078657   0.000000000
H  -0.887298043  -0.823991683   0.000000000
H  -0.581378637   0.681903431   0.886773106
```

MP2/cc-pVTZ

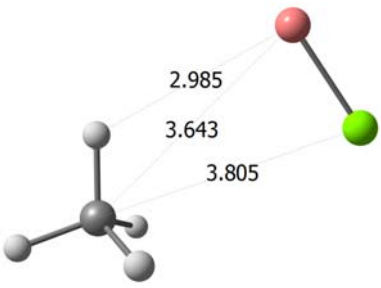


E=-164.891112
ZPE=0.049189

```
C  -2.101113000   0.011658000   0.000001000
B   1.566694000   0.804494000  -0.000004000
F   1.464483000  -0.459748000   0.000001000
H  -1.729852000  -0.491290000   0.887635000
H  -3.186276000  -0.010545000   0.000152000
H  -1.760958000   1.042693000  -0.002487000
H  -1.730045000  -0.495540000  -0.885300000
```

Chloroborylene (BCl)

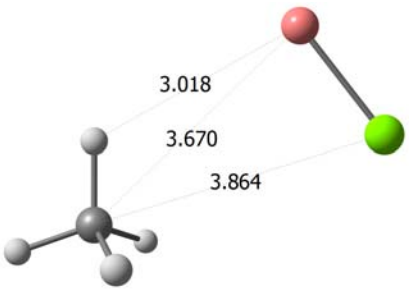
RI-B3LYP+D3/def2-QZVP



E=-525.4617182
ZPE=0.0473062

```
C   0.939444671  -0.349224742  -0.261435506
B  -1.918923443   1.354042695   1.222667569
Cl -2.776868531   0.391293587   0.083899291
```

RI-TPSS+D3/def2-QZVP



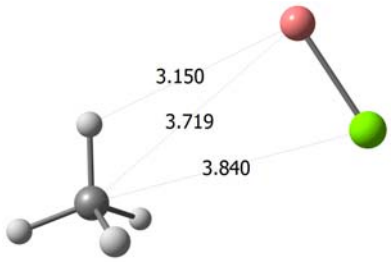
E=-525.5903972
ZPE=0.0468745

```
C   0.951773580  -0.351731158  -0.263255336
B  -1.934051477   1.363855181   1.220328489
Cl -2.823136535   0.393619866   0.095039848
```

```
H    0.548261466    0.051996914   -1.194105428
H    1.994759406   -0.584512885   -0.381668689
H    0.819788620    0.389318163    0.528986073
H    0.393537812   -1.252913737    0.001656695
```

```
H    0.561313437    0.057102162   -1.197082299
H    2.008687483   -0.594945747   -0.385536191
H    0.837822176    0.387354645    0.532637237
H    0.397591341   -1.255254949   -0.002131748
```

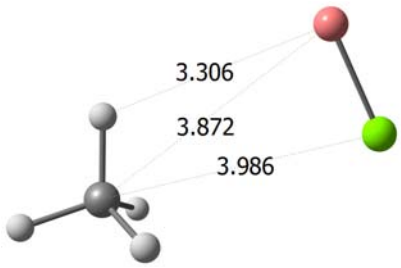
RI-MP2/def2-QZVP



E=-524.87356947602154
ZPE=0.0480207

```
C    0.958299011   -0.348676958   -0.258066273
B   -1.995091676    1.358478981    1.223596202
Cl -2.797112087    0.385467827    0.067258302
H    0.536610162    0.075596021   -1.162800473
H    1.988519792   -0.634110478   -0.439598814
H    0.921764330    0.387198960    0.538032821
H    0.387010469   -1.223954353    0.031578235
```

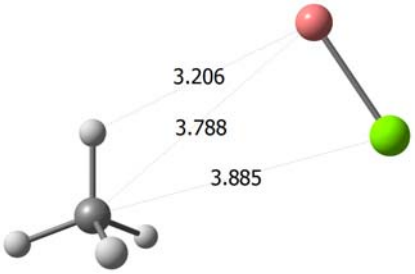
SCS-RI-MP2/def2-QZVP



E=-524.8845498322
ZPE=0.0478807

```
C    0.997561166   -0.363582342   -0.269213036
B   -2.095893206    1.397531084    1.254785506
Cl -2.893239275    0.421377811    0.092193451
H    0.574766462    0.060746781   -1.175009786
H    2.028903626   -0.649415401   -0.451784267
H    0.961838886    0.373372380    0.527541022
H    0.426062336   -1.240030313    0.021487105
```

MP2/cc-pVTZ

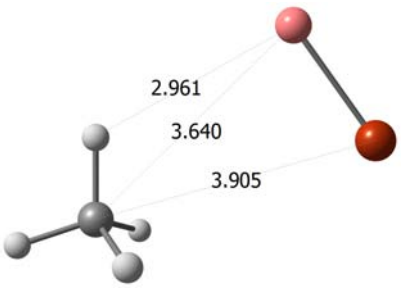


E=-524.8282421
ZPE=0.048003

```
C    2.608929000   -0.059549000   -0.000001000
B   -0.916768000    1.326104000   -0.000001000
Cl -1.265073000   -0.354973000    0.000000000
H    2.236123000   -0.565250000   -0.885526000
H    3.694162000   -0.083986000   -0.000016000
H    2.269984000    0.972016000   -0.002174000
H    2.236235000   -0.561467000    0.887720000
```

Bromoborylene (BBr)

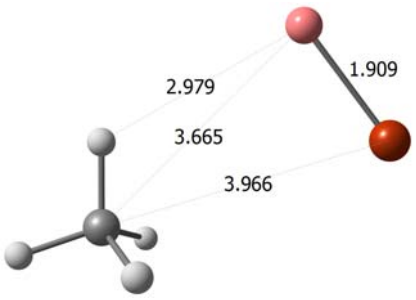
RI-B3LYP+D3/def2-QZVP



E=-2639.3730273
ZPE=0.0469711

```
C  -0.695666450   0.716001874  -0.306421367
B   2.235251891  -1.414039451   0.047950925
Br  1.240376713  -2.164148032   1.483983465
H   0.259988735   0.615368660  -0.817665460
H  -1.275610176   1.508552535  -0.774506176
H  -1.241951560  -0.222532035  -0.372731144
H  -0.522389159   0.960796449   0.739389757
```

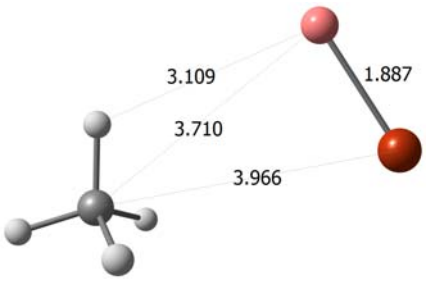
RI-TPSS+D3/def2-QZVP



E=-2639.4516999
ZPE=0.0465736

```
C  -0.703686189   0.724568788  -0.311013800
B   2.242679106  -1.424056718   0.052013811
Br  1.272543540  -2.196755067   1.503046837
H   0.257020670   0.617785550  -0.819546013
H  -1.278460086   1.523122568  -0.783437133
H  -1.256953010  -0.213826519  -0.380071118
H  -0.533144030   0.969161398   0.739007416
```

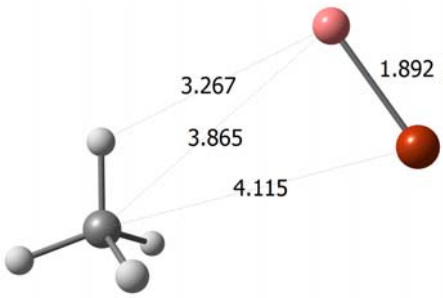
RI-MP2/def2-QZVP



E=-2637.77421436154600
ZPE=0.0476612

```
C  -0.701937888   0.732058956  -0.319663866
B   2.257621442  -1.466912219   0.088003927
Br  1.252183154  -2.193469735   1.510342736
H   0.230381331   0.685428113  -0.872382260
H  -1.331423525   1.509809996  -0.737735959
H  -1.212199709  -0.222451809  -0.389793369
H  -0.494624804   0.955536698   0.721228790
```

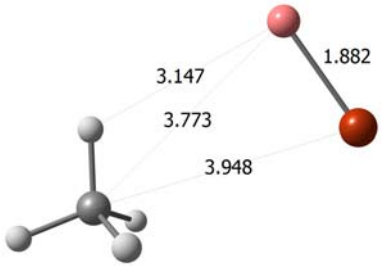
SCS-RI-MP2/def2-QZVP



E=-2637.7862158639
ZPE=0.0475198

```
C  -0.731477468   0.762613254  -0.332816878
B   2.335818603  -1.544796109   0.119727243
Br  1.322549701  -2.268925601   1.544425523
H   0.201876743   0.715813447  -0.886012090
H  -1.361527260   1.541323256  -0.751686302
H  -1.242834537  -0.192812960  -0.402991252
H  -0.524405781   0.986784714   0.709353755
```

MP2/cc-pVTZ

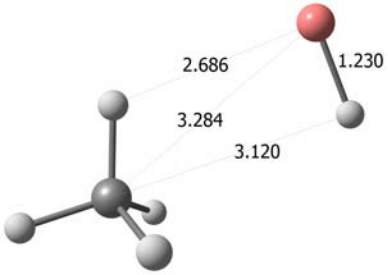


E=-2637.7981514
ZPE=0.047692

```
C  -3.099118000  -0.118382000  -0.000002000
B   0.262163000   1.594700000   0.000001000
Br  0.848006000  -0.194001000   0.000000000
H  -2.813870000   0.929430000  -0.002444000
H  -4.181707000  -0.198582000  -0.000529000
H  -2.699777000  -0.604232000  -0.885037000
H  -2.700970000  -0.599768000   0.888022000
```

Borylene (BH)

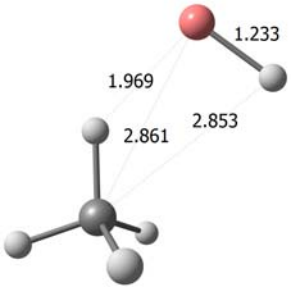
RI-B3LYP+D3/def2-QZVP



E=-65.7889815
ZPE=0.0512454

```
C  -0.894928503  -0.056002246   0.000000000
H  -0.687331649   0.536641627  -0.888452686
H  -1.940848235  -0.355371326   0.000000000
H  -0.274662344  -0.952702847   0.000000000
H  -0.687331649   0.536641627   0.888452686
B   2.364967211  -0.457129941   0.000000000
H   2.120135170   0.747923100   0.000000000
```

RI-TPSS+D3/def2-QZVP

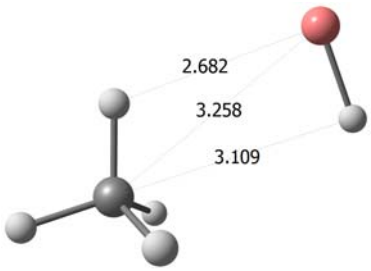


E=-65.8514655
ZPE=0.0517030

```
C  -0.800311267   0.010279887   0.000000000
H  -0.740504072   0.631800519  -0.893638422
H  -1.726936836  -0.566116298   0.000000000
H   0.028930268  -0.731478774   0.000000000
H  -0.740504072   0.631800519   0.893638422
B   1.994284093  -0.604549833   0.000000000
H   1.985041886   0.628263985   0.000000000
```

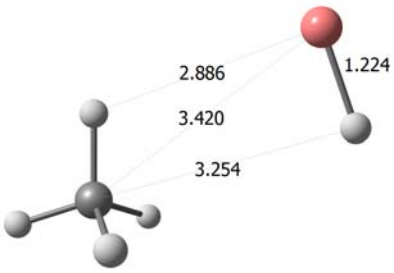
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-65.63727275994052
ZPE=0.0523243

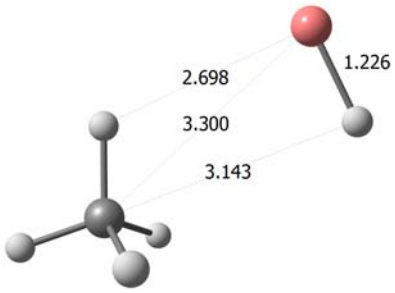
```
C   -0.888945266   -0.060098109    0.000000000
H   -0.673378409    0.527604630   -0.885787450
H   -1.936576242   -0.339569248    0.000000000
H   -0.285181275   -0.963099454    0.000000000
H   -0.673378409    0.527604630    0.885787450
B    2.346183810   -0.446861519    0.000000000
H    2.111275789    0.754419070    0.000000000
```



E=-65.6574290409
ZPE=0.0520610

```
C   -0.933390228   -0.069219198    0.000000000
H   -0.695348571    0.510576324   -0.886938304
H   -1.992411834   -0.307772314    0.000000000
H   -0.361463454   -0.993292549    0.000000000
H   -0.695348571    0.510576324    0.886938304
B    2.468066184   -0.423778734    0.000000000
H    2.209896474    0.772910145    0.000000000
```

MP2/cc-pVTZ



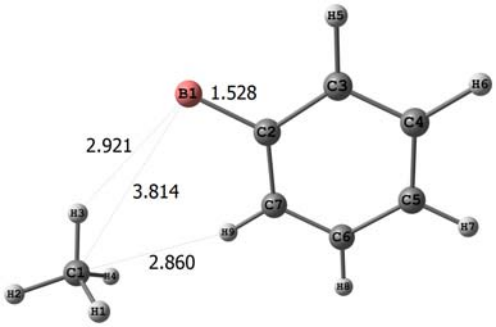
E=-65.6165427
ZPE=0.052276

```
C    1.215010000   -0.008913000   -0.000001000
H    1.051478000    0.595859000    0.886846000
H    2.234734000   -0.380866000    0.000497000
H    0.532404000   -0.855301000   -0.000662000
H    1.052528000    0.596397000   -0.886673000
B   -2.080009000   -0.181108000    0.000000000
H   -1.761161000    1.002925000   -0.000003000
```

Phenylborylene (BPh)

RI-B3LYP+D3/def2-QZVP

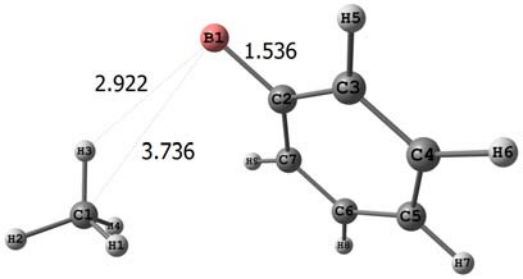
RI-TPSS+D3/def2-QZVP



dih B1C2C1H3=-0.6 degree
dih H3B1C2C7=18.6 degree

E=-296.83425015282
ZPE=0.1367190

C	-0.992380116	2.692433676	-2.120837330
B	-0.399294681	-1.068278132	-1.893566134
H	-0.069024996	2.843522050	-1.564730604
H	-1.079683024	3.457530054	-2.889437958
H	-0.979782702	1.708790555	-2.587279358
H	-1.842422476	2.764942559	-1.444322243
C	0.027134279	-1.086836779	-0.426131485
C	0.730236804	-2.193511647	0.081844996
C	1.121238626	-2.226179467	1.411815886
C	0.814806395	-1.156013649	2.248761896
C	0.118538059	-0.051927959	1.762154966
C	-0.273848410	-0.015177265	0.433036458
H	0.967434997	-3.024998399	-0.570155713
H	1.661981016	-3.078465162	1.799571212
H	1.120378913	-1.182376395	3.286035979
H	-0.113610777	0.773680670	2.420711689
H	-0.811701909	0.842865291	0.052527744

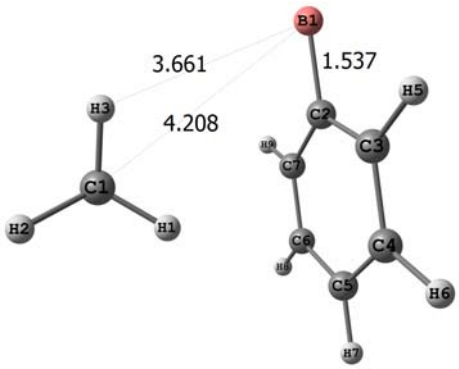


dih B1C2C1H3=-0.9 degree
dih H3B1C2C7=54.6 degree

E=-297.07750102288
ZPE=0.1347311

C	-0.543187472	2.432644282	-1.987200666
B	-1.107194820	-1.252691788	-1.744817958
H	0.347474225	2.137989597	-1.429208196
H	-0.282126283	3.205574238	-2.712371068
H	-0.947607083	1.562842413	-2.509983047
H	-1.292598101	2.822771146	-1.295213153
C	-0.406211956	-1.127098939	-0.383699270
C	0.718512134	-1.925687583	-0.084692250
C	1.358369000	-1.809436486	1.145206117
C	0.883610736	-0.896077970	2.090566723
C	-0.229484830	-0.097391860	1.812361560
C	-0.871322983	-0.210816011	0.583864666
H	1.085900275	-2.634440344	-0.822049444
H	2.223267718	-2.424422087	1.371855913
H	1.384128879	-0.805639608	3.049519403
H	-0.588509415	0.609425521	2.553425054
H	-1.733020025	0.412455480	0.362435616

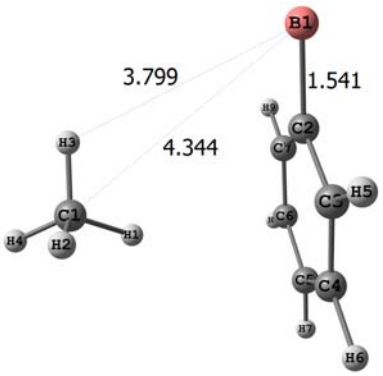
RI-MP2/def2-QZVP



dih B1C2C1H3=-27.4 degree
dih H3B1C2C7=93.8 degree

E=-296.2901289239
ZPE=0.1377741

SCS-RI-MP2/def2-QZVP



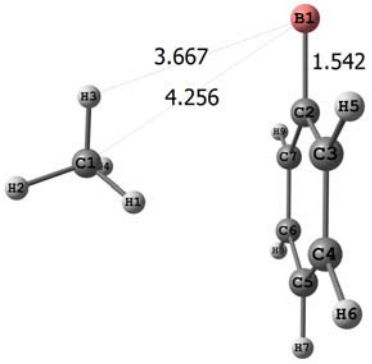
dih B1C2C1H3= 25.3 degree
dih H3B1C2C7= 86.4 degree

E=-296.2890807047
ZPE=0.1376273

C	0.067486929	1.950312586	-1.565532887
B	-1.857310595	-1.786619130	-1.372198424
H	0.602915082	1.368234226	-0.822201771
H	0.695130729	2.762721726	-1.916089524
H	-0.198180979	1.311006813	-2.400594734
H	-0.835659657	2.356095290	-1.122464737
C	-0.888179177	-1.276279225	-0.293257414
C	0.472530434	-1.612846420	-0.351681716
C	1.348937398	-1.139364081	0.615634287
C	0.872685142	-0.329437336	1.644582934
C	-0.476671615	0.010338262	1.712878961
C	-1.356457746	-0.460514673	0.747475566
H	0.838108549	-2.240495053	-1.154687408
H	2.397929323	-1.395803450	0.572504020
H	1.556690294	0.039336344	2.396221422
H	-0.834316014	0.640273635	2.514899708
H	-2.405638097	-0.196959516	0.794511718

C	0.010066000	2.031547562	-1.639211408
B	-1.765093934	-1.923674644	-1.359806418
H	0.093185997	1.686465783	-0.612581860
H	0.811333992	1.599022901	-2.231117647
H	-0.947090307	1.721455477	-2.047853315
H	0.082993778	3.114817173	-1.668210961
C	-0.830849587	-1.356702999	-0.273138754
C	0.561797347	-1.493400008	-0.393641214
C	1.403300124	-0.973647044	0.582580054
C	0.860626224	-0.314078386	1.684838981
C	-0.520392459	-0.171508316	1.817209991
C	-1.364223579	-0.690649464	0.842602599
H	0.980138042	-2.004423090	-1.251820260
H	2.475181164	-1.077700878	0.489551777
H	1.516336283	0.090816981	2.443448468
H	-0.930421626	0.341853710	2.675571587
H	-2.436887458	-0.580194759	0.941578379

MP2/cc-pVTZ



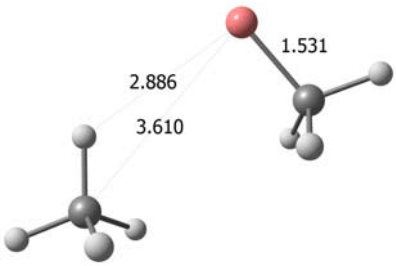
dih B1C2C1H3=-17.36 degree
dih H3B1C2C7=89.84 degree

E=-296.1974279
ZPE=0.137551

C	2.735903000	-0.933830000	-0.276339000
B	0.479449000	2.652878000	0.118927000
H	1.711875000	-1.124881000	-0.584123000
H	3.404567000	-1.632281000	-0.770681000
H	3.009225000	0.082173000	-0.545043000
H	2.816661000	-1.055175000	0.799781000
C	-0.146316000	1.244466000	0.086541000
C	-0.620121000	0.709264000	-1.123266000
C	-1.171147000	-0.567341000	-1.153423000
C	-1.252535000	-1.315291000	0.022168000
C	-0.786215000	-0.793708000	1.229551000
C	-0.234068000	0.482155000	1.263595000
H	-0.552997000	1.293324000	-2.033225000
H	-1.535994000	-0.981745000	-2.083249000
H	-1.680795000	-2.308380000	-0.002986000
H	-0.854033000	-1.382653000	2.133883000
H	0.131249000	0.890937000	2.198041000

Methylborylene (BCH_3)

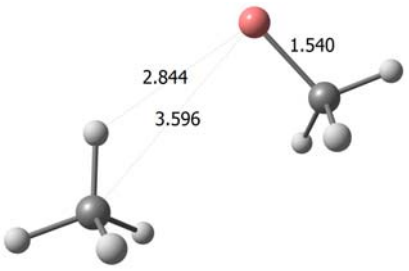
RI-B3LYP+D3/def2-QZVP



E=-105.0511149
ZPE=0.0805397

```
C  -0.597490862   1.546843023  -0.749408638
B   0.022686220  -2.000573878  -0.504346967
H   0.479000773   1.706624881  -0.741853416
H  -1.084741863   2.395360141  -1.224779954
H  -0.826204095   0.639303236  -1.305498546
H  -0.958170804   1.449794656   0.272787268
C   0.629277920  -1.522693992   0.817446809
H   1.163524148  -2.346558817   1.304943989
H   1.331817621  -0.700672451   0.640365141
H  -0.159699058  -1.167426798   1.490344313
```

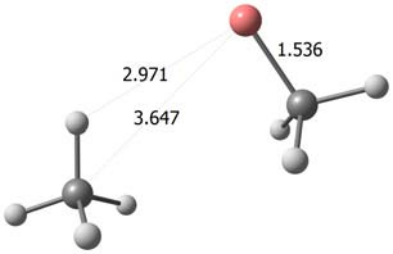
RI-TPSS+D3/def2-QZVP



E=-105.2242859
ZPE=0.0797380

```
C  -0.614872022   1.560564261  -0.754604397
B   0.013048326  -1.971474257  -0.513496076
H   0.460797579   1.744201149  -0.716957706
H  -1.106967848   2.391446145  -1.263073855
H  -0.808134597   0.634387619  -1.301525277
H  -1.006059816   1.474647233   0.261194725
C   0.647508881  -1.539704427   0.822147718
H   1.116424356  -2.401244518   1.319653534
H   1.415485201  -0.770974347   0.653603246
H  -0.117230059  -1.121848852   1.493058087
```

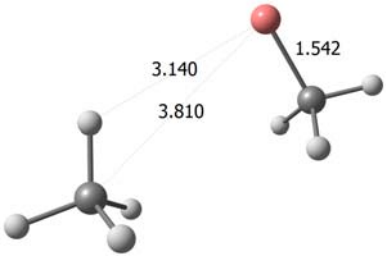
RI-MP2/def2-QZVP



E=-104.90714249977756
ZPE=0.0816591

```
C  -0.599810797   1.555453526  -0.760605288
B   0.050531670  -2.023483249  -0.499179923
H   0.476112157   1.692101343  -0.783360515
H  -1.080995709   2.427156072  -1.189950587
H  -0.866159575   0.675665401  -1.337138532
H  -0.928981894   1.433324890   0.265846248
C   0.632325670  -1.528614925   0.833879312
H   1.177544260  -2.340717597   1.319404341
H   1.313247528  -0.693477165   0.659496701
H  -0.173813311  -1.197408296   1.491608245
```

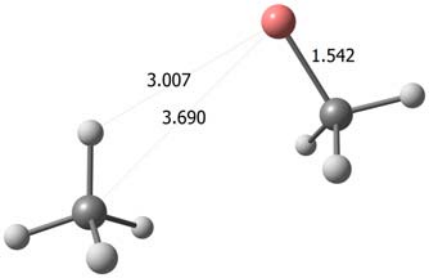
SCS-RI-MP2/def2-QZVP



E=-104.9272395862
ZPE=0.0816024

```
C  -0.620680171   1.616052731  -0.786303107
B   0.078349929  -2.115700514  -0.471856833
H   0.456391483   1.753777122  -0.810643712
H  -1.104079708   2.489048851  -1.213852770
H  -0.887718309   0.736041639  -1.364072643
H  -0.948186273   1.491738043   0.241831701
C   0.652358576  -1.588110855   0.858826187
H   1.207010662  -2.382581249   1.364546091
H   1.325270945  -0.747849190   0.671732862
H  -0.158717132  -1.252416579   1.509792224
```

MP2/cc-pVTZ

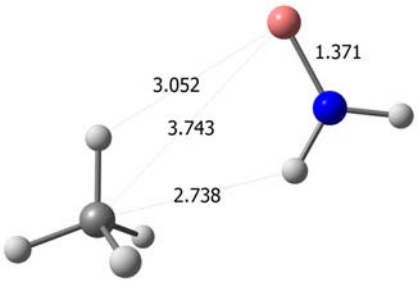


E=-104.8727694
ZPE=0.081604

```
C  -2.125298000  -0.023411000  -0.000114000
B   1.395941000   1.080546000  -0.000158000
H  -1.955426000  -0.426145000   0.994035000
H  -3.189547000   0.131327000  -0.147637000
H  -1.604781000   0.924420000  -0.101912000
H  -1.757927000  -0.724290000  -0.743921000
C   1.572124000  -0.451144000   0.000351000
H   2.624931000  -0.699920000   0.156625000
H   0.975705000  -0.896973000   0.799962000
H   1.246382000  -0.863818000  -0.957778000
```

Aminoborylene (BNH_2)

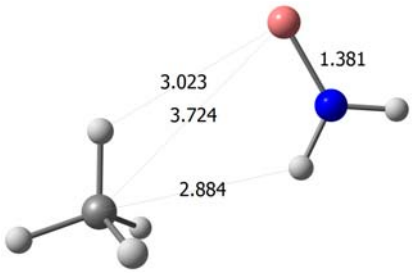
RI-B3LYP+D3/def2-QZVP



E=-121.2416799
ZPE=0.0710546

```
C  -1.517198926   0.367838403   0.000000000
B   2.200644816   0.805115709   0.000000000
N   1.884682103  -0.528635176   0.000000000
H  -1.359475371  -0.235832111   0.892550269
H  -2.539194433   0.739803563   0.000000000
H  -0.824314260   1.206858753   0.000000000
H  -1.359475371  -0.235832111  -0.892550269
H   2.584601852  -1.258173923   0.000000000
H   0.929729596  -0.861143107   0.000000000
```

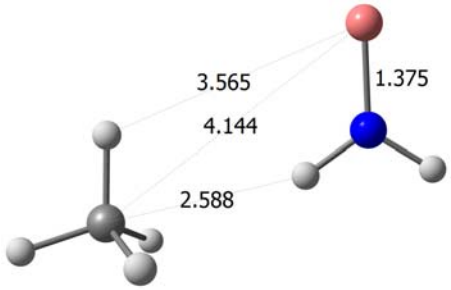
RI-TPSS+D3/def2-QZVP



E=-121.3333261
ZPE=0.0701299

```
C  -1.549204603   0.390764722   0.000000000
B   2.151471475   0.805683294   0.000000000
N   1.928970439  -0.557141187   0.000000000
H  -1.397809178  -0.217447996   0.894854863
H  -2.569505907   0.777537817   0.000000000
H  -0.842413641   1.223089201   0.000000000
H  -1.397809178  -0.217447996  -0.894854863
H   2.678726922  -1.242320698   0.000000000
H   0.997573675  -0.962717156   0.000000000
```

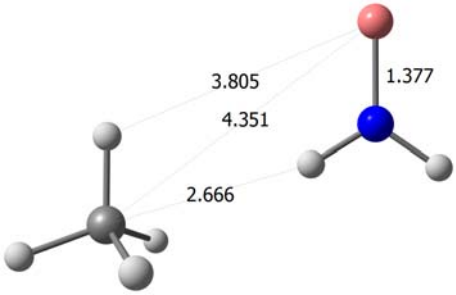
RI-MP2/def2-QZVP



E=-121.01549048196490
ZPE=0.0718279

```
C  -1.546413261   0.330323157   0.000000000
B   2.579432467   0.719752668   0.000000000
N   1.903694101  -0.478188470   0.000000000
H  -1.330809650  -0.252400659   0.890102916
H  -2.597351537   0.595671326   0.000000000
H  -0.948329701   1.235342353   0.000000000
H  -1.330809650  -0.252400659  -0.890102916
H   2.375162821  -1.369752737   0.000000000
H   0.895424411  -0.528346979   0.000000000
```

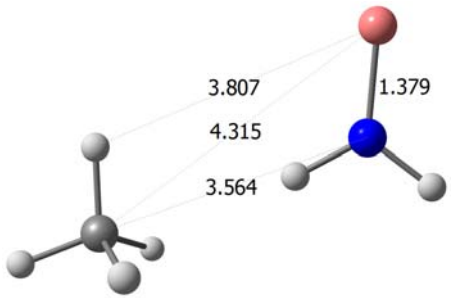
SCS-RI-MP2/def2-QZVP



E=-121.0288905081
ZPE=0.0718143

```
C  -1.598117142   0.331624148   0.000000000
B   2.740910159   0.659969542   0.000000000
N   1.961884880  -0.475743596   0.000000000
H  -1.369617890  -0.247826593   0.890540329
H  -2.655249556   0.576887771   0.000000000
H  -1.017669620   1.249659870   0.000000000
H  -1.369617890  -0.247826593  -0.890540329
H   2.353947058  -1.404655972   0.000000000
H   0.953530002  -0.442088576   0.000000000
```

MP2/cc-pVTZ

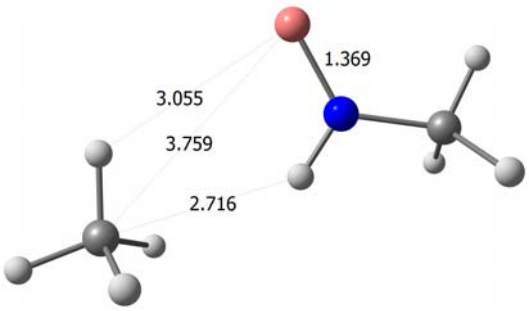


E=-120.9748357
ZPE=0.071695

```
C  -2.186841000   0.074476000  -0.000014000
B   2.072449000   0.765597000  -0.000024000
N   1.344809000  -0.406011000   0.000020000
H  -1.889008000  -0.469054000   0.892547000
H  -3.265951000   0.187930000   0.000347000
H  -1.723743000   1.056814000  -0.003672000
H  -1.890246000  -0.475106000  -0.889276000
H   1.779382000  -1.316941000  -0.000192000
H   0.334702000  -0.416410000   0.000309000
```

Methylaminoborylene (BNHMe)

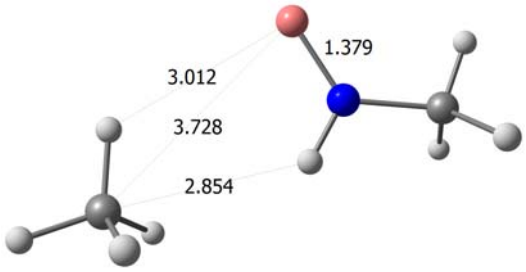
RI-B3LYP+D3/def2-QZVP



E=-160.5362302
ZPE=0.1005257

C	-2.485552106	0.102803529	0.000000000
B	0.783856553	-1.752879301	0.000000000
N	1.026303449	-0.405769643	0.000000000
C	2.343817181	0.238498075	0.000000000
H	-2.111757802	0.603006265	-0.892191995
H	-3.572453727	0.142856595	0.000000000
H	-2.159372292	-0.935333795	0.000000000
H	-2.111757802	0.603006265	0.892191995
H	0.227647311	0.216992571	0.000000000
H	2.470834702	0.856282186	0.887997276
H	3.117599830	-0.525744931	0.000000000
H	2.470834702	0.856282186	-0.887997276

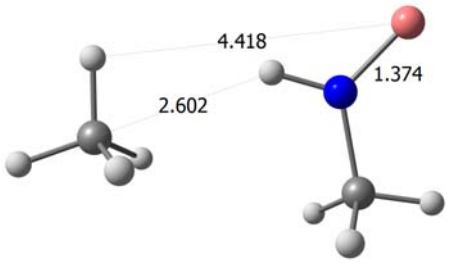
RI-TPSS+D3/def2-QZVP



E=-160.6640234
ZPE=0.0994015

C	-2.551397218	0.076485570	0.000000000
B	0.735545793	-1.682217062	0.000000000
N	1.050198009	-0.339387548	0.000000000
C	2.411868217	0.225230834	0.000000000
H	-2.193076962	0.591167808	-0.894616008
H	-3.642610035	0.078406642	0.000000000
H	-2.187135222	-0.952987561	0.000000000
H	-2.193076962	0.591167808	0.894616008
H	0.290628299	0.337814775	0.000000000
H	2.573781394	0.834505256	0.892438952
H	3.131493299	-0.594691784	0.000000000
H	2.573781394	0.834505256	-0.892438952

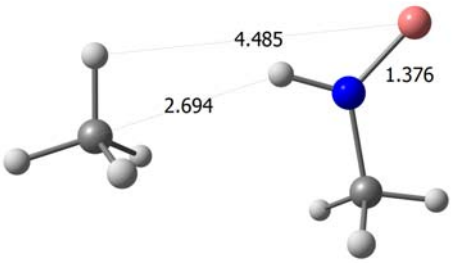
RI-MP2/def2-QZVP



E=-160.23817864598911
ZPE=0.1020331

C	-2.067561440	0.379987059	0.000000000
B	1.829937965	-2.181816924	0.000000000
N	1.117012639	-1.006760727	0.000000000
C	1.705006270	0.329507474	0.000000000
H	-1.492623506	0.619612093	-0.888658146
H	-2.980870899	0.963798685	0.000000000
H	-2.322788365	-0.674842346	0.000000000
H	-1.492623506	0.619612093	0.888658146
H	0.106527216	-1.049055948	0.000000000
H	1.405823726	0.881249251	0.886160660
H	2.786336174	0.237460039	0.000000000
H	1.405823726	0.881249251	-0.886160660

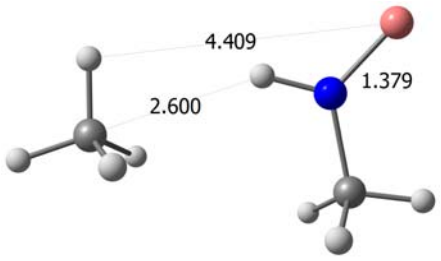
SCS-RI-MP2/def2-QZVP



E=-160.2543075202
ZPE=0.1019814

C	-2.141612899	0.385715493	0.000000000
B	1.848922556	-2.197275118	0.000000000
N	1.159373031	-1.006912745	0.000000000
C	1.768159554	0.324170314	0.000000000
H	-1.571618803	0.639303117	-0.889542744
H	-3.069902385	0.947893045	0.000000000
H	-2.369998442	-0.676501418	0.000000000
H	-1.571618803	0.639303117	0.889542744
H	0.148882640	-1.031651554	0.000000000
H	1.475365946	0.879715872	0.886952052
H	2.848681659	0.216524002	0.000000000
H	1.475365946	0.879715872	-0.886952052

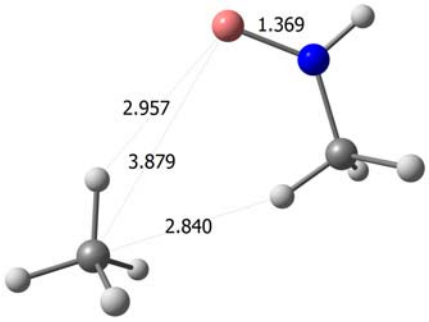
MP2/cc-pVTZ



E=-160.1847087
ZPE=0.101870

```
C  -2.562783000   0.274053000   0.000000000
B   2.016879000   1.160126000   0.000000000
N   0.929046000   0.312868000   0.000000000
C   0.996867000  -1.147224000   0.000000000
H  -2.124977000  -0.169872000   0.889659000
H  -3.632110000   0.089555000   0.000000000
H  -2.388579000   1.346438000   0.000000000
H  -2.124977000  -0.169872000  -0.889659000
H   0.000000000   0.714502000   0.000000000
H   0.519193000  -1.556106000  -0.886857000
H   2.040037000  -1.450223000   0.000000000
H   0.519193000  -1.556106000   0.886857000
```

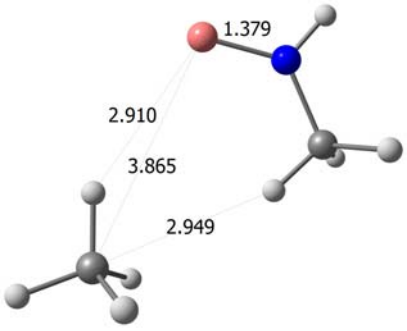
RI-B3LYP+D3/def2-QZVP



E=-160.5358786
ZPE=0.1005312

```
C  -2.322372993  -0.024976182   0.000000000
B   1.097496178  -1.856377745   0.000000000
N   1.917752834  -0.760793146   0.000000000
C   1.506832497   0.648516953   0.000000000
H  -1.708526024  -0.923935756   0.000000000
H  -3.374103017  -0.303620532   0.000000000
H  -2.107631696   0.564718375   0.889642440
H  -2.107631696   0.564718375  -0.889642440
H   1.879490689   1.157311914   0.887937114
H   1.879490689   1.157311914  -0.887937114
```

RI-TPSS+D3/def2-QZVP



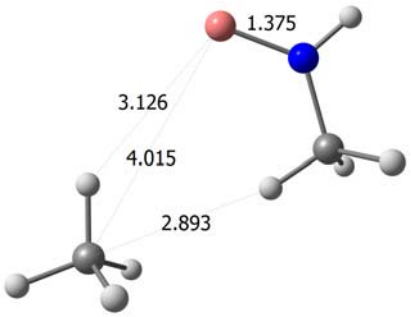
E=-160.6638601
ZPE=0.0993864

```
C  -2.368199880  -0.036866170   0.000000000
B   1.055204629  -1.830851394   0.000000000
N   1.927335731  -0.762790441   0.000000000
C   1.561113689   0.666412823   0.000000000
H  -1.702590571  -0.903569856   0.000000000
H  -3.405809799  -0.375837177   0.000000000
H  -2.186561822   0.566199796   0.892462944
H  -2.186561822   0.566199796  -0.892462944
H   1.952632251   1.160574492   0.892344060
H   1.952632251   1.160574492  -0.892344060
```

```
H    0.421800650    0.704867821    0.000000000
H    2.917401895   -0.927741980    0.000000000
```

```
H    0.474323519    0.749196555    0.000000000
H    2.926481825   -0.959242917    0.000000000
```

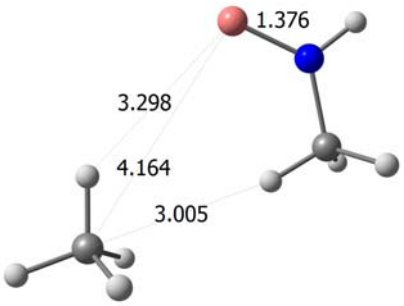
RI-MP2/def2-QZVP



E=-160.23754264338032
ZPE=0.1019201

```
C   -2.377743489   -0.011417128    0.000000000
B    1.184059807   -1.863609475    0.000000000
N    1.996090616   -0.754509198    0.000000000
C    1.528007341    0.629833784    0.000000000
H   -1.799056291   -0.929129957    0.000000000
H   -3.435411910   -0.250739622    0.000000000
H   -2.143316660    0.568305328    0.886805143
H   -2.143316660    0.568305328   -0.886805143
H    1.874969979    1.151919412    0.886486131
H    1.874969979    1.151919412   -0.886486131
H    0.443088841    0.631951156    0.000000000
H    2.997658449   -0.892829041    0.000000000
```

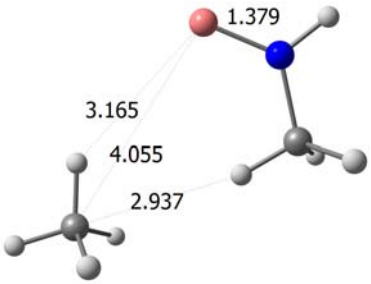
SCS-RI-MP2/def2-QZVP



E=-160.2538197467
ZPE=0.1018723

```
C   -2.453091947   -0.007115834    0.000000000
B    1.266095764   -1.879821707    0.000000000
N    2.059350238   -0.755589908    0.000000000
C    1.572275898    0.625737581    0.000000000
H   -1.894961904   -0.938726959    0.000000000
H   -3.517210736   -0.222285374    0.000000000
H   -2.204799143    0.567930066    0.887674093
H   -2.204799143    0.567930066   -0.887674093
H    1.913823069    1.151873173    0.887324192
H    1.913823069    1.151873173   -0.887324192
H    0.486756448    0.613735171    0.000000000
H    3.062738388   -0.875539446    0.000000000
```

MP2/cc-pVTZ



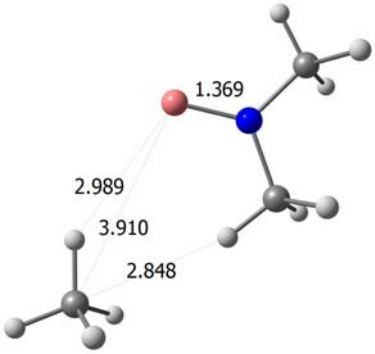
E=-160.1841296
ZPE=0.101802

```
C   -2.809167000    0.059957000    0.000000000
B    0.922041000   -1.527333000    0.000000000
N    1.649989000   -0.356280000    0.000000000
C    1.083220000    0.992395000    0.000000000
H   -2.160854000   -0.811285000    0.000000000
H   -3.846434000   -0.260446000    0.000000000
H   -2.619842000    0.656728000    0.887710000
H   -2.619842000    0.656728000   -0.887710000
```

```
H   1.391289000   1.539669000   0.887185000
H   1.391289000   1.539669000  -0.887185000
H   0.000000000   0.915945000   0.000000000
H   2.659951000  -0.420495000   0.000000000
```

Dimethylaminoborylene ($BNMe_2$)

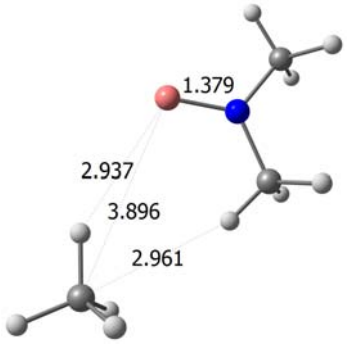
RI-B3LYP+D3/def2-QZVP



E=-199.8345276
ZPE=0.1290034

```
C  -3.137284662   0.215231051   0.000000000
B   0.314420436  -1.621853014   0.000000000
N   1.185972799  -0.565888069   0.000000000
C   0.725574188   0.820682337   0.000000000
C   2.632397602  -0.770490520   0.000000000
H  -2.522849502  -0.683171596   0.000000000
H  -4.189279699  -0.062580512   0.000000000
H  -2.921987650   0.805074989   0.889447565
H  -2.921987650   0.805074989  -0.889447565
H   3.078561138  -0.319377642   0.888160389
H   2.857869872  -1.835595944   0.000000000
H   3.078561138  -0.319377642  -0.888160389
H   1.090870514   1.340040961   0.887879111
H   1.090870514   1.340040961  -0.887879111
H  -0.361709033   0.852189651   0.000000000
```

RI-TPSS+D3/def2-QZVP

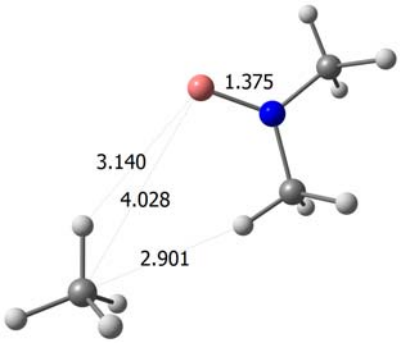


E=-199.9984330
ZPE=0.1275186

```
C  -3.184318587   0.190003478   0.000000000
B   0.288167604  -1.575589375   0.000000000
N   1.197086606  -0.538302424   0.000000000
C   0.775450626   0.868061110   0.000000000
C   2.643064587  -0.792987967   0.000000000
H  -2.504473240  -0.665366682   0.000000000
H  -4.216688498  -0.164818488   0.000000000
H  -3.011966234   0.796122464   0.892274399
H  -3.011966234   0.796122464  -0.892274399
H   3.102778083  -0.356393199   0.892625047
H   2.820978185  -1.870722846   0.000000000
H   3.102778083  -0.356393199  -0.892625047
H   1.156906564   1.375169377   0.892289522
H   1.156906564   1.375169377  -0.892289522
H  -0.314704107   0.919925910   0.000000000
```

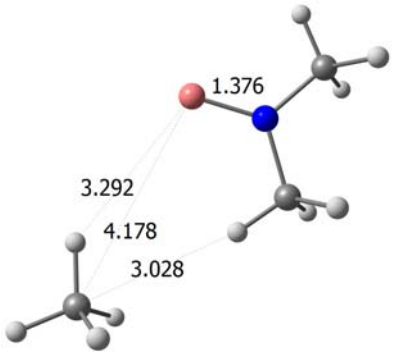
RI-MP2/def2-QZVP

SCS-RI-MP2/def2-QZVP



E=-199.46573566748475
ZPE=0.1309399

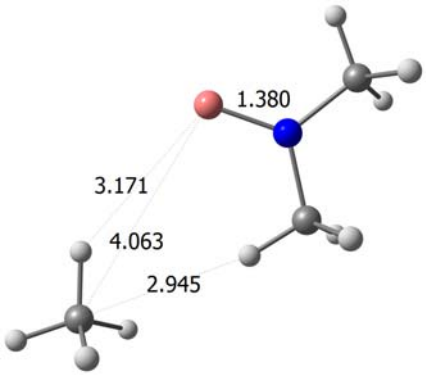
C	-3.191598153	0.229654490	0.000000000
B	0.369892537	-1.653036718	0.000000000
N	1.226598114	-0.577388223	0.000000000
C	0.740219517	0.792703859	0.000000000
C	2.669756980	-0.750564408	0.000000000
H	-2.619505963	-0.692160925	0.000000000
H	-4.251196110	-0.001240077	0.000000000
H	-2.952388664	0.807567477	0.886732280
H	-2.952388664	0.807567477	-0.886732280
H	3.102635422	-0.290640768	0.886793114
H	2.911948152	-1.809771262	0.000000000
H	3.102635422	-0.290640768	-0.886793114
H	1.094770476	1.315830590	0.886676336
H	1.094770476	1.315830590	-0.886676336
H	-0.346149542	0.796288667	0.000000000



E=-199.4839582160
ZPE=0.1309258

C	-3.287936652	0.243148010	0.000000000
B	0.426103254	-1.670074688	0.000000000
N	1.276907386	-0.588714290	0.000000000
C	0.779757429	0.782164647	0.000000000
C	2.725701430	-0.751107469	0.000000000
H	-2.713096964	-0.678134578	0.000000000
H	-4.348209855	0.009202126	0.000000000
H	-3.049418348	0.822431027	0.887609227
H	-3.049418348	0.822431027	-0.887609227
H	3.155448961	-0.287919156	0.887395242
H	2.975256464	-1.809123555	0.000000000
H	3.155448961	-0.287919156	-0.887395242
H	1.130288388	1.308111434	0.887342971
H	1.130288388	1.308111434	-0.887342971
H	-0.307120492	0.777393187	0.000000000

MP2/cc-pVTZ



E=-199.399598
ZPE=0.130823

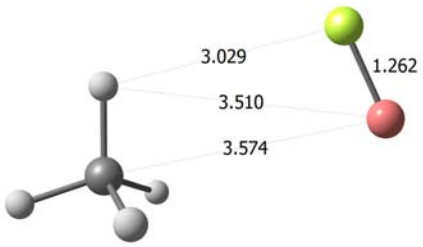
C	3.499176000	-0.106382000	0.000153000
B	-0.352962000	-1.399523000	-0.000223000
N	-1.032885000	-0.198599000	-0.000057000
C	-0.337582000	1.080557000	-0.000134000
C	-2.487491000	-0.143475000	0.000174000
H	2.781724000	-0.921655000	0.000323000
H	4.507225000	-0.509330000	-0.012479000

```
H    3.350332000    0.510774000   -0.881367000
H    3.366468000    0.497164000    0.893577000
H   -2.844463000    0.378902000   -0.887242000
H   -2.892492000   -1.152841000    0.000192000
H   -2.844183000    0.378824000    0.887749000
H   -0.605619000    1.654027000   -0.887439000
H   -0.605498000    1.653983000    0.887233000
H    0.736895000    0.913754000   -0.000195000
```

4. Geometries of van der Waals complexes with methane B

Fluoroborylene (BF)

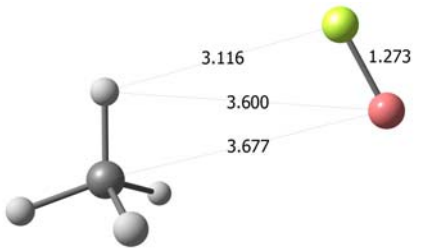
RI-B3LYP+D3/def2-QZVP



E=-165.1839042
ZPE=0.0485504

```
C    0.989979336   -0.039315912    0.000000000
B   -2.550410043   -0.526202580    0.000000000
F   -2.399507843    0.726344411    0.000000000
H    2.077802789   -0.030464544    0.000000000
H    0.631850627   -0.556797687   -0.887634774
H    0.618434518    0.983233999    0.000000000
H    0.631850627   -0.556797687    0.887634774
```

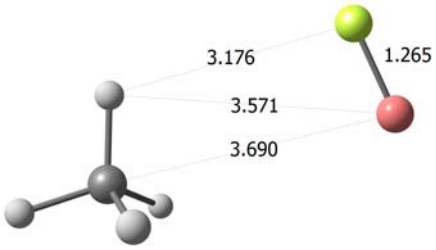
RI-TPSS+D3/def2-QZVP



E=-165.2788240
ZPE=0.0479957

```
C    1.018137128   -0.041128958    0.000000000
B   -2.626472917   -0.527394070    0.000000000
F   -2.464872499    0.735756532    0.000000000
H    2.109408763   -0.027003682    0.000000000
H    0.661422845   -0.561743706   -0.890754321
H    0.640953841    0.983257589    0.000000000
H    0.661422845   -0.561743706    0.890754321
```

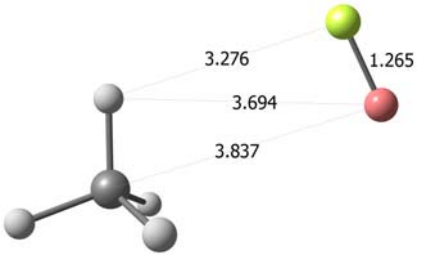
RI-MP2/def2-QZVP



E=-164.94401860205582
ZPE=0.0491826

```
C    1.033013554   -0.049841432    0.000000000
B   -2.628465449   -0.505143204    0.000000000
F   -2.539827197    0.756410786    0.000000000
```

SCS-RI-MP2/def2-QZVP



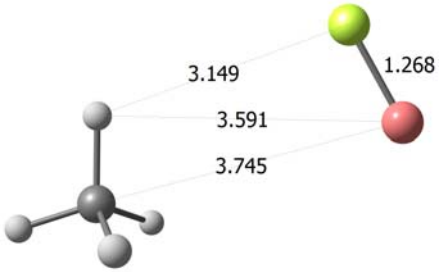
E=-164.9511008701
ZPE=0.0490779

```
C    2.334226042   -0.221875187    0.000029888
B   -1.476494712   -0.667950522   -0.000759425
F   -1.349141204    0.590233359    0.000606082
```

```
H    2.116240288  -0.003137021   0.000000000
H    0.694831625  -0.577536541  -0.884972335
H    0.629375548   0.956783952   0.000000000
H    0.694831625  -0.577536541   0.884972335
```

```
H    3.418354153  -0.165657302  -0.000218204
H    1.999960877  -0.753032161  -0.886023811
H    1.921210315   0.782426236  -0.000141738
H    2.000344204  -0.752566515   0.886507208
```

MP2/cc-pVTZ

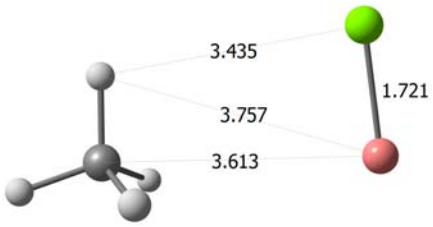


E=-164.8910992
ZPE=0.049132

```
C   -0.610039000   -2.036296000    0.000000000
B    1.219914000    1.231410000    0.000000000
F    0.000000000    1.578803000    0.000000000
H   -1.092157000   -3.008772000    0.000000000
H    0.010025000   -1.940724000    0.885969000
H   -1.367229000   -1.258276000    0.000000000
H    0.010025000   -1.940724000   -0.885969000
```

Chloroborylene (BCl)

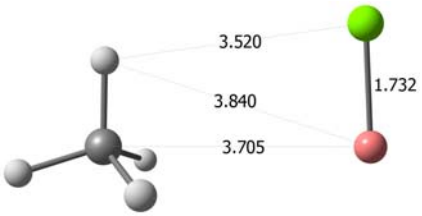
RI-B3LYP+D3/def2-QZVP



E=-525.4615698
ZPE=0.0471739

```
C   -1.013895285    0.186222035    0.000000000
B    2.284842234   -1.286852647    0.000000000
Cl   2.782924700    0.360290822    0.000000000
H   -2.096981707    0.288552570    0.000000000
H   -0.700976484   -0.360458254    0.887064956
H   -0.554936973    1.172703732    0.000000000
H   -0.700976484   -0.360458254   -0.887064956
```

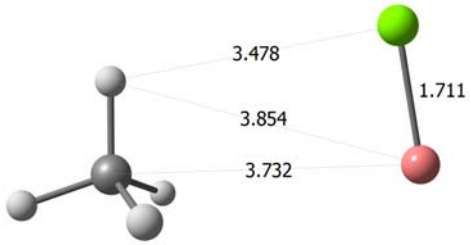
RI-TPSS+D3/def2-QZVP



E=-525.5902845
ZPE=0.0467554

```
C   -1.039214157    0.190832508    0.000000000
B    2.350105146   -1.305010464    0.000000000
Cl   2.844578480    0.354651491    0.000000000
H   -2.125584764    0.295571233    0.000000000
H   -0.726426571   -0.357904841    0.890289047
H   -0.577031563    1.179764915    0.000000000
H   -0.726426571   -0.357904841   -0.890289047
```

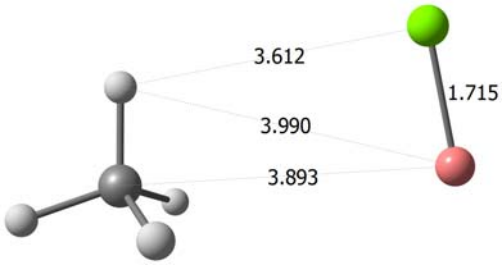
RI-MP2/def2-QZVP



E=-524.87347842431984
ZPE=0.0479418

```
C  -1.037419727   0.191933774   0.000000000
B   2.380459791  -1.306841732   0.000000000
Cl  2.808386034   0.349755718   0.000000000
H  -2.115783229   0.305675022   0.000000000
H  -0.732325568  -0.355834897   0.884890063
H  -0.570991732   1.171147012   0.000000000
H  -0.732325568  -0.355834897  -0.884890063
```

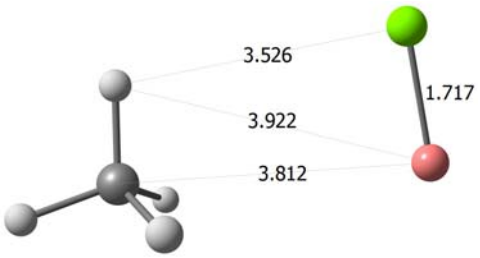
SCS-RI-MP2/def2-QZVP



E=-524.8844800270
ZPE=0.0478090

```
C  -2.877568115   0.186765424  -0.000000225
B   0.702872231  -1.342809570   0.000007905
Cl  1.110994773   0.322711247  -0.000006743
H  -3.956193853   0.310320535   0.000000809
H  -2.577064157  -0.364060210   0.886164920
H  -2.402045869   1.163067418   0.000003560
H  -2.577064969  -0.364052851  -0.886170226
```

MP2/cc-pVTZ



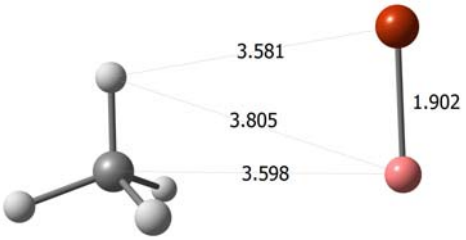
E=-524.828149
ZPE=0.047880

```
C  -0.764442000  -2.508627000   0.000000000
B   1.528482000   0.536136000   0.000000000
Cl  0.000000000   1.318093000   0.000000000
H  -1.132132000  -3.529972000   0.000000000
H  -0.159221000  -2.342488000   0.885849000
H  -1.605181000  -1.821550000   0.000000000
H  -0.159221000  -2.342488000  -0.885849000
```

Bromoborylene (BBr)

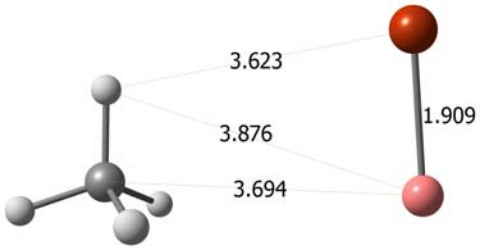
RI-B3LYP+D3/def2-QZVP

RI-TPSS+D3/def2-QZVP



E=-2639.3728716
ZPE=0.0468073

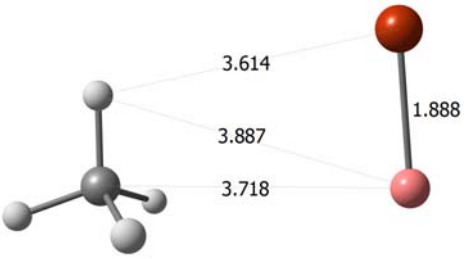
C	1.030957489	0.150226007	0.000000000
B	-2.273245521	-1.274459522	0.000000000
Br	-2.879214634	0.528385478	0.000000000
H	2.118673868	0.172948825	0.000000000
H	0.679121236	-0.372165358	-0.887137680
H	0.644586325	1.167229923	0.000000000
H	0.679121236	-0.372165358	0.887137680



E=-2639.4515761
ZPE=0.0464596

C	1.053020921	0.152958832	0.000000000
B	-2.346399683	-1.291419208	0.000000000
Br	-2.916416361	0.530801844	0.000000000
H	2.143753922	0.192205554	0.000000000
H	0.707941833	-0.375976932	-0.890391094
H	0.650157540	1.167406843	0.000000000
H	0.707941833	-0.375976932	0.890391094

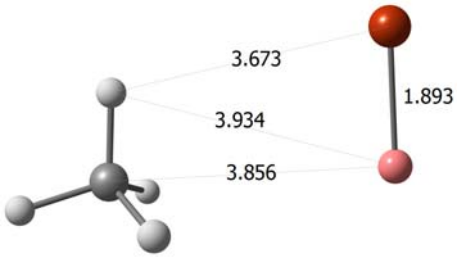
RI-MP2/def2-QZVP



E=-2637.77411201205041
ZPE=0.0475722

C	1.055744424	0.153511053	0.000000000
B	-2.371784815	-1.287284847	0.000000000
Br	-2.908085403	0.522454402	0.000000000
H	2.139106645	0.201343518	0.000000000
H	0.717849248	-0.374577153	-0.884983408
H	0.649320653	1.159130180	0.000000000
H	0.717849248	-0.374577153	0.884983408

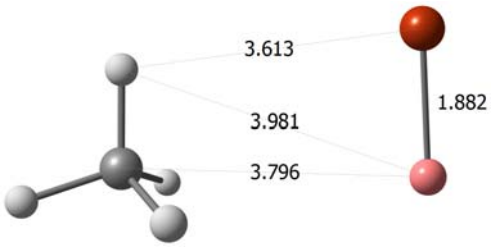
SCS-RI-MP2/def2-QZVP



E=-2637.7861342769
ZPE=0.0474521

C	3.418154727	-0.153765186	-0.000000130
B	-0.161256823	-1.587829265	0.000006233
Br	-0.678880764	0.232603245	-0.000005597
H	4.497400140	-0.035130475	0.000000259
H	3.114986684	-0.703282649	-0.886098086
H	2.946580487	0.824411195	0.000003407
H	3.114986791	-0.703289027	0.886093914

MP2/cc-pVTZ

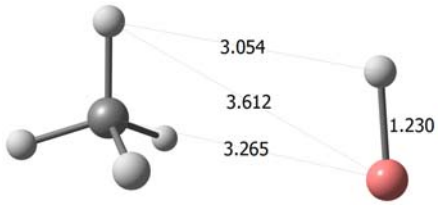


E=-2637.7980469
ZPE=0.047585

```
C  -0.810361000  -3.003351000   0.000000000
B   1.620129000  -0.087859000   0.000000000
Br  0.000000000   0.870685000   0.000000000
H  -1.154426000  -4.032938000   0.000000000
H  -0.208920000  -2.823326000   0.885828000
H  -1.666212000  -2.334990000   0.000000000
H  -0.208920000  -2.823326000  -0.885828000
```

Borylene (BH)

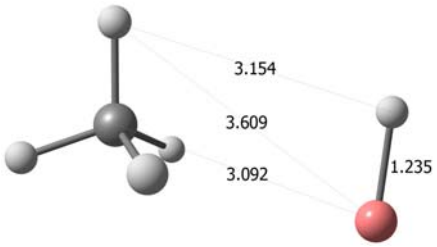
RI-B3LYP+D3/def2-QZVP



E=-65.7889230
ZPE=0.0511391

```
C   0.883076981   0.116182865   0.000000000
H   1.857213586   0.600427245   0.000000000
H   0.336088371   0.423047762   0.890515175
H   1.009328237  -0.963728896   0.000000000
H   0.336088371   0.423047762  -0.890515175
B  -2.377608133   0.292463475   0.000000000
H  -2.044187413  -0.891440214   0.000000000
```

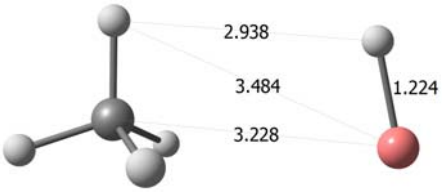
RI-TPSS+D3/def2-QZVP



E=-65.8504837
ZPE=0.0508023

```
C  -0.852855790   0.068829942   0.000000000
H  -1.850156076  -0.374236352   0.000000000
H  -0.321727475  -0.266029331   0.896002537
H  -0.925197209   1.156974764   0.000000000
H  -0.321727475  -0.266029331  -0.896002537
B   2.121533875  -0.777069829   0.000000000
H   2.150130154   0.457560141   0.000000000
```

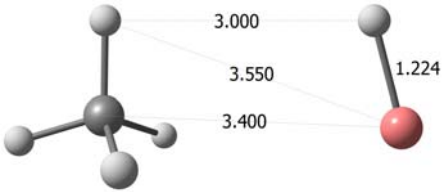
RI-MP2/def2-QZVP



E=-65.63718959368065
ZPE=0.0522341

```
C  -0.882217284   0.024171691  -0.000017736
H  -1.943600686  -0.197494079   0.000051985
H  -0.431228136  -0.409579798   0.887092980
H  -0.735608491   1.098174840  -0.000198543
H  -0.431285033  -0.409900677  -0.887001241
```

SCS-RI-MP2/def2-QZVP



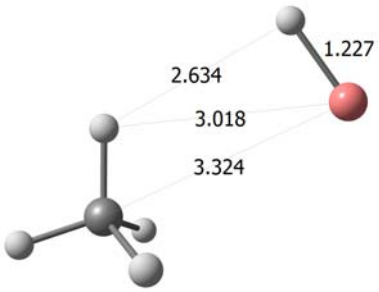
E=-65.6573605893
ZPE=0.0519557

```
C  -0.930383848   0.010535672   0.000000000
H  -2.006571846  -0.131816873   0.000000000
H  -0.509942677  -0.454302672   0.887472616
H  -0.706168494   1.072699268   0.000000000
H  -0.509942677  -0.454302672  -0.887472616
```

```
B    2.271630496  -0.661899518  -0.000397024
H    2.152309136   0.556527542   0.000469580
```

```
B    2.409461203  -0.628567540   0.000000000
H    2.253548339   0.585754818   0.000000000
```

MP2/cc-pVTZ

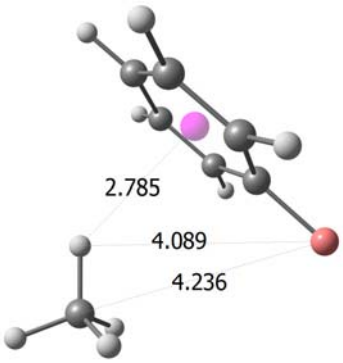


E=-65.6163607
ZPE=0.051952

```
C    0.075355000  -1.231584000   0.000000000
H   -0.050815000  -2.309784000   0.000000000
H    0.628002000  -0.932421000   0.885456000
H   -0.904026000  -0.761607000   0.000000000
H    0.628002000  -0.932421000  -0.885456000
B    0.075355000   2.092571000   0.000000000
H   -1.130069000   1.862881000   0.000000000
```

Phenylborylene (BPh)

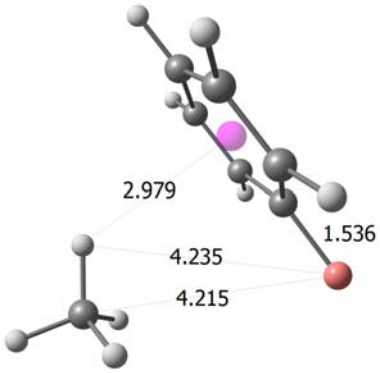
RI-B3LYP+D3/def2-QZVP



E=-296.8345472
ZPE=0.1367336

```
C    2.030663008   1.571892591  -0.000099850
B    1.295263030  -2.600208406   0.000020220
H    0.947789119   1.473881572  -0.000013298
H    2.304730123   2.624844702  -0.000094839
H    2.436377580   1.089940559   0.886611096
```

RI-TPSS+D3/def2-QZVP



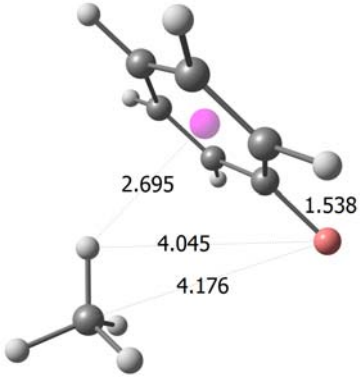
E=-297.0777569
ZPE=0.1347689

```
C    2.078782503   1.593590260  -0.000017860
B    1.340381841  -2.556025101   0.000056400
H    0.990021829   1.664688055   0.000178423
H    2.513760343   2.594689362   0.000065565
H    2.405861669   1.052229065   0.889217977
```

```
H    2.436232982    1.089985237   -0.886900852
C    0.157554842   -1.579626601    0.000029343
C   -0.366939199   -1.098444760    1.211543443
C   -1.387995834   -0.160741997    1.209971866
C   -1.896024689    0.306145274    0.000052912
C   -1.387910832   -0.160620430   -1.209876085
C   -0.366876338   -1.098343417   -1.211472951
H    0.032237309   -1.459416353    2.151126473
H   -1.788224584    0.210164136    2.143388816
H   -2.691132927    1.039423034    0.000061284
H   -1.788083183    0.210374225   -2.143282695
H    0.032339588   -1.459249366   -2.151064876
```

```
H    2.405558376    1.052510074   -0.889536271
C    0.166219337   -1.565610823    0.000033058
C   -0.374154054   -1.095683211    1.215941488
C   -1.423207188   -0.182419050    1.214201378
C   -1.945156304    0.272462824   -0.000018241
C   -1.423144226   -0.182413393   -1.214212110
C   -0.374090738   -1.095677581   -1.215901286
H    0.036237042   -1.448096013    2.158411026
H   -1.835426803    0.178652425    2.150831573
H   -2.762680363    0.986526053   -0.000036709
H   -1.835313014    0.178662088   -2.150863101
H    0.036349757   -1.448085033   -2.158351319
```

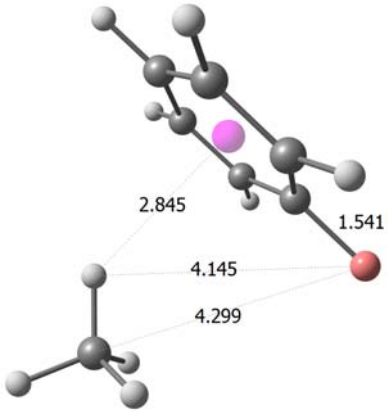
RI-MP2/def2-QZVP



E=-296.2901207125
ZPE=0.1377498

```
C    1.978327493    1.534418147   -0.000474765
B    1.318722561   -2.588796238    0.000099724
H    0.897572145    1.434554517   -0.000206251
H    2.249225270    2.584879042   -0.000571723
H    2.384397305    1.055506385    0.884016978
H    2.383960652    1.055456415   -0.885139464
C    0.176155598   -1.559916400    0.000150021
C   -0.343756545   -1.083007749    1.212701318
C   -1.366363150   -0.143804317    1.210466344
C   -1.874613705    0.323448451    0.000248197
C   -1.366551000   -0.143882865   -1.210017865
C   -0.343946794   -1.083106680   -1.212356980
H    0.056371245   -1.447241671    2.150613184
H   -1.767653908    0.226608524    2.143061096
H   -2.669885202    1.055827589    0.000290185
H   -1.767987778    0.226468870   -2.142574721
H    0.056025813   -1.447412018   -2.150305277
```

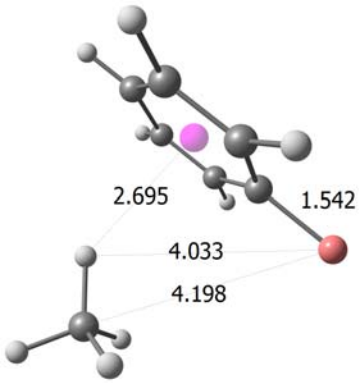
SCS-RI-MP2/def2-QZVP



E=-296.2890729600
ZPE=0.1375418

```
C    2.261561901    1.958190158    0.000002228
B    1.483498834   -2.270029176    0.000024775
H    1.179389185    1.863980729    0.000037962
H    2.537569526    3.008655810    0.000010948
H    2.665844936    1.477252008    0.885751231
H    2.665784414    1.477282489   -0.885790883
C    0.343742442   -1.232569424    0.000009078
C   -0.177701344   -0.752575623    1.212639856
C   -1.199579203    0.189276915    1.211240182
C   -1.707626344    0.657887691   -0.000012099
C   -1.199585247    0.189242726   -1.211253819
C   -0.177708936   -0.752611429   -1.212632502
H    0.220152477   -1.117144363    2.151488478
H   -1.600351227    0.559661949    2.144308446
H   -2.502339117    1.391258232   -0.000020599
H   -1.600362855    0.559600897   -2.144330346
H    0.220134820   -1.117212123   -2.151472939
```

MP2/cc-pVTZ

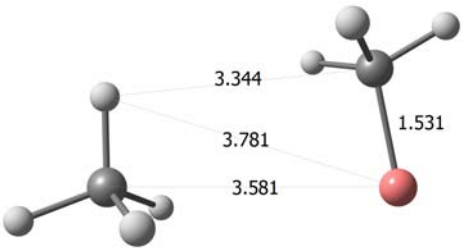


E=-296.1974087
ZPE=0.137499

```
C   2.890088000  -0.300413000   0.000000000
B  -0.615067000  -2.610597000   0.000000000
H   2.063784000   0.404792000   0.000000000
H   3.832979000   0.238363000   0.000000000
H   2.830003000  -0.926142000   0.885428000
H   2.830003000  -0.926142000  -0.885428000
C  -0.629385000  -1.068871000   0.000000000
C  -0.630140000  -0.361677000   1.214185000
C  -0.630140000   1.028988000   1.212264000
C  -0.629769000   1.720551000   0.000000000
C  -0.630140000   1.028988000  -1.212264000
C  -0.630140000  -0.361677000  -1.214185000
H  -0.627760000  -0.903206000   2.152495000
H  -0.629621000   1.575420000   2.145398000
H  -0.628925000   2.802355000   0.000000000
H  -0.629621000   1.575420000  -2.145398000
H  -0.627760000  -0.903206000  -2.152495000
```

Methylborylene (BCH_3)

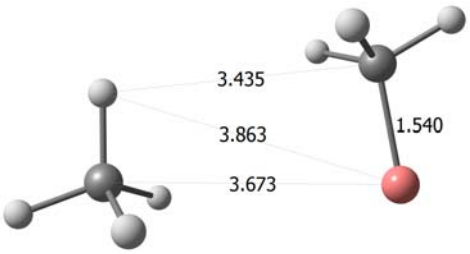
RI-B3LYP+D3/def2-QZVP



E=-105.1314312
ZPE=0.0804387

```
C   1.737494335  -0.448179040   0.000000000
B  -1.800626223  -1.001274868   0.000000000
C  -1.733456972   0.528436766   0.000000000
H   2.798840971  -0.686626907   0.000000000
```

RI-TPSS+D3/def2-QZVP



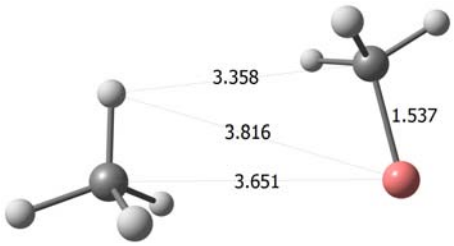
E=-105.2240722
ZPE=0.0795457

```
C   1.782800729  -0.459352607   0.000000000
B  -1.850280089  -1.000731181   0.000000000
C  -1.779379408   0.538120630   0.000000000
H   2.847653778  -0.698180846   0.000000000
```

```
H    1.270974922  -0.872964837  -0.886287737
H    1.609349619   0.632587310   0.000000000
H    1.270974922  -0.872964837   0.886287737
H   -2.746863345   0.946719551   0.000000000
H   -1.203344111   0.887133431   0.889524989
H   -1.203344111   0.887133431  -0.889524989
```

```
H    1.315078046  -0.885117451  -0.889670720
H    1.654043088   0.625005486   0.000000000
H    1.315078046  -0.885117451   0.889670720
H   -2.792516445   0.966447179   0.000000000
H   -1.246238875   0.899463123   0.891358006
H   -1.246238875   0.899463123  -0.891358006
```

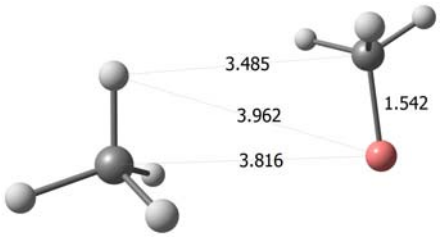
RI-MP2/def2-QZVP



E=-104.90705243787730
ZPE=0.0815866

```
C    1.758291468  -0.453126212   0.000000000
B   -1.852754409  -0.994470716   0.000000000
C   -1.752566772   0.538764203   0.000000000
H    2.822029472  -0.663291615   0.000000000
H    1.305550227  -0.888198004  -0.884386970
H    1.604265377   0.620752764   0.000000000
H    1.305550227  -0.888198004   0.884386970
H   -2.755990496   0.969793677   0.000000000
H   -1.217187547   0.878986954   0.888492536
H   -1.217187547   0.878986954  -0.888492536
```

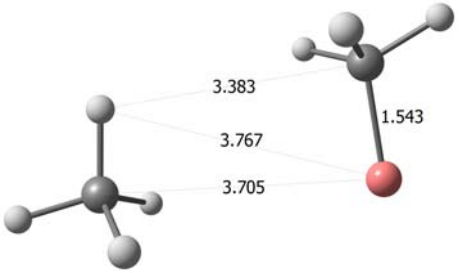
SCS-RI-MP2/def2-QZVP



E=-104.9271733989
ZPE=0.0815457

```
C    2.265207329  -0.257893867   0.000002095
B   -1.515472810  -0.778592433  -0.000034949
C   -1.373931123   0.757252765  -0.000000045
H    3.330332633  -0.467830961  -0.000004493
H    1.812159706  -0.692976116  -0.885777110
H    2.110555806   0.817236415  -0.000025528
H    1.812180342  -0.692927618   0.885815672
H   -2.364202936   1.219899335   0.000012716
H   -0.828900028   1.084667043   0.888697424
H   -0.828904581   1.084706597  -0.888685781
```

MP2/cc-pVTZ



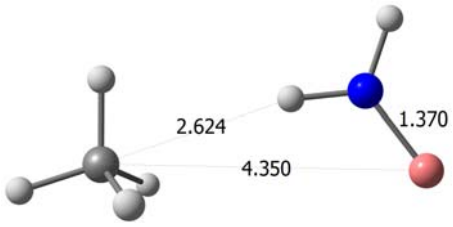
E=-104.8726507
ZPE=0.081448

```
C   -0.605487000  -2.061570000   0.000000000
B    1.413891000   1.044309000   0.000000000
C    0.000000000   1.660985000   0.000000000
H   -0.956572000  -3.088782000   0.000000000
H   -0.001988000  -1.886253000   0.885459000
H   -1.460124000  -1.391240000   0.000000000
H   -0.001988000  -1.886253000  -0.885459000
H    0.079681000   2.751182000   0.000000000
H   -0.547769000   1.341655000  -0.890155000
```

```
H  -0.547769000   1.341655000   0.890155000
```

Aminoborylene (BNH_2)

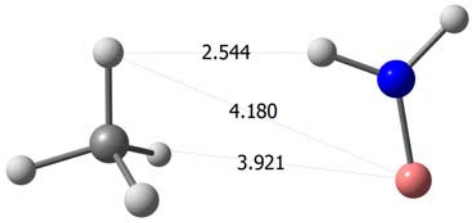
RI-B3LYP+D3/def2-QZVP



E=-121.2415974
ZPE=0.0708304

```
C  -1.609070547   0.168268094   0.000000000
B   2.430927916  -1.444807775   0.000000000
N   1.995308157  -0.145856316   0.000000000
H  -2.695539306   0.215408235   0.000000000
H  -1.275295506  -0.360983520   0.890569913
H  -1.212273612   1.182655530   0.000000000
H  -1.275295506  -0.360983520  -0.890569913
H   2.626775951   0.643910380   0.000000000
H   1.014462457   0.102388897   0.000000000
```

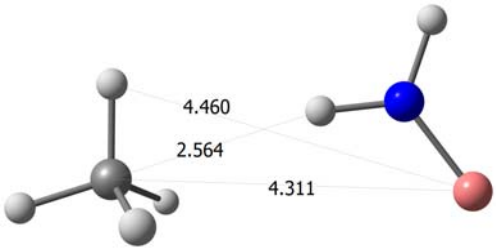
RI-TPSS+D3/def2-QZVP



E=-121.3331855
ZPE=0.0699598

```
C  -1.609804939   0.103104456   0.000000000
B   1.994065718  -1.441369085   0.000000000
N   2.017837641  -0.060921319   0.000000000
H  -2.700355406   0.070512588   0.000000000
H  -1.232858655  -0.401599753   0.891418068
H  -1.287617297   1.147868380   0.000000000
H  -1.232858655  -0.401599753  -0.891418068
H   2.877867576   0.479539560   0.000000000
H   1.173724018   0.504464920   0.000000000
```

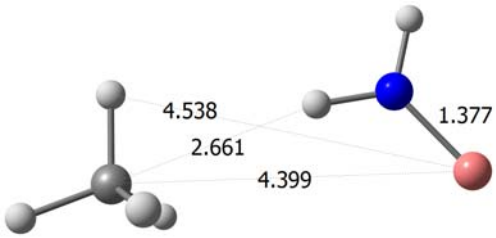
RI-MP2/def2-QZVP



E=-121.0154701961
ZPE=0.0718051

```
C  -1.584548584   0.162309686   0.000000000
B   2.421327337  -1.431740785   0.000000000
N   1.962465055  -0.135237130   0.000000000
H  -2.667767926   0.201054089   0.000000000
H  -1.248352768  -0.362691006   0.888135518
H  -1.197032801   1.176342543   0.000000000
H  -1.248352768  -0.362691006  -0.888135518
H   2.583290457   0.659721804   0.000000000
H   0.978930106   0.092736841   0.000000000
```

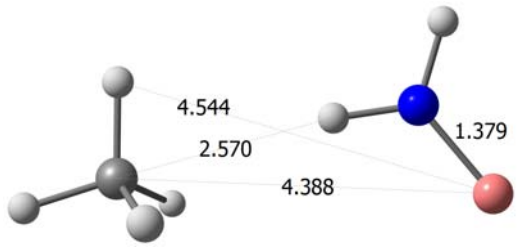
SCS-RI-MP2/def2-QZVP



E=-121.0288789753
ZPE=0.0717923

```
C  -2.083846168   0.394419474   0.000004446
B   2.012534232  -1.210249751   0.000177279
N   1.557991023   0.089837278  -0.000033558
H  -3.168292194   0.434805140  -0.000017228
H  -1.747380234  -0.131654752   0.888915655
H  -1.693092869   1.408694792   0.000125744
H  -1.747338342  -0.131459787  -0.889006373
H   2.180754040   0.882846503  -0.000158349
H   0.576451198   0.323306260  -0.000007615
```

MP2/cc-pVTZ

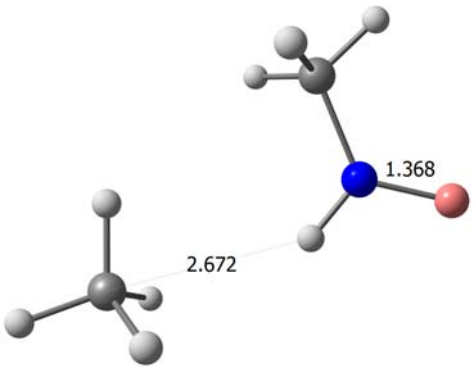


E=-120.9748046
ZPE=0.071641

```
C  -1.552927000  -1.568151000   0.000000000
B   2.055037000   0.928444000   0.000000000
N   0.703722000   1.204406000   0.000000000
H  -2.176474000  -2.456137000   0.000000000
H  -0.929228000  -1.572966000   0.889393000
H  -2.191160000  -0.688665000   0.000000000
H  -0.929228000  -1.572966000  -0.889393000
H   0.342416000   2.146858000   0.000000000
H   0.000000000   0.479716000   0.000000000
```

Methylaminoborylene (BNHMe)

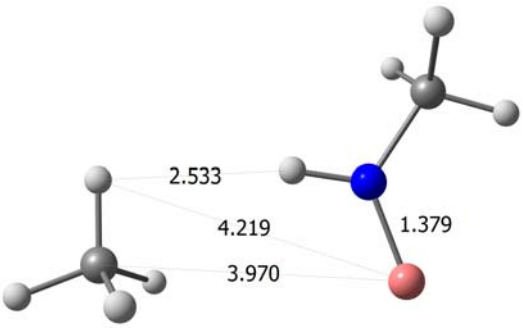
RI-B3LYP+D3/def2-QZVP



E=-160.5364079
ZPE=0.1005716

```
C  -2.049758882  -0.557293346   0.000000000
B   1.676891475   2.341764741   0.000000000
N   1.066950982   1.117053945   0.000000000
C   1.732747488  -0.189482556   0.000000000
H  -2.968335883  -1.139259492   0.000000000
H  -2.024469110   0.067083377  -0.891450798
H  -1.197128967  -1.233279933   0.000000000
H  -2.024469110   0.067083377   0.891450798
H   0.054128879   1.089151106   0.000000000
H   1.461476276  -0.759159242  -0.887741784
```

RI-TPSS+D3/def2-QZVP

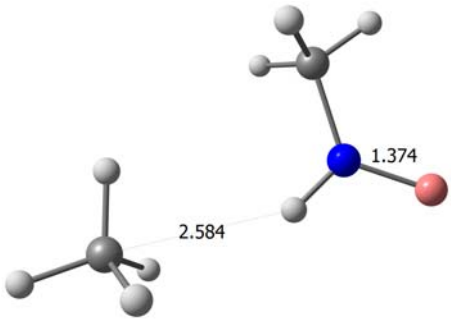


E=-160.6638771
ZPE=0.0991889

```
C  -2.512970869  -0.312046336   0.000000000
B   0.783765307   1.899337926   0.000000000
N   1.037393417   0.543915984   0.000000000
C   2.371498983  -0.083275269   0.000000000
H  -3.589435744  -0.490126302   0.000000000
H  -2.240399013   0.256045434  -0.891369675
H  -1.995207794  -1.274948259   0.000000000
H  -2.240399013   0.256045434   0.891369675
H   0.247676273  -0.098051178   0.000000000
H   2.504735596  -0.699506700  -0.892418430
```

```
H    2.810490575  -0.044502727   0.000000000
H    1.461476276  -0.759159242   0.887741784
H    3.128607267   0.702115962   0.000000000
H    2.504735596  -0.699506700   0.892418430
```

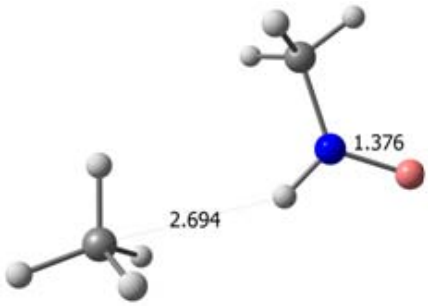
RI-MP2/def2-QZVP



E=-160.2381531579
ZPE=0.1019857

```
C   -2.077799335  -0.516670555   0.000002159
B    1.606031168   2.307670911  -0.000134968
N    1.038841657   1.055894977  -0.000038540
C    1.782718922  -0.200468799   0.000033370
H   -3.026735053  -1.040724626   0.000049777
H   -2.016285014   0.102841565  -0.889005197
H   -1.270194168  -1.241340806  -0.000304297
H   -2.015973236   0.102439307   0.889268147
H    0.030477323   0.977453685  -0.000021712
H    1.551730925  -0.783529647  -0.886516494
H    2.845410826   0.019837951  -0.000009828
H    1.551775985  -0.783403963   0.886677583
```

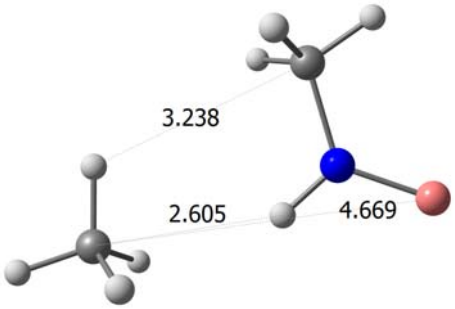
SCS-RI-MP2/def2-QZVP



E=-160.2542989521
ZPE=0.1019730

```
C   -2.342724852  -0.655954976   0.000000373
B    1.446205526   2.211269019  -0.000149946
N    0.866291888   0.963832707  -0.000032925
C    1.592347215  -0.307128198   0.000032297
H   -3.295977385  -1.174685114   0.000047172
H   -2.276412087  -0.035673384  -0.889674968
H   -1.538592703  -1.386365093  -0.000300669
H   -2.276109377  -0.036070824   0.889930286
H   -0.142285836   0.897477596   0.000003927
H    1.350561693  -0.886373367  -0.887169245
H    2.658837591  -0.102899657  -0.000011519
H    1.350611127  -0.886253815   0.887325217
```

MP2/cc-pVTZ



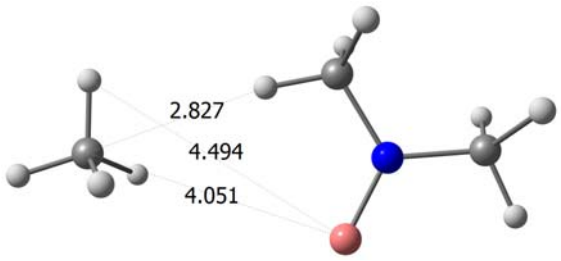
E=-160.1847402
ZPE=0.101916

```
C   -2.568292000  -0.274439000   0.000000000
B    2.016006000  -1.162076000   0.000000000
N    0.930251000  -0.312102000   0.000000000
C    1.002271000   1.147883000   0.000000000
H   -3.653412000  -0.274713000   0.000000000
H   -2.214469000  -0.787004000   0.890311000
H   -2.210946000   0.751219000   0.000000000
```

```
H  -2.214469000  -0.787004000  -0.890311000
H   0.000000000  -0.710720000   0.000000000
H   0.525690000   1.557272000   0.887228000
H   2.046252000   1.448106000   0.000000000
H   0.525690000   1.557272000  -0.887228000
```

Dimethylaminoborylene ($BNMe_2$)

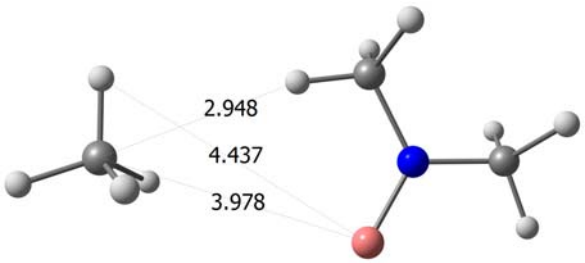
RI-B3LYP+D3/def2-QZVP



E=-199.8341208
ZPE=0.1287769

```
C  -3.169673416   0.204591423   0.000000000
B   0.627951326   1.614478638   0.000000000
N   1.292157511   0.416856266   0.000000000
H  -4.215409259   0.504731969   0.000000000
H  -2.678618858   0.602158682  -0.885477524
H  -3.108486355  -0.882473766   0.000000000
H  -2.678618858   0.602158682   0.885477524
C   2.751564661   0.353769226   0.000000000
C   0.585719812  -0.861732457   0.000000000
H   3.107954315  -0.171207330  -0.888169258
H   3.167683710   1.359834868   0.000000000
H   3.107954315  -0.171207330   0.888169258
H   0.849356108  -1.439373690  -0.887890848
H   0.849356108  -1.439373690   0.887890848
H  -0.488891123  -0.693211486   0.000000000
```

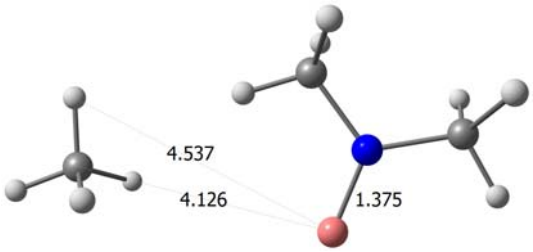
RI-TPSS+D3/def2-QZVP



E=-199.9980257
ZPE=0.1272698

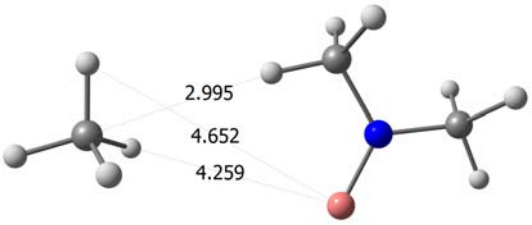
```
C  -3.199407547   0.252586615   0.000000000
B   0.561076339   1.550826240   0.000000000
N   1.282797699   0.375089624   0.000000000
H  -4.237325421   0.590615162   0.000000000
H  -2.692379758   0.633912116  -0.887965187
H  -3.177063699  -0.839685108   0.000000000
H  -2.692379758   0.633912116   0.887965187
C   2.751058271   0.386350881   0.000000000
C   0.633604569  -0.941416687   0.000000000
H   3.132167952  -0.120275956  -0.892666821
H   3.105056863   1.419797815   0.000000000
H   3.132167952  -0.120275956   0.892666821
H   0.925298414  -1.505061478  -0.892252147
H   0.925298414  -1.505061478   0.892252147
H  -0.449970274  -0.811313910   0.000000000
```

RI-MP2/def2-QZVP



E=-199.4654891143
ZPE=0.1307862

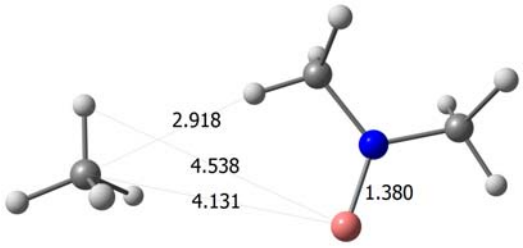
SCS-RI-MP2/def2-QZVP



E=-199.4837630295
ZPE=0.130785

C	-3.202149612	0.212271200	0.000000000	C	-3.296820452	0.217523745	0.000000000
B	0.673010054	1.627686228	0.000000000	B	0.721364786	1.629093490	0.000000000
N	1.321249877	0.414634527	0.000000000	N	1.368511676	0.414465457	0.000000000
H	-4.251756150	0.484981058	0.000000000	H	-4.348368841	0.487852134	0.000000000
H	-2.723638684	0.620395064	-0.883553185	H	-2.819071860	0.626728692	-0.884953095
H	-3.114641776	-0.869399352	0.000000000	H	-3.205869654	-0.865173753	0.000000000
H	-2.723638684	0.620395064	0.883553185	H	-2.819071860	0.626728692	0.884953095
C	2.771809555	0.323926381	0.000000000	C	2.823306783	0.320434024	0.000000000
C	0.595150668	-0.844732462	0.000000000	C	0.638631359	-0.847798984	0.000000000
H	3.114478394	-0.206766283	-0.886722606	H	3.165404387	-0.210756296	-0.887421654
H	3.201649263	1.321815943	0.000000000	H	3.254125739	1.318507194	0.000000000
H	3.114478394	-0.206766283	0.886722606	H	3.165404387	-0.210756296	0.887421654
H	0.848901865	-1.423460921	-0.886687601	H	0.891464466	-1.427256309	-0.887266601
H	0.848901865	-1.423460921	0.886687601	H	0.891464466	-1.427256309	0.887266601
H	-0.473805028	-0.651519242	0.000000000	H	-0.430475384	-0.652335484	0.000000000

MP2/cc-pVTZ



E=-199.3993576
ZPE=0.130653

C	0.771508000	-3.428964000	0.000000000
B	1.321615000	0.665388000	0.000000000
N	0.000000000	1.063711000	0.000000000
H	1.258716000	-4.399112000	0.000000000
H	1.070377000	-2.874689000	0.884306000
H	-0.305658000	-3.570382000	0.000000000
H	1.070377000	-2.874689000	-0.884306000
C	-0.373139000	2.470674000	0.000000000
C	-1.094990000	0.104545000	0.000000000
H	-0.961060000	2.704243000	0.887488000
H	0.522743000	3.087328000	0.000000000
H	-0.961060000	2.704243000	-0.887488000
H	-1.713394000	0.239754000	0.887329000
H	-1.713394000	0.239754000	-0.887329000
H	-0.695992000	-0.906896000	0.000000000

Computational Boron Chemistry

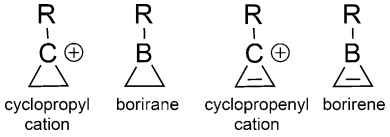
Ring Enlargement of Three-Membered Boron Heterocycles upon Reaction with Organic π Systems: Implications for the Trapping of Borylenes

Małgorzata Krasowska* and Holger F. Bettinger*[a]

Abstract: New low-energy pathways for the reaction between substituted boriranes and borirenes with unsaturated hydrocarbons (ethyne or ethene) were discovered using density functional and coupled cluster theory. The interaction between the π bond of the hydrocarbon and the empty p orbital of the boron center leads to ring expansion of the three-membered to a five-membered boron heterocycle. The reactions are strongly exothermic and have low or even no barriers. They involve intermediates with a pentacoordinate boron center with two hydrocarbon molecules coordinating to boron akin to metal-olefin complexes. These borylene complexes are shallow minima on the potential energy surfaces. But significantly higher barriers for ring formation are computed for 1,5-cyclooctadiene and dibenzocyclooctatetraene complexes of borylenes, making these complexes likely detectable under appropriate experimental conditions. Our computational findings have implications for the interpretation of trapping experiments of thermally generated small borylenes with excess of small π systems. Because of very low barriers for reactions of three-membered boron heterocycles with π systems and the at least locally large excess of the latter under such conditions, formation of five-membered boron heterocycles should be considered.

Introduction

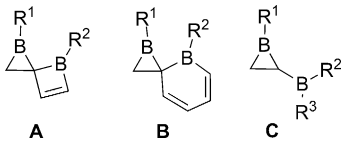
Boriranes and borirenes, also known as boracyclopropanes and boracyclopropenes, are rather rare three-membered boron heterocycles that are isoelectronic to the cyclopropyl and cyclopropenyl cations, respectively (Scheme 1).[1,2] Boriranes are alicyclic compounds, whereas borirenes exhibit aromatic character.[1–4] Both possess one empty p orbital on boron atom that is able to accept a pair of electrons.



Scheme 1. Borirane and borirene are isoelectronic to cyclopropyl and cyclopropenyl cations.

A number of experimental[5–26] and theoretical[3,27–34] investigations have been performed to elucidate the properties of these highly strained heterocycles. They were identified as products or intermediates in spectroscopic[35–37] and crossed beam[38–41] experiments. Most of the known stable boriranes were generated with base (pyridine,[5] THF,[6] or NHC[7,8]) coordinated to the boron atom through a dative bond. Likewise, intramolecularly stabilized derivatives of boranorcaradienes were extensively studied.[42–48] Uncoordinated boriranes were so far synthesized only as 1,4-diboraspiro[2.3]hex-5-ene (**A**),[9–11] 1.4-diboraspiro[2.5]octa-5,7-diene (**B**),[11] and 2-borylborirane (**C**) (Scheme 2).[12,13] The heteroaromatic character of borirenes makes them more stable and easier to handle compared with boriranes and many examples of uncoordinated[14–21] as well as Lewis base coordinated[22] borirenes are known. Anionic three-membered boron heterocycles (borate salts) are also known.[49–56] These involve boratiranes,[49–51] boratirenes,[51–53] and boratanorcaradienes[54–56] that were all obtained photochemically by irradiation of phenylborates and were further structurally characterized.

In the late 1960s Timms performed a series of experiments in which boron trihalides (BF_3, BCl_3) were passed over solid boron at high temperature to yield boron subhalides (haloborylenes BF and BCl) followed by a low temperature co-condensation of the obtained compounds with ethynes and propenes.[57,58] The major products of this co-condensation of borylenes and ethynes were identified as 1,4-diboracyclohexa-



Scheme 2. Synthesized uncoordinated boriranes.

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dienes and 1,4-diboracyclohexanes in the reactions of borylenes with propenes. Although neither borirenes nor boriranes could be isolated under these conditions, they were suggested as conceivable transient intermediates that result from the facile reaction of the borylene with the π system, in agreement with recently computed barrier heights reported by us.[59,60] Facile dimerization of the three-membered rings was invoked to explain the observed six-membered rings. Indeed, low barriers for borirene dimerization were computed.[33]

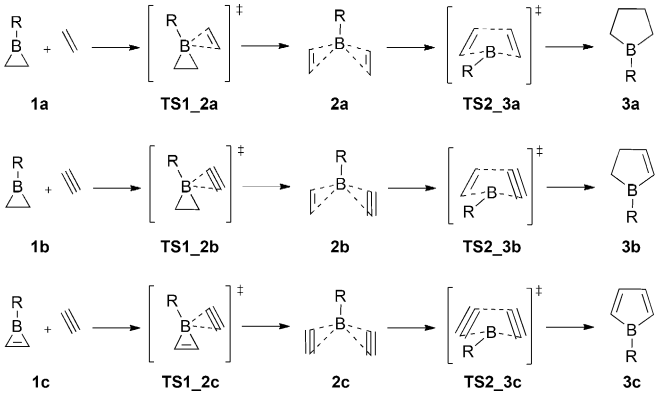
Here we report computational investigations of the reactions of the three-membered rings with an additional unsaturated hydrocarbon molecule. We obtain sufficiently low barriers for the latter reaction to conclude that under conditions of large excess of unsaturated hydrocarbons their bimolecular reaction with three-membered boron heterocycles to five-membered heterocycles (borolanes, 2,3-dihydroboroles, boroles) is at least competitive to dimerization. We hence suggest that the co-condensation of borylenes and small organic unsaturated hydrocarbons should be investigated experimentally in more detail.

Computational Details

All stationary points on the potential energy surfaces were optimized using the hybrid meta exchange-correlation density functional M06-2X[61] in conjunction with the 6-311+G** basis set.[62–65] The nature of stationary points (minimum or first-order saddle points) was confirmed by subsequent frequency analyses performed at the same level of theory. Additionally, energies were further recomputed with coupled-cluster theory using single, double, and a perturbative estimate of triple excitations, CCSD(T),[66] in combination with the polarized triple-ζ def2-TZVP basis set.[67] The frozen core as well as the resolution of the identity (RI) approximations[68,69] with the corresponding auxiliary basis set[70] were applied in coupled cluster computations. DFT calculations were performed using the Gaussian 09 program.[71] The energy refinement at the RI-CCSD(T) level of theory was carried out with the Turbomole program.[72] All energy data given in the text were obtained at the CCSD(T)/def2-TZVP//M06-2X/6-311+G**+ZPVE level of theory unless noted otherwise. Bader's QTAIM analysis[73] was performed using the AIMAll package,[74] and the results are provided as Supporting Information. Wiberg bond indices[75] were calculated with the NBO 3.1[76] program as implemented in Gaussian09. Figures of molecular structures and orbitals were prepared using the CYLView[77] and Chemcraft[78] programs.

Results and Discussion

To study the reactions of three membered boron compounds with unsaturated hydrocarbons we have chosen two types of cyclic boron compounds: borirane and borirene with various substituents on boron atom (R=H, F, Cl, Me, Ph, NH_2). As model unsaturated hydrocarbons ethyne and ethene were chosen.



Scheme 3. Reactions of boriranes and borirenes with ethene and ethyne.

Reactions of boriranes and borirenes with ethene and ethyne

All studied reactions of boriranes and borirenes with both ethene and ethyne under formation of heterocycles **3a**–**c** are strongly exothermic (Scheme 3, Table 1). The reactions are stepwise and involve, besides weakly bound van der Waals complexes (see Figure S1 for structures), intermediates **2a**–**2c** (see Figure 1) with boron in an unusual pentacoordinate bonding arrangement (see below).

Formation of intermediates **2a** and **2b** on the potential energy surface, which proceeds through transition states **TS1_2a** and **TS1_2b** (see Figure 2), involves extremely low or even no barriers (parent borirane) for almost all boriranes. Except for amino substituted derivatives, intermediates **2a** and **2b** are considerably stabilized with respect to reactants by 14 to 21 kcal mol^{-1}. The decreased electrophilicity of the boron centers in the amino derivatives results in almost thermoneutral processes and somewhat higher barriers (up to 11 kcal mol^{-1}). All of the transition states **TS1_2** are of C_s symmetry. The distances between boron atom of borirane and carbon atoms from π system of ethyne are from 2.146 Å for NH_2 substituted borirane to 2.552 Å for Cl-borirane. The distances between B atom and C atoms of ethene vary from 2.272 Å for aminoborirane to 2.651 Å also for chloroborirane.

Contrary to the reactions of boriranes, the formation of intermediates **2c** from the heteroaromatic borirenes is endothermic (with the exception of aminoborirene) with moderately high barriers (Table 2). The lowest barrier for formation of inter-

Table 1. Energies relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory.

R	Borirane+ethyne					Borirane+ethene				
	vdW[a]	TS1_2b	2b	TS2_3b	3b	vdW[a]	TS1_2a	2a	TS2_3a	3a
F	−1.4	−0.6	−15.0	−14.5	−81.4	−1.4	−1.2	−14.4	−13.4	−61.9
Cl	−1.3	−0.1	−17.0	−15.9	−79.4	−1.5	−0.3	−17.4	−15.1	−59.4
H			−19.7	−17.6	−76.4			−21.3	−18.3	−56.0
Ph	−1.5	−0.1	−13.8	−12.9	−75.1	−2.2	−1.2	−16.0	−12.5	−55.2
Me	−1.8	−1.0	−14.1	−12.7	−75.3	−1.3	−0.7	−15.2	−13.6	−55.4
NH_2	−0.3	10.9	4.1	4.3	−74.5	-0.9	9.7	3.2	5.6	−56.0

[a] van der Waals complex formed between borirane and hydrocarbon.

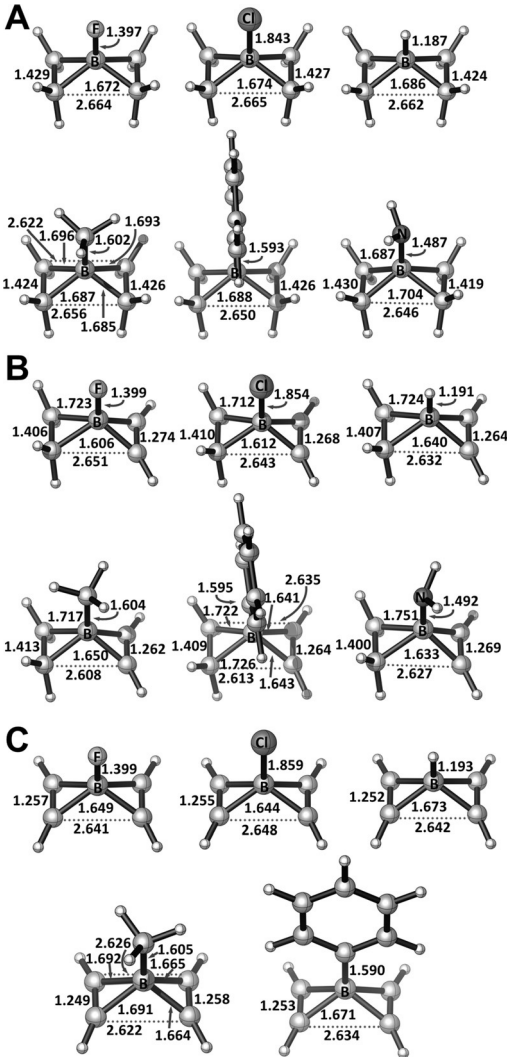


Figure 1. Optimized geometries (M06-2X/6-311+G**) of intermediates **2a** (A), **2b** (B) and **2c** (C). Important bond lengths and distances are given in Å.

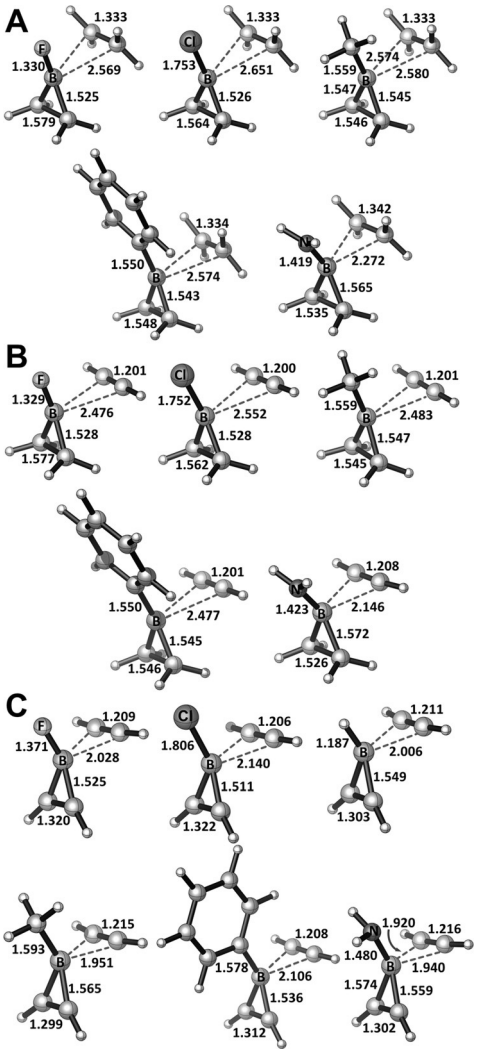


Figure 2. Optimized geometries (M06-2X/6-311+G**) of transition states **TS1_2a** (A), **TS1_2b** (B) and **TS1_2c** (C). Important distances are given in Å.

Table 2. Energies relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory.

R	vdW[a]	TS1_2c	2c	TS2_3c	3c
F	−0.4	12.5	10.6	10.3	−63.6
Cl	−1.1	12.9	9.8	10.2	−59.9
H	−0.2	13.7	12.3	13.4	−51.3
Ph	−0.7	15.2	12.7	13.5	−56.0
Me	−1.1	17.2	16.2	16.5	−53.7
NH_2	−1.7	26.3			−65.9

[a] van der Waals complex formed between borirene and ethyne.

mediate **2c** is calculated for fluoroborirene (12.5 kcal mol^{-1}), whereas the highest barrier is found for methylborirene (17.2 kcal mol^{-1}). The aminoborirene **TS1_2c** does not lead to intermediate **2c** but directly to aminoborole **3c**. This process is highly exothermic, although the reaction barrier is significantly higher (26.3 kcal mol^{-1}) than the reaction barriers of other substituted borirenes. All of the transition states in **TS1_2c** are of C_s symmetry except aminoborirene in which the amino group on boron atom is somewhat twisted, which is also the cause of the difference in boron–carbon (ethyne) distances in this system.

Intermediates **2** lie in rather shallow potential energy minima. The barriers for collapse to products **3** through **TS2_3** (Figure 3) are at most 2 kcal mol^{-1} for **2b**, 4 kcal mol^{-1} for **2a**, and even lower (< 1 kcal mol^{-1}) for **2c**. Hence, these intermediates are not expected to be observable in conventional experiments, and even under matrix isolation conditions it may be challenging. The structure of the **TS2_3** differs slightly from the intermediate as the borylene unit is shifted towards two carbon atoms from two different hydrocarbon units whereas the other pair of carbon atoms is brought closer together so that the distance between the atoms is decreased from about 2.6 to about 2.2–2.3 Å. Representative reaction profiles are given for the reactions of chloroborirane and chloroborirene in Figures 4–6.

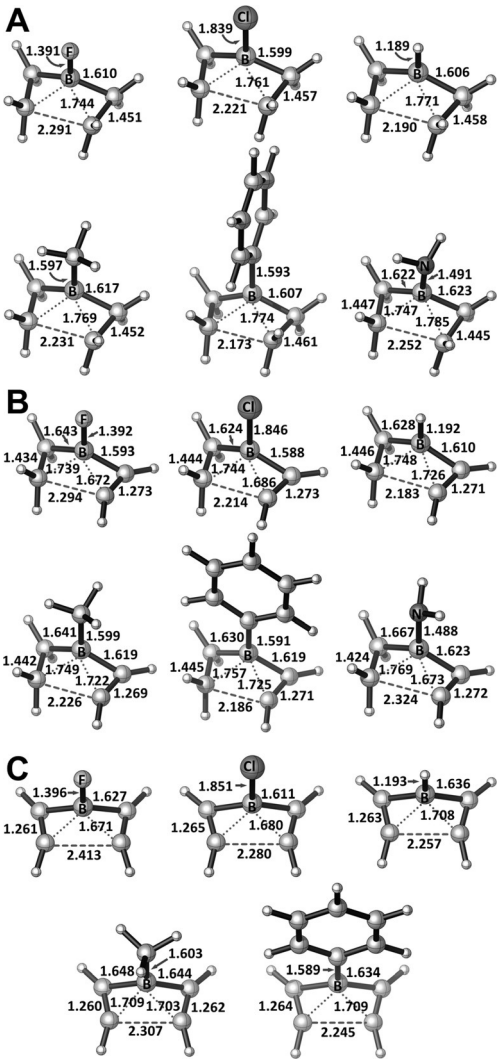


Figure 3. Optimized geometries (M06-2X/6-311 + G**) of transition states **TS2_3a** (A), **TS2_3b** (B) and **TS2_3c** (C). Important distances are given in Å.

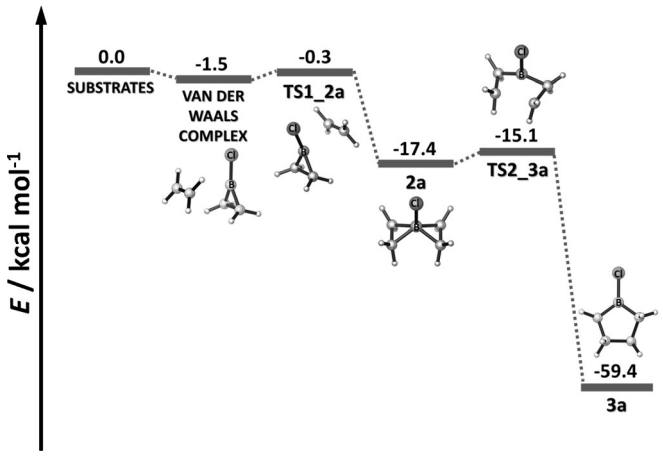


Figure 4. Schematic representation of reaction between chloroborirane and ethene as calculated at the CCSD/def2-TZVP//M06-2X/6-311 + G** + ZPVE level of theory.

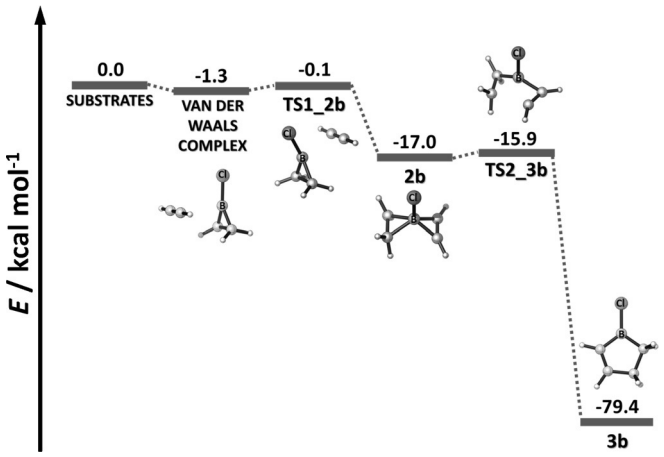


Figure 5. Schematic representation of reaction between chloroborirane and ethyne as calculated at the CCSD/def2-TZVP//M06-2X/6-311 + G** + ZPVE level of theory.

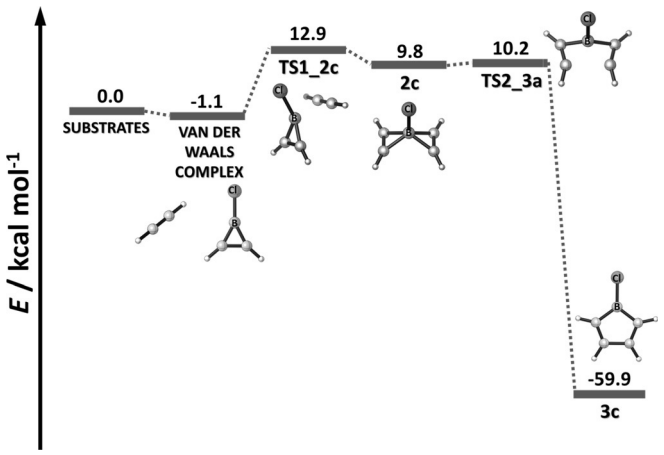
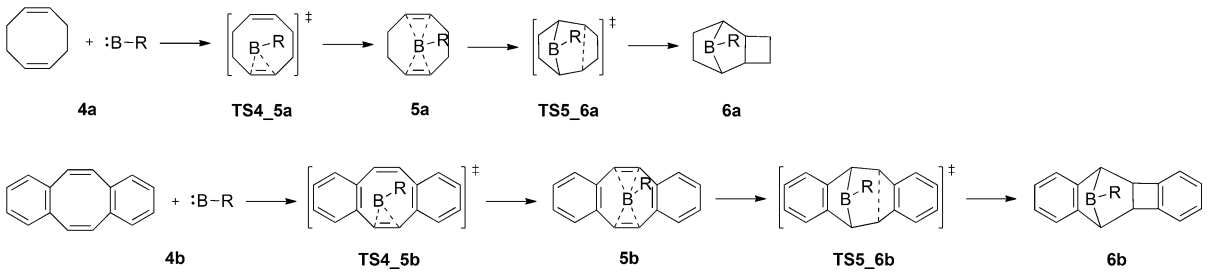


Figure 6. Schematic representation of reaction between chloroborirene and ethyne as calculated at the CCSD/def2-TZVP//M06-2X/6-311 + G** + ZPVE level of theory.

Reactions of borylenes with 1,5-cyclooctadiene and dibenzo[*a*,*e*]cyclooctatetraene

Intermediates **2** have a unique structure but they are expected to be not observable directly in experiments. To assess if an analogue of intermediate **2** could be sufficiently stabilized for experimental detection or even isolation, 1,5-cyclooctadiene (COD) and dibenzo[*a*,*e*]cyclooctatetraene (DBCOT), which are commonly used ligands in organometallic chemistry, were selected (Scheme 4).

Barriers for the formation of intermediates **5** are low, not exceeding 5 kcal mol^{-1}, and reaction energies are substantial (Table 3; see the Supporting Information, Figure S2 for structures of **TS4_5**). Structures of intermediates **5** (Figure 7) resemble the structure of intermediates **2**. Contrary to intermediates **2**, barriers for formation of cyclized products **6a** and **6b** are significantly heightened to 10–16 kcal mol^{-1}. The ring closure is endothermic for dibenzo[*a*,*e*]cyclooctatetraene (except for R = NH_2) and exothermic for 1,5-cyclooctadiene with the exception of the parent system (see the Supporting Information, Fig-



Scheme 4. Reactions of borylenes with 1,5-cyclooctadiene (top) and dibenzo[*a*,*e*]cyclooctatetraene (bottom).

Table 3. Energies relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for the reactions of borylenes with COD and DBCOT.

R	Olefin	TS4_5	5	TS5_6	6
Cl	COD	3.5	−65.4	−54.4	−67.6
	DBCOT	3.9	−65.6	−51.1	−60.9
H	COD	not found	−90.5	−78.2	−85.3
	DBCOT	not found	−90.8	−74.3	−81.6
Me	COD	−0.1	−77.6	−67.7	−78.6
	DBCOT	0.0	−78.7	−65.4	−73.9
NH_2	COD[a]	5.0	−51.8	−42.7	−72.9
	DBCOT[b]	4.6	−53.9	−41.4	−66.1

[a] Additional borirane intermediate (−50.7) and TS (−48.3) for formation of **5a** were located. [b] Additional borirane intermediate (−56.1) and TS (−52.1) for formation of **5b** were located.

ure S3 for structures of **TS5_6**). Significantly heightened barriers for conversion of **5** to **6**, compared with the barriers for intermediate **2** into product **3**, is most likely due to the presence of the strained four-membered ring in product **6**. The substantially higher barriers for disappearance of intermediates **5** should make them observable species. It is beyond the scope of the present paper to probe additional steric and electronic effects for further increase of barrier heights.

Structure and bonding of pentacoordinate boron compounds 2 and 5

Boranes are well known to coordinate to π systems of organic compounds, for example, the borane-olefin complex involved in hydroboration.[79] We have previously identified computationally borylene-olefin and borylene-alkyne van der Waals complexes as shallow minima involved in the cycloaddition reaction.[60] The pentacoordinate compounds **2** and **5** may be considered as diolefin and dialkyne π-complexes of borylenes reminiscent of transition-metal π-complexes. The structural parameters are in agreement with this assessment. The CC bonds in **2aH** (R=H) and **2cH** (R=H) are longer by roughly 0.1 Å than in the free hydrocarbons, but they are roughly 0.1 Å shorter than in the monocyclic boron compounds. On the other hand, the B–C distances of around 1.67–1.69 Å are significantly longer than those in borirane (1.53 Å) or borirene (1.47 Å). The ethylene unit in **2aH** is pyramidalized as measured by the angle of the HCH plane and the CC bond (22.9°). As expected, the pyramidalization is less than in borirane (33.6°). Likewise, the bending of the CCH angle in **2cH** is less (30°) than that observed in borirene (41.2°). In agreement with structural parameters that significantly deviate from those of covalent bonds in borirane and borirene, fractional BC bonding is supported by Wiberg bond indices (WBI) of 0.64 for the four BC bonds in **2aH** and **2cH**. For comparison, the WBI are close to 1 in borirane (0.94) and borirene (1.14). Furthermore, the significant lengthening of the CC bonds compared to free hydrocarbons and the shorter BC distances than in more conventional borane-olefin complexes are indicative of a pronounced degree of back donation from the boron center to the unsaturated hydrocarbons. This view is supported by the analysis of the molecular orbitals of systems **2**.

The HOMO of **2aH** and **2cH** are characterized by a bonding interaction between a boron p_B orbital and the π* orbitals of

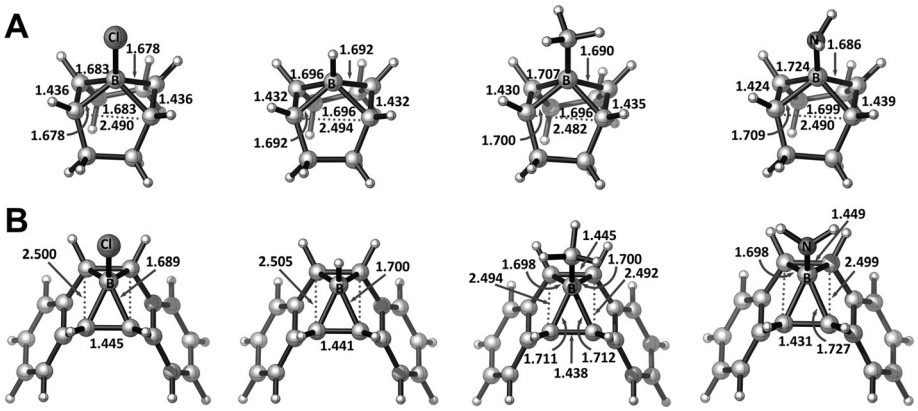


Figure 7. Optimized geometries (M06-2X/6-311+G**) of intermediates **5a** (A) and **5b** (B). Important bond lengths and distances are given in Å.

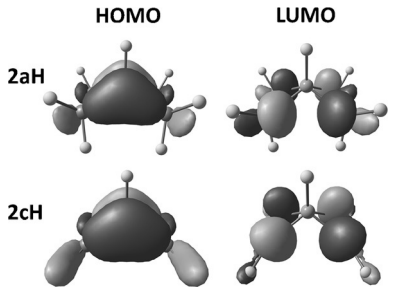
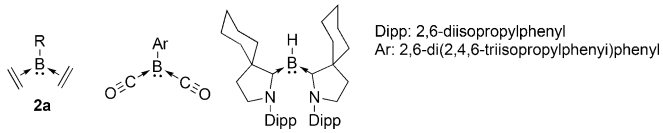


Figure 8. Frontier molecular orbitals of **2aH** and **2cH** computed at M06-2X/6-311+G** level of theory.

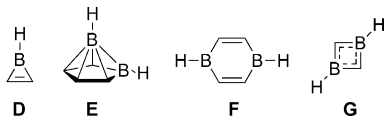
the hydrocarbon moieties whereas the LUMO is the antibonding combination of π* orbitals without contribution from the BH unit (Figure 8). The rotational barrier of an ethene unit is 22.2 kcal mol^{-1} in agreement with operation of a strong stereoelectronic effect such as back-donation. The electronic structure of **2** and **5** is thus related to the known $(CAAC)_2BH$[80] and L_2BR (L = CO, CNR)[81] compounds that can be considered as borylene complexes akin to transition-metal complexes (Scheme 5).



Scheme 5.

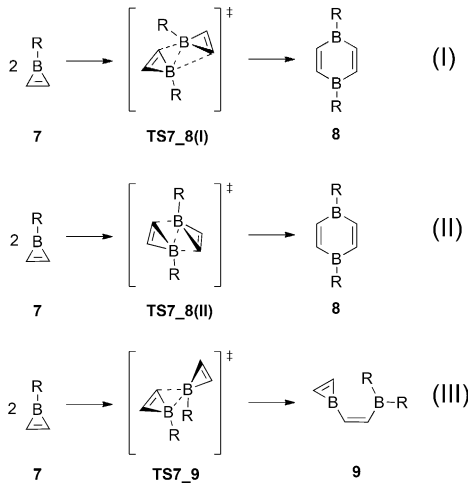
Dimerization of borirenes and boriranes

Our analysis indicates that certain boriranes and borirenes may react very quickly with small unsaturated hydrocarbons, in particular if there is a (locally) large excess of the latter as is likely the case in Timms co-condensation experiments. In his experiments with chloro- or fluoroborylene and alkynes and alkenes, Timms suggested that borirene or borirane could be an intermediate for the formation of 1,4-dibora-2,5-cyclohexadienes and 1,4-dibora-2,5-cyclohexanes, although he could not detect it directly.[57,58] The facile dimerization of parent borirene was confirmed by a computational investigation of Schleyer and co-workers.[33] They studied comprehensively dimerization pathways of parent borirene **D** to 1,4-diboracyclohexa-2,5-diene **F** and to 2,3,4,5-tetracarba-*nido*-hexaborane **E** as well as the disproportionation reaction of two borirene molecules to 1,3-diboretene **G** and ethyne by computational means (Scheme 6).[33] The *nido*-carborane turned out to be energetically most stable isomer at MP3/6-31G//3-21G and HF/6-31G*//3-21G levels of theory, although the low-energy pathway for its formation from two borirene molecules could not be located. Borirene dimerization to 1,4-diboracyclohexa-2,5-diene **F**, which lies just a few kcal mol^{-1} above *nido*-carborane **E**, was analyzed in detail by symmetry and orbital interactions arguments.[33] From these considerations two non-planar four-center transition states for low-energy pathways were found: one transition state (11 kcal mol^{-1}) of C_2 symmetry where the empty p orbital on boron overlaps with both π orbitals of CC and a σ orbital of a B–C bond and a second transition state (19 kcal mol^{-1}) of C_i symmetry in which the overlap of boron acceptor orbital and CC π orbital is poor.



Scheme 6.

Following Schleyer and co-workers, we performed a computational study of the dimerization processes of chloro- and fluoroborirene, which are important in view of Timms experiments, and of parent borirene as a reference. For this purpose we adopted both C_2 and C_i transition state geometries provided by Schleyer and co-workers as a starting point for our study. During the re-optimization the symmetry of both transition states could not be retained, although the resulting C_1 geometries resemble the previously reported structures. Thus we were able to find three low-energy pathways. Two of them led to 1,4-diboracyclohexadiene as expected, whereas the third path is a boration reaction (Scheme 7) that was not considered previously by Schleyer and co-workers. Path I and II differ in the structure of the transition states (see Figure 9). Barrier heights calculated for diboracyclohexadiene formation are in agreement with the previous computations by Schleyer et al. Path II is favored, but the boration reaction is competitive (Table 4).



Scheme 7. Dimerization pathways of borirenes.

Additionally, we studied dimerization reactions of boriranes for the first time (Scheme 8, Figure 10). Two low-energy pathways were found for this process: one for dimerization to 1,4-diboracyclohexane (path IV) and one for a boration reaction (path V). Structures of transition states **TS10_11** for reaction IV resemble the transitions states **TS7_8(II)** found in pathway II for borirene dimerization to 1,4-diboracyclohexadiene. The reaction of the parent borirane has no barrier but proceeds

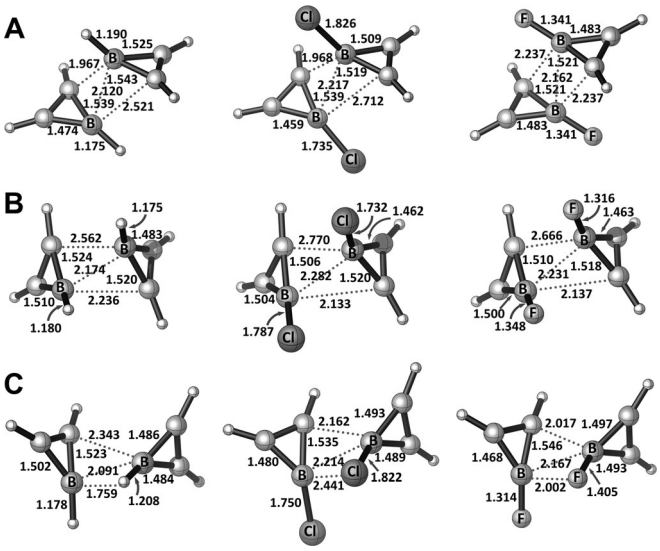
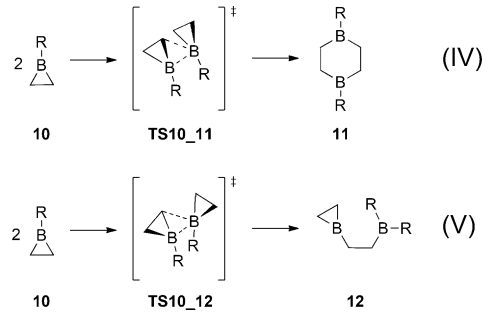


Figure 9. Optimized geometries (M06-2X/6-311+G**) of transition states **TS7_8(I)** (A), **TS7_8(II)** (B), and **TS7_9** (C). Important distances are given in Å.

Table 4. Energies relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for dimerization of borirenes (see Scheme 7 for pathways).

R	Path I		Path II		Path III	
	TS7_8(I)	**8**	**TS7_8(II)**	**8**	**TS7_9**	**9**
H	16.4	−55.7	10.7	−55.7	12.1	−27.7
Cl	18.5	−74.1	12.8	−74.1	16.7	−39.8
F	14.3	−81.2	10.5	−81.2	14.4	−52.6



Scheme 8. Dimerization pathways of boriranes.

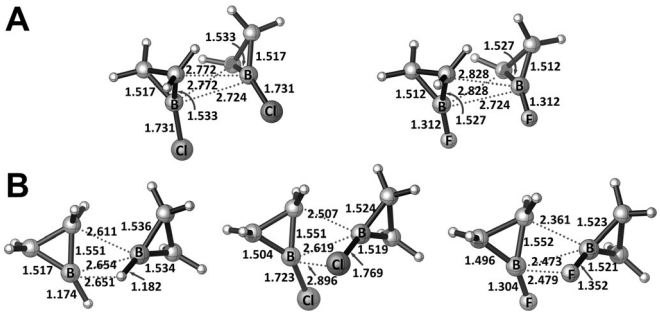


Figure 10. Optimized geometries (M06-2X/6-311+G**) of transition states **TS10_11** (A) and **TS10_12** (B). Important distances are given in Å.

through a cyclic intermediate in which the distance between boron atoms is smaller than 2 Å (see the Supporting Information, Figure S6). Both borirane dimerization pathways have extremely low barriers, but diboracyclohexane formation is significantly more exothermic than boration (V) (Table 5).

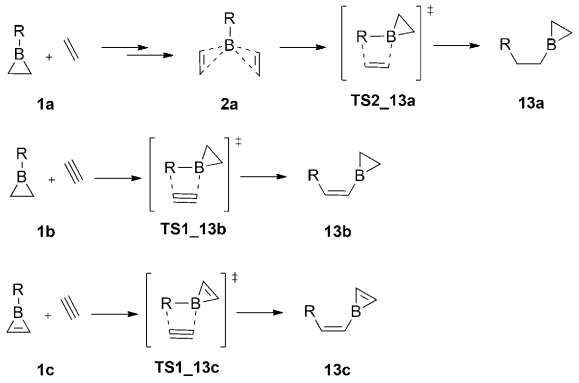
Table 5. Energies relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for dimerization of boriranes (see Scheme 8 for pathways).

R	Path IV			Path V		
	vdW^{IV}[a]	**TS10_11**	**11**	**vdW^{V}**[b]	**TS10_12**	**12**
H[c,d]			−77.7	−1.9	−2.5	−38.8
Cl	−1.3	−0.6	−86.2	−1.9	0.1	−46.3
F	−1.0	−1.0	−92.1	−1.4	0.5	−57.3

[a] vdW^{IV} refers to van der Waals complex formed between two borirane molecules in path IV.[b] vdW^{V} refers to van der Waals complex formed between two borirane molecules in path V. [c] Additional intermediate (−65.8) and TS (−67.3) for formation of **11** were located (the Supporting Information, Figure S6 A). [d] Additional intermediate (−44.8) and TS (−37.3) for formation of **12** were located (the Supporting Information, Figure S6 B).

Boration of unsaturated hydrocarbons by boriranes and borirenes

As we found boration reactions involving boriranes and borirenes to be energetically competitive, we also investigated boration reactions of ethene and ethyne as an alternative to borolane, 2,3-dihydroborole, and borole formation (Scheme 9).



Scheme 9. Boration reactions.

Boration of ethyne by borirane has the lowest barriers among all boration reactions studied here. In transition structures **TS1_13** hydrocarbon is parallel to B–R bond contrary to **TS1_2** where hydrocarbon is perpendicular to B–R bond (Figure 11). Barriers for boration reaction are much higher than barriers for ring expansion reactions (Table 6). Due to unfavorable energetics boration reactions are unlikely to occur.

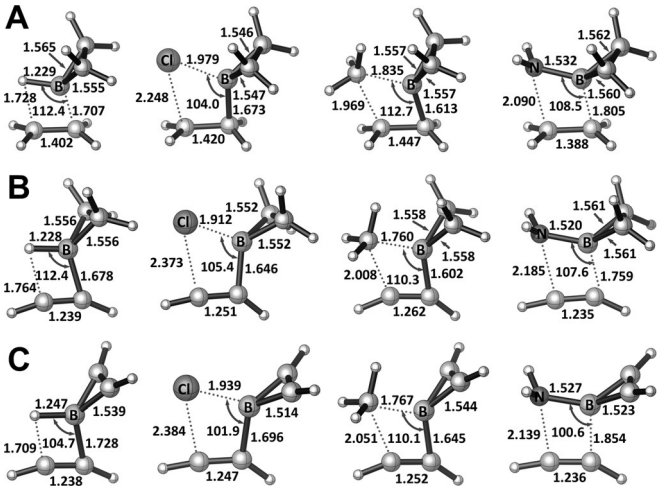


Figure 11. Optimized geometries (M06-2X/6-311+G**) of transition states **TS2_13a** (A), **TS1_13b** (B), and **TS1_13c** (C). Important distances are given in Å.

Table 6. Reaction energies (with respect to separate reactants) in kcal mol^{-1} calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory for boration.[a]

R	Borirane + ethene			Borirane + ethyne			Borirene + ethyne		
	2a	**TS2_13a**	**13a**	**vdW**[b]	**TS1_13b**	**13b**	**vdW**[d]	**TS1_13c**	**13c**
H	−21.3	0.7	−31.9	−19.7[c]	4.9	−46.1	−0.1	34.6	−42.8
Cl	−17.4	19.6	1.5	−1.1	15.2	−13.1	−1.1	31.3	−14.6
Me	−15.2	25.1	−19.7	−0.9	22.5	−36.5	−0.2	48.9	−34.9
NH_2	−0.5[h]	33.3	14.0	−0.7	31.1	−14.1	−1.5	40.0	−18.3

[a] See Scheme 9. [b] vdW refers to van der Waals complex formed between borirane and ethyne (see Supporting Information, Figure S7A. [c] Reaction starts with intermediate **2b**. [d] vdW refers to van der Waals complex formed between borirene and ethyne (see Supporting Information, Figure S7B). [e] Additional intermediate (3.5) and TS (13.7) for formation of **13a** were located (see Supporting Information, Figure S8A). [f] Additional intermediate (−8.7) and TS (−0.7) for formation of **13b** were located (see Supporting Information, Figure S8B). [g] Additional intermediate (−0.5) and TS (−0.9) for formation of **13c** were located (see Supporting Information, Figure S8C). [h] Reaction starts with vdW complex.

Conclusion

The computational study of the reactivity of boron-substituted boriranes and borirenes (R = H, F, Cl, Me, Ph, and NH_2) towards unsaturated hydrocarbons (ethyne or ethene) allows us to draw the following conclusions:

1. The newly found reaction that leads to ring expansion of the three-membered to five-membered heterocycles, borolanes (**3a**), dihydroboroles (**3b**), or boroles (**3c**) is based on the interaction between the empty p orbital of the boron atom and the π bond of the unsaturated hydrocarbon.
2. The reaction is step-wise and proceeds through the intermediate **2**, which can be regarded as a borylene complexed to two unsaturated hydrocarbon molecules, similar to transition metal olefin or alkyne complexes. Intermediates **2** thus fall into the category of L_2BR compounds where two neutral two-electron donor ligands (such as cyclic (alkyl)-(amino)carbenes CAAC, carbon monoxide, isonitriles) stabilize a borylene.
3. For most of the substituted boriranes the reaction barriers for formation of intermediates **2a** and **2b** are extremely low (below 1 kcal mol^{-1}) or there are no barriers in case of parent borirane. The reactions of aminoborirane have higher barriers (about 11 kcal mol^{-1}) and are slightly endothermic due to the reduced Lewis acidity of boron. In case of borirenes, formation of intermediates **2c** is an endothermic process with barrier heights ranging from 12.9 to 28.0 kcal mol^{-1}. Formation of intermediates **2** is substantially exothermic.
4. Barrier heights for collapse of intermediates **2** to five-membered heterocycles **3** by C–C bond formation are very low (not exceeding 3.5 kcal mol^{-1}) and smallest for the reaction of borirene with ethyne (below 1 kcal mol^{-1}).
5. Barriers for C–C bond formation can be significantly increased up to 17 kcal mol^{-1} by using diolefins 1,5-cyclooctadiene and dibenzo[*a*,*e*]cyclooctatetraene (DBCOT). Based on barrier heights, the corresponding $(DBCOT)_2BR$ complexes should be observable experimentally.
6. Boration reactions of the unsaturated hydrocarbons by boriranes and borirenes have significantly higher barriers and are expected not to be competitive with formation of **3**.
7. Two pathways for dimerization of parent, chloro-, and fluoroborirenes to 1,4-dibora-2,5-cyclohexadienes were found with barrier heights in the range of 10–18 kcal mol^{-1}. An additional pathway, with comparable barriers heights, is the ring-opening boration of a borirene C–B bond by borirene.
8. One pathway for dimerization of boriranes (R = H, Cl, F) was identified, and that proceeds with very low barriers.
9. The facile reaction of the three membered boron heterocycles, in particular boriranes, with unsaturated hydrocarbons is relevant in the context of the co-condensation of thermolytically generated borylenes and small unsaturated hydrocarbons as performed by Timms. The expected high local concentrations of hydrocarbon in these experiments are expected to favor formation of five-membered heterocycle over the dimerization, although this also is a low barrier process. The five-membered heterocycles are not expected to be particularly stable and may have reacted further during processing of the reaction mixture.

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Supporting Information

Ring Enlargement of Three-Membered Boron Heterocycles upon Reaction with Organic π Systems: Implications for the Trapping of Borylenes

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Table S1. Energies ΔE_0 and Gibbs free energies ΔG (298.15 K) relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory. Corrections to ΔE_0 and ΔG are taken from M06-2X/6-311+G** calculations.

R	vdW[b]		TS1_2b		2b		TS2_3b		3b	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
F	6.0	-1.4	8.2	-0.6	-5.3	-15.0	-4.4	-14.5	-71.7	-81.4
Cl	5.7	-1.3	8.7	-0.1	-7.3	-17.0	-5.7	-15.9	-69.7	-79.4
H					-10.4	-19.7	-7.9	-17.6	-66.9	-76.4
Ph	5.7	-1.5	8.8	-1.0	-4.7	-13.8	-2.8	-12.9	-65.1	-75.1
Me	5.8	-1.8	8.4	-1.0	-4.2	-14.1	-2.0	-12.7	-65.2	-75.3
NH_2	6.3	-0.3	20.1	10.9	13.5	4.1	14.3	4.3	-65.1	-74.5
R	**vdW[a]**		**TS1_2a**		**2a**		**TS2_3a**		**3a**	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
F	6.8	-1.4	7.9	-1.2	-3.2	-14.4	-2.2	-13.4	-51.1	-61.9
Cl	6.4	-1.5	9.4	-0.3	-6.0	-17.4	-3.8	-15.1	-48.5	-59.4
H					-10.5	-21.3	-7.6	-18.3	-45.4	-56.0
Ph	5.3	-2.2	8.0	-1.2	-5.7	-16.0	-0.9	-12.5	-44.0	-55.2
Me	7.0	-1.3	9.6	-0.7	-4.2	-15.2	-1.9	-13.6	-44.1	-55.4
NH_2	6.0	-0.9	19.9	9.7	13.8	3.2	16.6	5.6	-45.2	-56.0
R	**vdW[c]**		**TS1_2c**		**2c**		**TS2_3c**		**3c**	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
F	5.3	-0.4	21.6	12.5	20.1	10.6	20.1	10.3	-53.5	-63.6
Cl	4.8	-1.1	22.0	12.9	19.5	9.8	20.0	10.2	-49.8	-59.9
H	5.1	-0.2	22.5	13.7	21.6	12.3	22.9	13.4	-41.4	-51.3
Ph	5.2	-0.7	24.6	15.2	23.0	12.7	23.8	13.5	-45.3	-56.0
Me	5.4	-1.1	27.7	17.2	26.2	16.2	27.1	16.5	-43.1	-53.7
NH_2	4.6	-1.7	35.4	26.3					-55.7	-65.9

[a] van der Waals complex formed between borirane and ethene
[b] van der Waals complex formed between borirane and ethyne
[c] van der Waals complex formed between borirene and ethyne

Table S2. Energies ΔE_0 and Gibbs free energies ΔG (298.15 K) relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory. Corrections to ΔE_0 and ΔG are taken from M06-2X/6-311+G** calculations.

R	TS4_5a		5a		TS5_6a		6a	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
Cl	14.5	3.5	-53.2	-65.4	-42.0	-54.4	-56.0	-67.6
H			-79.9	-90.5	-67.3	-78.2	-74.9	-85.3
Me	10.8	-0.1	-65.6	-77.6	-55.0	-67.7	-66.8	-78.6
NH_2	16.2	5.0	-39.3	-51.8	-29.9	-42.7	-60.5	-72.9
R	**TS4_5b**		**5b**		**TS5_6b**		**6b**	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
Cl	14.3	3.9	-53.4	-65.6	-39.0	-51.1	-49.6	-60.9
H			-80.1	-90.8	-63.9	-74.3	-71.5	-81.6
Me	10.5	0.0	-67.0	-78.7	-53.4	-65.4	-62.4	-73.9
NH_2	15.4	4.6	-41.6	-53.9	-29.1	-41.4	-54.3	-66.1

Table S3. Energies ΔE_0 and Gibbs free energies ΔG (298.15 K) relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory. Corrections to ΔE_0 and ΔG are taken from M06-2X/6-311+G** calculations.

R	TS7_8(I)		TS7_8(II)		8		TS7_9		9	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
H	26.7	16.4	20.9	10.7	-44.9	-55.7	11.6	12.1	-18.3	-27.7
Cl	29.4	18.5	24.0	12.8	-62.1	-74.1	11.6	16.7	-29.5	-39.8
F	25.2	14.3	21.4	10.5	-69.4	-81.2	11.9	14.4	-42.8	-52.6

Table S4. Energies ΔE_0 and Gibbs free energies ΔG (298.15 K) relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory. Corrections to ΔE_0 and ΔG are taken from M06-2X/6-311+G** calculations.

R	vdW		TS10_11		11		vdW		TS10_12		12	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
H					-66.6	-77.7	7.0	-1.9	6.5	-2.5	-29.3	-38.8
Cl	7.7	-1.3	10.5	-0.6	-74.4	-86.2	7.3	-1.9	11.3	0.1	-35.7	-46.3
F	8.3	-1.0	9.6	-1.0	-80.7	-92.1	7.5	-1.4	11.0	0.5	-47.3	-57.3

Table S5. Energies ΔE_0 and Gibbs free energies ΔG (298.15 K) relative to separate reactants (in kcal mol^{-1}) calculated at the CCSD(T)/def2-TZVP//M06-2X/6-311+G** level of theory. Corrections to ΔE_0 and ΔG are taken from M06-2X/6-311+G** calculations.

R	TS2_13a		13a		vdW		TS1_13b		13b	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
H	11.0	0.7	-22.9	-31.9			14.2	4.9	-37.6	-46.1
Cl	30.2	19.6	10.8	1.5	5.8	-1.1	25.0	15.2	-4.4	-13.1
Me	36.9	25.1	-9.5	-19.7	6.9	-0.9	33.3	22.5	-26.8	-36.5
NH_2	43.8	33.3	23.5	14.0	6.1	-0.7	40.6	31.1	-5.3	-14.1

R	vdW		TS1_13c		13c	
	ΔG	**ΔE_0**	**ΔG**	**ΔE_0**	**ΔG**	**ΔE_0**
H	5.5	-0.1	43.5	34.6	-34.3	-42.8
Cl	4.8	-1.1	40.8	31.3	-6.1	-14.6
Me	7.1	-0.2	59.9	48.9	-24.9	-34.9
NH_2	3.5	-1.5	49.2	40.0	-9.4	-18.3

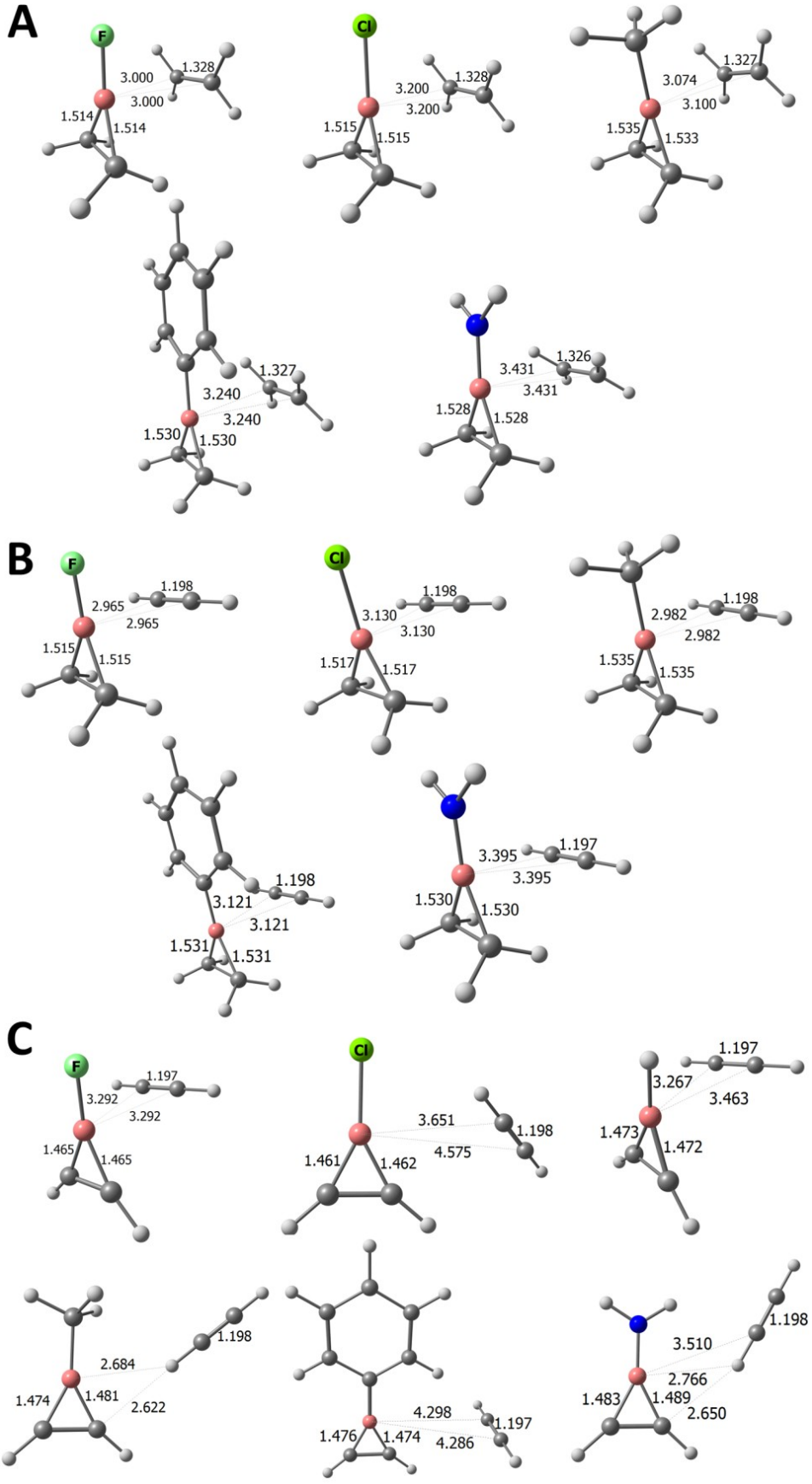

Figure S1. Optimized geometries (M06-2X/6-311+G**) of van der Waals complexes found in ring expansion reaction. Important distances are given in Å.

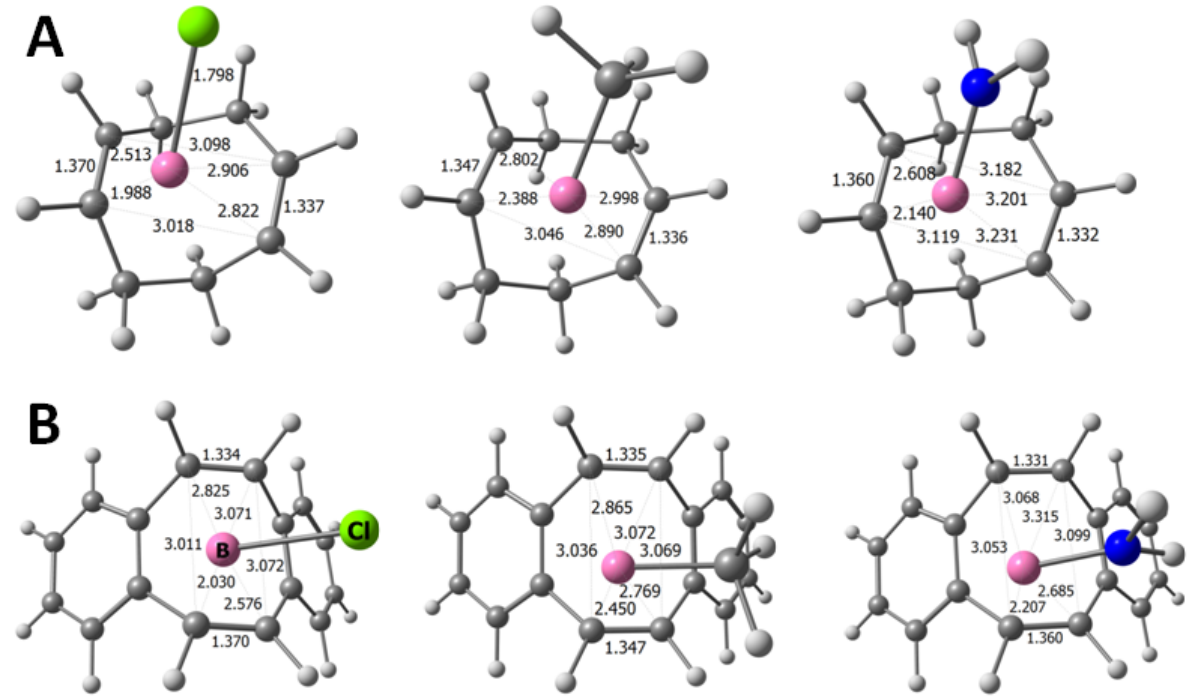

Figure S2. Optimized geometries (M06-2X/6-311+G**) of transition states **TS4_5a** (A) and **TS4_5b** (B). Important distances are given in Å.

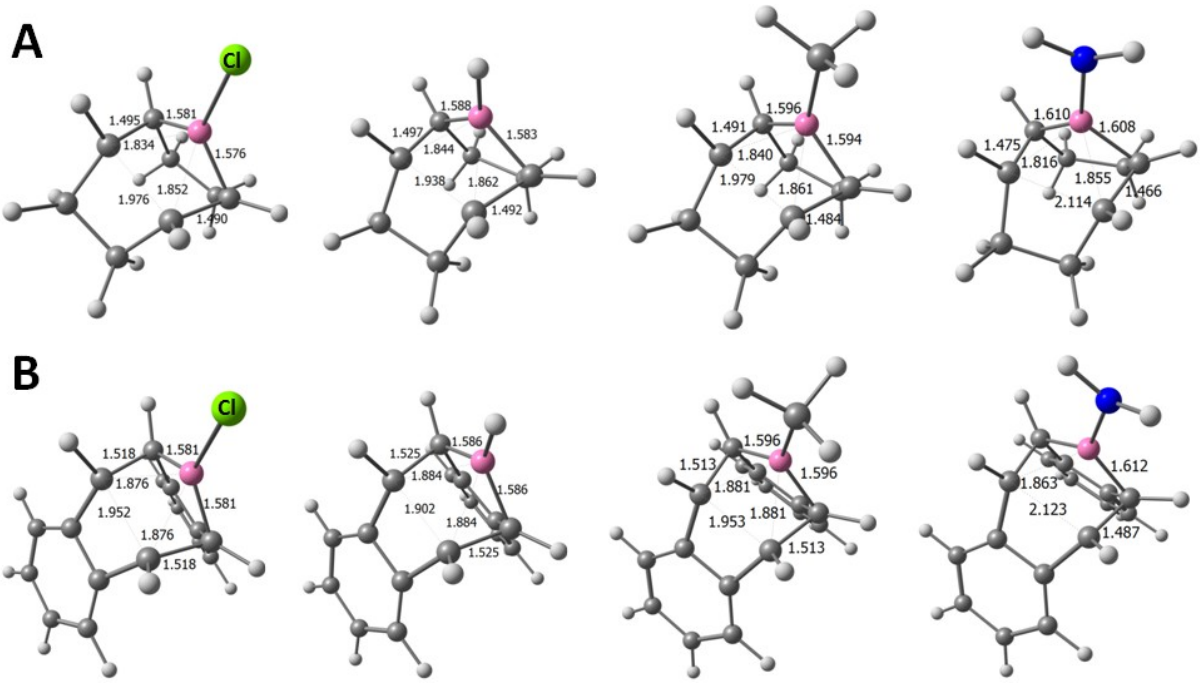

Figure S3. Optimized geometries (M06-2X/6-311+G**) of transition states **TS5_6a** (A) and **TS5_6b** (B). Important distances are given in Å.

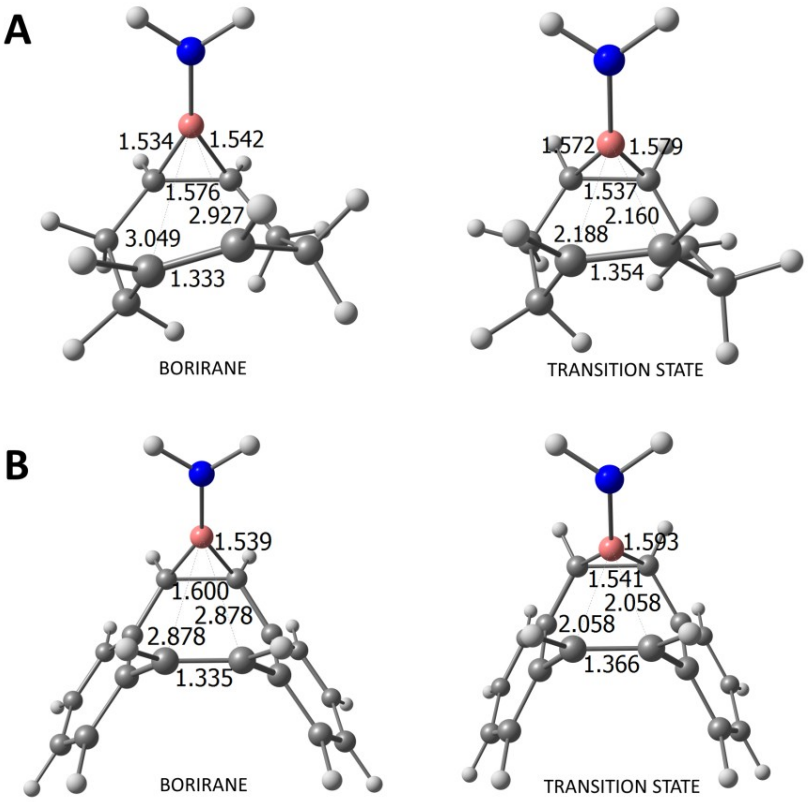

Figure S4. Optimized geometries (M06-2X/6-311+G**) of borirane intermediate and transition state found for formation of **5a** (A) and **5b** (B). Important distances are given in Å.

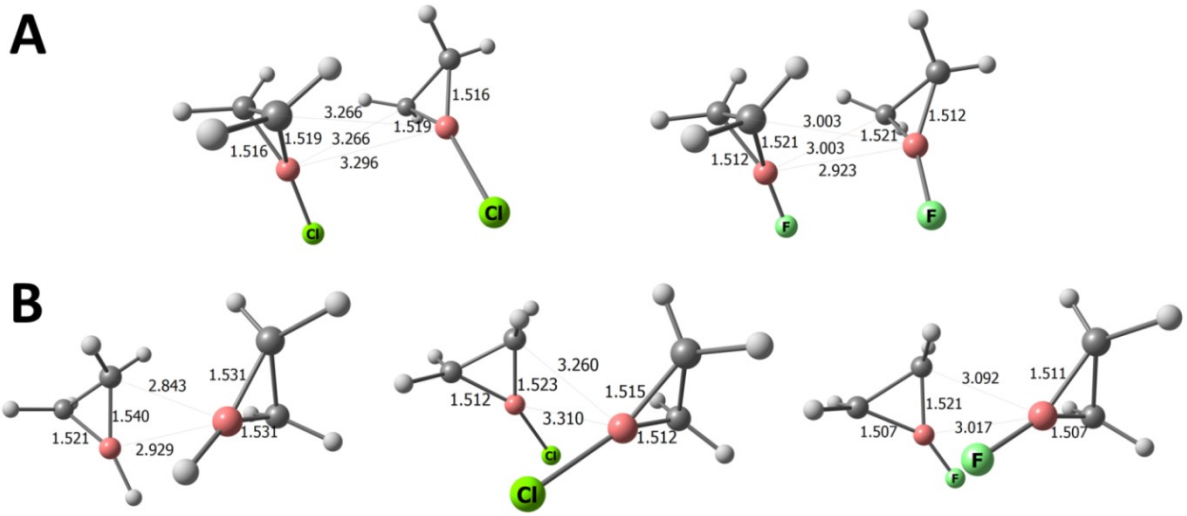

Figure S5. Optimized geometries (M06-2X/6-311+G**) of van der Waals complexes found in path IV (A) and V (B) for borirane dimerization. Important distances are given in Å.

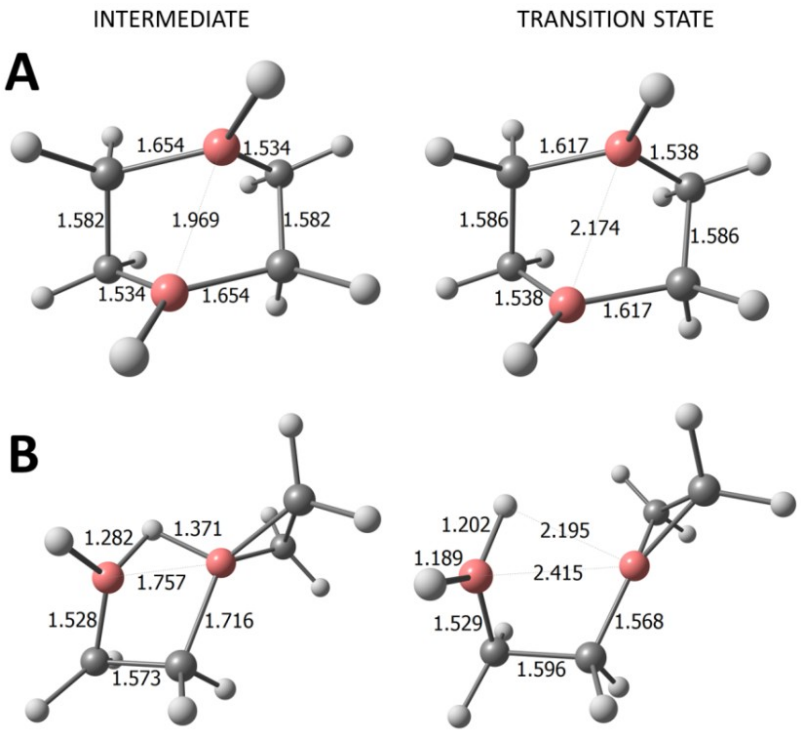

Figure S6. Optimized geometries (M06-2X/6-311+G**) of additional intermediate and transition state found for formation of **11** (A) and **12** (B). Important distances are given in Å.

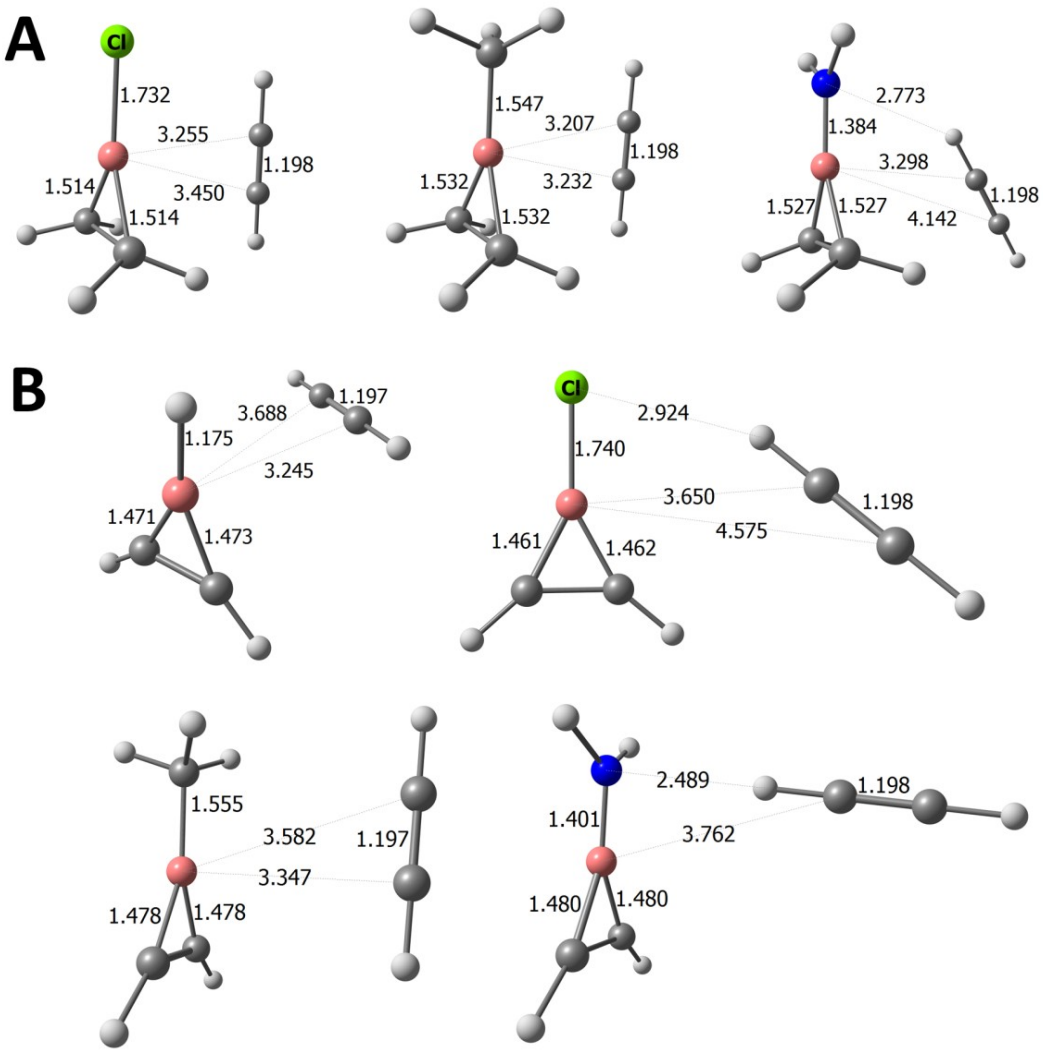

Figure S7. Optimized geometries (M06-2X/6-311+G**) of van der Waals complexes found in boration reactions. Important distances are given in Å.

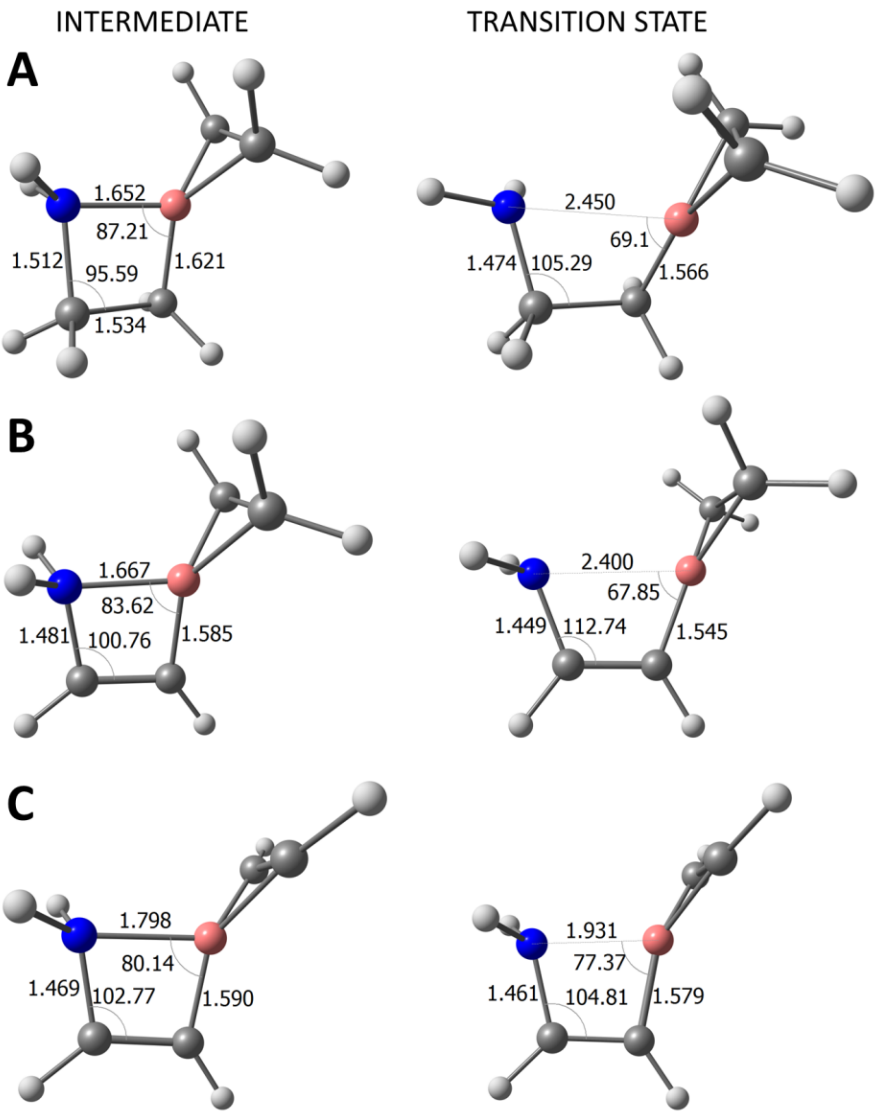

Figure S8. Optimized geometries (M06-2X/6-311+G**) of intermediate and transition state found for formation of **13a** (A) and **13b** (B) and **13c** (C). Important distances are given in Å.

Distortion of hydrocarbon units in intermediates 2.

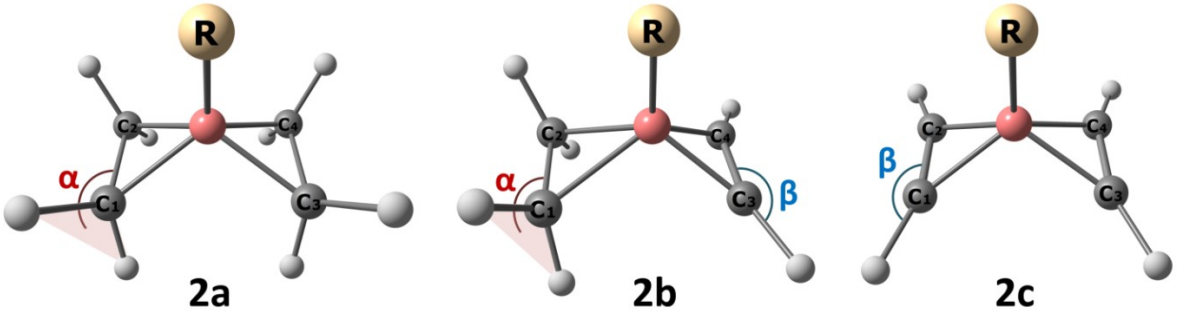

Table S6. Selected geometrical data for intermediates 2a and 2b computed at M06-2X/6-311+G** level of theory.

R	2a						2b					
	d^{C1C2}	d^{C3C4}	α1	α2	α3	α4	d^{C1C2}	d^{C3C4}	α1	α2	β1	β2
H	1.424		158.2				1.407	1.264	161.9		152.3	
F	1.429		159.2				1.406	1.274	163.8		150.5	
Cl	1.427		159.2				1.410	1.268	162.7		152.7	
Me	1.424	1.426	157.9	158.0	157.8	157.7	1.413	1.262	160.6		152.9	
Ph	1.426	1.426	158.0	158.0			1.409	1.264	161.8	161.0	152.4	152.4
NH_2	1.430	1.419	157.1		159.7		1.400	1.269	163.6		150.6	

Table S7. Selected geometrical data for intermediate 2c computed at M06-2X/6-311+G** level of theory.

R	d^{C1C2}	d^{C3C4}	β1	β2	β1	β2
H	1.252		155.8			
F	1.257		155.0			
Cl	1.255		155.9			
Me	1.249	1.258	156.7	156.7	153.8	153.8
Ph	1.253		155.9			

Table S8. Selected geometrical data for borirane and borirene computed at M06-2X/6-311+G** level of theory.

R	Borirane			Borirene		
	d^{BC1}	d^{C1C2}	α	d^{BC1}	d^{C1C2}	β
H	1.526	1.545	146.4	1.471	1.349	138.8
F	1.510	1.591	142.6	1.463	1.362	136.5
Cl	1.514	1.569	144.8	1.463	1.355	138.1
Me	1.530	1.552	145.2	1.476	1.349	137.9
Ph	1.528	1.554	144.8	1.475	1.349	138.1
NH_2	1.528	1.565	143.3	1.484	1.345	137.8

Free acetylene d(CC)=1.197 Å

Free ethylene d(CC)=1.326 Å

QTAIM analysis of intermediates 2

In addition to molecular orbital analysis, quantum theory of atoms in molecules (QTAIM)[1] was performed at the M062X/6-311+G** level of theory to describe bonding in intermediates **2** (Table S9). Moreover, QTAIM analysis was carried out on borirane, borirene, borole, and dimethylborane to provide reference data. Computed molecular graphs of intermediates **2** show that the boron atom is connected to each carbon atom of two hydrocarbon subunits by bond paths (BP) and corresponding bond critical points (BCP) were found. BCPs on B-C bond paths lie closer to the boron atom (see Figure S9; BCP is situated closer to the atom with lower electronegativity[2]). Bond paths in borirane and borirene are somewhat curved outwardly (exocyclic BP) and the convex shape of molecules is revealed. This is in agreement with molecular graphs obtained for cyclopropane molecule[3, 4] and is an indication of molecular strain. Comparing the three-membered boron heterocycles with less strained borole, it is easy to recognize that the B-C bond paths of latter are no longer convex (see Figure S10.). B-C bond paths of intermediates **2** are, on the other hand, curved inwardly (concave or endocyclic BP). Properties at BCP can reveal the nature of the bond type. Electron density ρ at BCP greater than 0.20 au is typical for covalent bonds, and ρ < 0.10 au characterizes closed-shell interactions (ionic bonds, van der Waals complexes, hydrogen bonds). In intermediates **2** the electron density at BCP(B-C) amounts to 0.128 au in **2aH** and to 0.125 au in **2cH**. These values of ρ places B-C bonds of intermediates **2** between covalent bonds and closed-shell interactions, although the magnitude 10^{-1} au is significant and suggests that these bonds have some covalent character. These values are lower than the values of ρ at the BCP(B-C) of boracycles (borirane, borirene, and borole) and acyclic dimethylborane. In all of these compounds electron density is equal to or greater than 0.18 au which is lower than typical value for covalent bond (>0.20 au), but could be typical for boron-carbon bonds. The values of electron density at BCP(C-C) are heightened from 0.222 in borirane to 0.279 au in **2aH** and from 0.323 in borirene to 0.375 au in **2cH**. Another useful property that can be computed at BCP is Laplacian of the electron density $\nabla^2\rho$, which has negative sign in covalent bonds and is positive in closed-shell interactions, but can be also positive in strongly polar bonds, dative bonds (for dative C-B bonds see Frenking et al.[5]) or so called charge-shift bonds.[6, 7] Sign of Laplacian of electron density $\nabla^2\rho$ in BCP(B-C) in all intermediates **2** is positive and values are smaller when boron is connected to ethene unit (0.057 au in **2aH** and 0.082 au in **2bH**) which still is an indication of partial covalent character of the bond. In **2cH** $\nabla^2\rho$ at BCP(B-C) is also positive and the value is higher (0.190 au). $\nabla^2\rho$ at BCP(B-C) of borirane is slightly negative (-0.059 au) but in borirene is highly positive (0.293 au). In borole and $HBMe_2$ $\nabla^2\rho$ at BCP(B-C) is negative (about -0.23 au).

The ring critical points (RCP) in borirane and borirene are close to BCPs of B-C bond paths. The electron density value at these RCPs is smaller by only less than 0.02 au than electron density at BCP(C-B). This indicates that the electron density is distributed basically throughout the ring plane. Cremer and Kraka[3, 8] describe it as *surface delocalization*

associated with π character of CC bonds (electron density spreads either towards ring center and outside of the ring in cyclopropane and other strained rings). In borole the distance between BCP(C-B) and RCP is larger and the ρ value of the latter is much smaller (0.044 au) than in the case of three-membered boracycles. This indicates that electron density in borole is distributed in the bonding region only. Narrowing the BCP1-B-BCP2 angle in intermediates **2** (concave bond paths) brings the BCP(B-C) and RCP closer and causes almost identical values of ρ at RCP and at BCP(B-C) (see Table S6), although the electron density is still distributed throughout the ring plane (see Figure S9C-F). This stays in agreement with the Laplacian distributions shown in Figure S9. Borirane and borirene both exhibit extended bond ellipticities ε at BCP(B-C), 0.991 and 0.781, respectively, which are larger than ellipticities of B-C bond in borole and $HBMe_2$ (~0.3). Extended ellipticity is another manifestation of the π character of the B-C bonds in three-membered boracycles as in case of cyclopropane.[3] Extremely large bond ellipticities were found for B-C bonds of intermediates **2** with the largest value of 15.7 in **2cH**. The enormous values of ε are associated with the elongation of B-C bonds compared to three-membered boracycles. Large ε values were associated with facile bond rupture and were also e.g. found in QTAIM analysis performed on cyclopropylcarbinyl cation ($C_4H_7^+$).[9]

The shape of the molecular graphs (exo- or endocyclic B-C bond paths) can be associated with the strength of σ-donation from multiple CC bonds and π-back donation in metallacycle[10] or other three-membered rings.[3] The stronger the electron donation from the CC bond and the weaker π-back donation, the more curved inwardly the bond paths become until T-shape is reached and ring structure is lost as for pure σ-donation without any back donation. The situation is reversed when back donation dominates: the bond paths are convex (like in cyclopropane) or close to being straight as in metallacycles where convex structure is hardly reached.[10] Judging from the shape of molecular graphs, in borirane and borirene pure boracycle structure predominates. The situation changes when two unsaturated hydrocarbon units are connected to the boron center, like in intermediates **2**. Narrowing of the ring structure of molecular graph of **2** the back donation is still present but donation from CC bond to boron is now dominant. Weaker back donation is present in **2cH** than in **2aH** as the B-C bond paths are narrower. Delocalization indices obtained from QTAIM calculations correlate quite well with calculated Wiberg bond orders for the non-polar CC bonds, but are lower in case of B-C bonds.

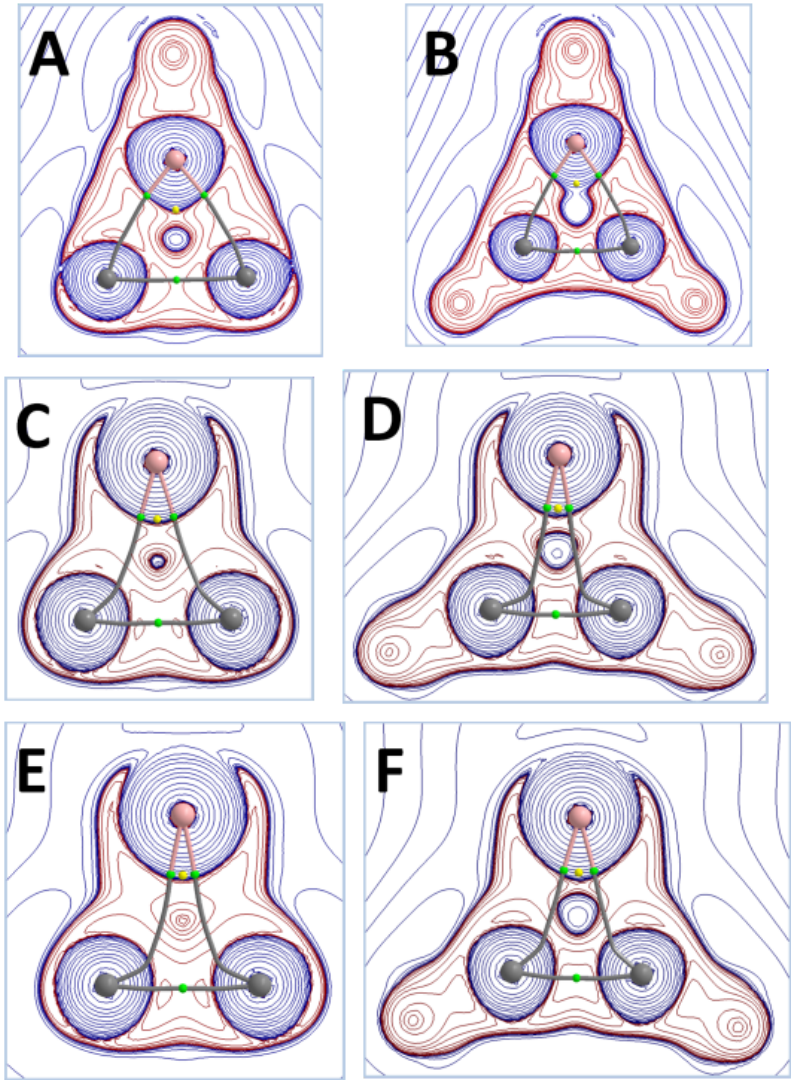

Figure. S9. Molecular graphs and Laplacian $\nabla^2\rho$ contour maps in the BCC plane of borirane (A), borirene (B), **2aH** (C), **2cH** (D), **2bH** ethene part (E), and **2bH** ethyne part (F). Red contour lines denote the region where the electronic charge is concentrated ($\nabla^2\rho < 0$) and blue lines indicate electronic charge depletion ($\nabla^2\rho > 0$). Bond critical points (BCP) are marked as green circles and ring critical points (RCP) as yellow circles. Hydrogen atoms and corresponding bond paths are omitted for clarity.

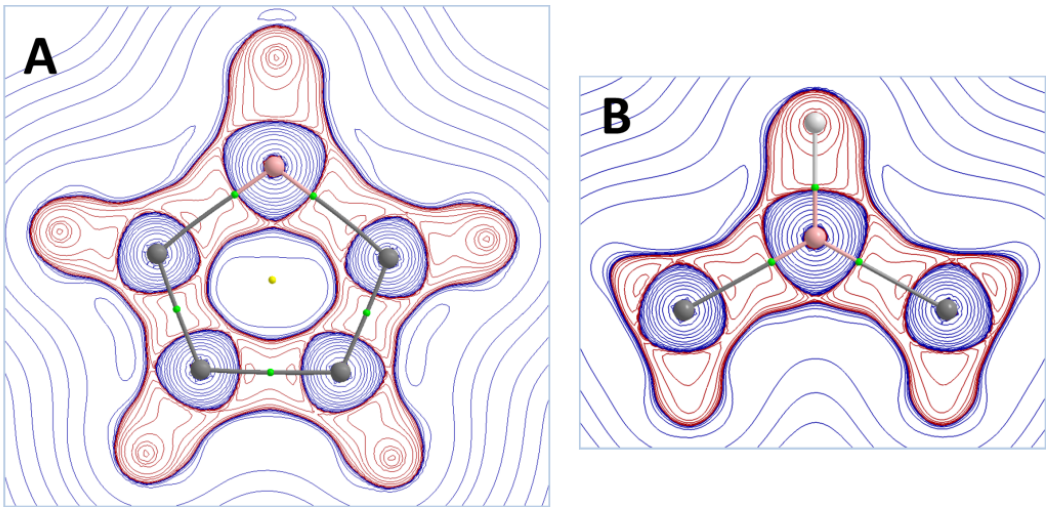

Figure S10. Molecular graphs and Laplacian $\nabla^2\rho$ distribution of borole (A) and dimethylborane (B). Red contour lines denote the region where the electronic charge is concentrated ($\nabla^2\rho < 0$) and blue lines indicate electronic charge depletion ($\nabla^2\rho > 0$). Bond critical points (BCP) are marked as green circles and ring critical points (RCP) as yellow circles. Hydrogen atoms and corresponding bond paths are omitted for clarity.

Table S9. Properties of electron density at bond and ring critical points obtained from AIM computations at the M06-2X/6-311+G** level of theory.

Molecule	BCP	ρ^a	$\nabla^2\rho^b$	ε^c	$\delta(A,B)^d$	Wiberg	$\delta(C1\text{-}C3)^d$
2aH	C1-C2	0.279	-0.660	0.328	1.327	1.226	0.172
	B-C1	0.128	+0.057	6.16	0.403	0.641	
	B-H	0.175	-0.159	0.111	0.615	0.970	
	RCP	0.128	+0.093				
2bH	C1-C2	0.289	-0.715	0.326	1.379	1.293	0.177
	C3-C4	0.368	-1.038	0.119	2.204	2.141	
	B-C1	0.119	+0.082	15.0	0.365	0.589	
	B-C3	0.134	+0.172	6.89	0.424	0.688	
	B-H	0.175	-0.169	0.125	0.618	0.964	
	RCP1	0.119	+0.103				
	RCP2	0.134	+0.216				
2cH	C1-C2	0.375	-1.071	0.119	2.258	2.208	0.179
	B-C1	0.125	+0.190	15.7	0.395	0.639	
	B-H	0.175	-0.177	0.138	0.622	0.965	
	RCP	0.125	+0.216				
borirane	C1-C2	0.222	-0.341	0.592	1.202	0.992	
	B-C1	0.183	-0.059	0.991	0.541	0.939	
	B-H	0.182	-0.378	0.311	0.679	0.975	
	RCP	0.166	+0.032				
borirene	C1-C2	0.323	-0.762	0.029	2.030	1.720	
	B-C1	0.185	+0.293	0.781	0.572	1.143	
	B-H	0.181	-0.351	0.180	0.670	0.978	
	RCP	0.174	+0.442				
borole	B-C1	0.177	-0.227	0.318	0.530	0.911	0.189
	B-H	0.184	-0.318	0.275	0.585	0.983	
	RCP	0.044	+0.252				
$HBMe_2$	B-C1	0.183	-0.233	0.304	0.548		0.141
	B-H	0.179	-0.276	0.329	0.552		
ethyne	C1-C2	0.410	-1.235	0.000	2.851		
ethene	C1-C2	0.343	-1.024	0.331	1.904		

[a] electron density (e $bohr^{-3}$).
[b] Laplacian of electron density (e $bohr^{-5}$).
[c] bond ellipticity.
[d] delocalization index between atoms A(boron or carbon) and B.

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Geometries

Reactions of borirane and borirene with unsaturated hydrocarbons

Hydrocarbons

Ethene

E(HF)=-78.5635539607
ν1=838.2

C	0.000000000	0.000000000	0.662818000
C	0.000000000	0.000000000	-0.662818000
H	0.000000000	0.923212000	1.231258000
H	0.000000000	-0.923212000	1.231258000
H	0.000000000	-0.923212000	-1.231258000
H	0.000000000	0.923212000	-1.231258000

Ethyne

E(HF)=-77.3162766994
ν1=719.3

C	0.000000000	0.000000000	0.598461000
C	0.000000000	0.000000000	-0.598461000
H	0.000000000	0.000000000	1.662693000
H	0.000000000	0.000000000	-1.662693000

Boriranes

H-borirane

E(HF)=-103.978814992
ν1=439.0

C	0.000000000	0.772711000	-0.351919000
B	0.000000000	0.000000000	0.963923000
C	0.000000000	-0.772711000	-0.351919000
H	0.903816000	1.273637000	-0.684460000
H	-0.903816000	1.273637000	-0.684460000
H	0.903816000	-1.273637000	-0.684460000
H	-0.903816000	-1.273637000	-0.684460000
H	0.000000000	0.000000000	2.141258000

F-borirane

E(HF)=-203.291360575
ν1=235.2

C	0.000000000	0.795434000	-0.944417000
B	0.000000000	0.000000000	0.339474000
F	0.000000000	0.000000000	1.652191000
C	0.000000000	-0.795434000	-0.944417000
H	0.904561000	1.271802000	-1.308523000
H	-0.904561000	1.271802000	-1.308523000
H	0.904561000	-1.271802000	-1.308523000
H	-0.904561000	-1.271802000	-1.308523000

Cl-borirane

E(HF)=-563.634529536
ν1=199.3

C	0.000000000	0.784553000	-1.485424000
B	0.000000000	0.000000000	-0.190628000
Cl	0.000000000	0.000000000	1.535261000
C	0.000000000	-0.784553000	-1.485424000
H	0.905654000	1.273036000	-1.830301000
H	-0.905654000	1.273036000	-1.830301000
H	0.905654000	-1.273036000	-1.830301000
H	-0.905654000	-1.273036000	-1.830301000

Me-borirane

E(HF)=-143.302550514
ν1=110.0

C	1.802807740	-0.002973832	0.000000000
B	0.257919744	-0.026529284	0.000000000
C	-1.060369500	0.004108888	0.775988000
C	-1.060369500	0.004108888	-0.775988000
H	-1.384800769	0.914771227	1.269992000
H	-1.422587796	-0.892996830	1.268725000

Borirenes

H-borirene

E(HF)=-102.776170082
ν1=674.3

C	0.000000000	0.674509000	-0.379684000
C	0.000000000	-0.674509000	-0.379684000
B	0.000000000	0.000000000	0.927527000
H	0.000000000	1.487001000	-1.091975000
H	0.000000000	-1.487001000	-1.091975000
H	0.000000000	0.000000000	2.102517000

F-borirene

E(HF)=-202.081536721
ν1=410.4

C	0.000000000	0.680954000	-1.018563000
B	0.000000000	0.000000000	0.276415000
F	0.000000000	0.000000000	1.596370000
C	0.000000000	-0.680954000	-1.018563000
H	0.000000000	1.464892000	-1.763322000
H	0.000000000	-1.464892000	-1.763322000

Cl-borirene

E(HF)=-562.425631142
ν1=318.9

C	0.000000000	0.677560000	-1.572719000
C	0.000000000	-0.677560000	-1.572719000
B	0.000000000	0.000000000	-0.275636000
Cl	0.000000000	0.000000000	1.461118000
H	0.000000000	1.482186000	-2.294092000
H	0.000000000	-1.482186000	-2.294092000

Me-borirene

E(HF)=-142.096865498
ν1=34.6

C	-0.001557000	-1.721016000	0.000000000
B	-0.015177000	-0.166196000	0.000000000
C	-0.001557000	1.146807000	0.674616000
C	-0.001557000	1.146807000	-0.674616000
H	0.003972000	1.871556000	-1.477216000
H	0.003972000	1.871556000	1.477216000

H -1.384800769 0.914771227 -1.269992000 H -1.422587796 -0.892996830 -1.268725000 H 2.250377830 -0.438463327 0.894592000 H 2.250377830 -0.438463327 -0.894592000 H 2.082102926 1.060740525 0.000000000	H -0.472130000 -2.144295000 0.888629000 H -0.472130000 -2.144295000 -0.888629000 H 1.040228000 -2.059128000 0.000000000
Ph-borirane	Ph-borirene
E(HF)=-335.013246578 ν1=79.6 C 0.000000000 1.205238000 0.627795000 C 0.000000000 0.000000000 -0.092551000 C 0.000000000 -1.205238000 0.627795000 C 0.000000000 -1.208697000 2.016714000 C 0.000000000 0.000000000 2.708860000 C 0.000000000 1.208697000 2.016714000 B 0.000000000 0.000000000 -1.622237000 C 0.000000000 -0.776887000 -2.938287000 C 0.000000000 0.776887000 -2.938287000 H -0.904133000 -1.267384000 -3.284953000 H 0.904133000 -1.267384000 -3.284953000 H -0.904133000 1.267384000 -3.284953000 H 0.904133000 1.267384000 -3.284953000 H 0.000000000 -2.142208000 0.081052000 H 0.000000000 -2.145172000 2.561713000 H 0.000000000 0.000000000 3.792951000 H 0.000000000 2.145172000 2.561713000 H 0.000000000 2.142208000 0.081052000	E(HF)=-333.804773880 ν1=49.3 C 0.000000000 1.202487000 0.532299000 C 0.000000000 0.000000000 -0.187440000 C 0.000000000 -1.202487000 0.532299000 C 0.000000000 -1.206136000 1.922227000 C 0.000000000 0.000000000 2.617266000 C 0.000000000 1.206136000 1.922227000 B 0.000000000 0.000000000 -1.728258000 C 0.000000000 -0.674473000 -3.039944000 C 0.000000000 0.674473000 -3.039944000 H 0.000000000 1.478833000 -3.761947000 H 0.000000000 -1.478833000 -3.761947000 H 0.000000000 -2.142313000 -0.009485000 H 0.000000000 -2.144378000 2.464508000 H 0.000000000 0.000000000 3.701198000 H 0.000000000 2.144378000 2.464508000 H 0.000000000 2.142313000 -0.009485000
NH_2-borirane	NH_2-borirene
E(HF)=-159.400241494 ν1=255.8 C 0.000000000 0.782375000 -1.015535000 C 0.000000000 -0.782375000 -1.015535000 B 0.000000000 0.000000000 0.297386000 N 0.000000000 0.000000000 1.677833000 H -0.904578000 -1.262390000 -1.373899000 H -0.904578000 1.262390000 -1.373899000 H 0.904578000 1.262390000 -1.373899000 H 0.904578000 -1.262390000 -1.373899000 H 0.000000000 -0.846091000 2.225132000 H 0.000000000 0.846091000 2.225132000	E(HF)=-158.180098390 ν1=338.3 C 0.000000000 0.672632000 -1.097009000 C 0.000000000 -0.672632000 -1.097009000 B 0.000000000 0.000000000 0.225874000 N 0.000000000 0.000000000 1.621169000 H 0.000000000 1.473408000 -1.823426000 H 0.000000000 -1.473408000 -1.823426000 H 0.000000000 -0.844676000 2.166702000 H 0.000000000 0.844676000 2.166702000
Van der Waals complexes	
VdW R-borirane + ethene	VdW R-borirane + ethyne
VdW F-borirane + ethene	VdW F-borirane + ethyne
E(HF)=-281.861385026 ν1=56.0 C 0.529004000 -1.517832000 0.793834000 B -0.538879000 -0.795462000 0.000000000 F -1.713519000 -0.196794000 0.000000000 C 0.529004000 -1.517832000 -0.793834000 H 0.309242000 -2.468173000 1.270382000 H 1.343148000 -0.981180000 1.267597000 H 0.309242000 -2.468173000 -1.270382000 H 1.343148000 -0.981180000 -1.267597000 C 0.529004000 1.928330000 0.664035000 H -0.395327000 1.917437000 1.231309000 C 0.529004000 1.928330000 -0.664035000 H 1.452923000 1.943153000 -1.231783000 H 1.452923000 1.943153000 1.231783000 H -0.395327000 1.917437000 -1.231309000	E(HF)=-280.613413017 ν1=71.2 C 0.570561000 -1.370399000 0.793782000 B -0.530681000 -0.696708000 0.000000000 F -1.742844000 -0.185306000 0.000000000 C 0.570561000 -1.370399000 -0.793782000 H 0.388511000 -2.327280000 1.273595000 H 1.372442000 -0.807064000 1.257056000 H 0.388511000 -2.327280000 -1.273595000 H 1.372442000 -0.807064000 -1.257056000 C 0.570561000 1.990179000 0.598959000 C 0.570561000 1.990179000 -0.598959000 H 0.561821000 1.991315000 -1.663868000 H 0.561821000 1.991315000 1.663868000
Cl-borirane + ethene	Cl-borirane + ethyne
E(HF)=-642.203881507 ν1=57.6 C 0.952037000 -1.477624000 0.784220000	E(HF)=-640.955921981 ν1=63.2 C 1.007102000 -1.327196000 0.784063000

B -0.197044000 -0.876628000 0.000000000 Cl -1.805269000 -0.229437000 0.000000000 C 0.952037000 -1.477624000 -0.784220000 H 0.823981000 -2.437314000 1.275227000 H 1.684683000 -0.839441000 1.265346000 H 0.823981000 -2.437314000 -1.275227000 H 1.684683000 -0.839441000 -1.265346000 C 0.952037000 2.035057000 0.663800000 H 0.031688000 1.951645000 1.232110000 C 0.952037000 2.035057000 -0.663800000 H 1.872598000 2.122298000 -1.230650000 H 1.872598000 2.122298000 1.230650000 H 0.031688000 1.951645000 -1.232110000	B -0.157094000 -0.751042000 0.000000000 Cl -1.802781000 -0.216058000 0.000000000 C 1.007102000 -1.327196000 -0.784063000 H 0.892274000 -2.285772000 1.280783000 H 1.741711000 -0.682603000 1.252965000 H 0.892274000 -2.285772000 -1.280783000 H 1.741711000 -0.682603000 -1.252965000 C 1.007102000 2.092083000 0.598880000 C 1.007102000 2.092083000 -0.598880000 H 0.997170000 2.093150000 -1.663765000 H 0.997170000 2.093150000 1.663765000
Me-borirane + ethene	Me-borirane + ethyne
E(HF)=-221.871620721 ν1=24.7 C -1.355182000 -0.871946000 0.830206000 C -1.378807000 -0.934951000 -0.719065000 B -0.919579000 0.340851000 0.000014000 C -0.635130000 1.861365000 -0.079620000 C 1.990326000 -0.405555000 -0.650385000 C 2.085751000 -0.081625000 0.633394000 H -2.310399000 -0.859633000 1.346425000 H -0.614429000 -1.489581000 1.326106000 H -2.353273000 -0.947328000 -1.198778000 H -0.669502000 -1.605554000 -1.190672000 H 2.043371000 0.950138000 0.964460000 H 2.035974000 -1.437796000 -0.979945000 H 2.212691000 -0.836509000 1.401441000 H 1.863277000 0.347011000 -1.421016000 H -0.196147000 2.283597000 0.825461000 H -0.039777000 2.147064000 -0.949435000 H -1.615636000 2.340616000 -0.211295000	E(HF)=-220.624522573 ν1=83.3 C 0.658762000 -1.386210000 0.775299000 B -0.480427000 -0.709617000 0.000000000 C 0.658762000 -1.386210000 -0.775299000 H 0.471538000 -2.332494000 1.274646000 H 1.440748000 -0.805512000 1.251801000 H 0.471538000 -2.332494000 -1.274646000 H 1.440748000 -0.805512000 -1.251801000 C 0.658762000 1.980647000 0.598995000 C 0.658762000 1.980647000 -0.598995000 H 0.655504000 1.976258000 -1.663782000 H 0.655504000 1.976258000 1.663782000 C -1.931735000 -0.169767000 0.000000000 H -2.185618000 0.406506000 -0.891206000 H -2.582086000 -1.056074000 0.000000000 H -2.185618000 0.406506000 0.891206000
Ph-borirane + ethene	Ph-borirane + ethyne
E(HF)=-413.582850041 ν1=17.3 C -1.401676000 -2.346458000 0.776888000 B -0.979025000 -1.098483000 0.000000000 C -1.401676000 -2.346458000 -0.776888000 H -2.369704000 -2.378695000 1.267221000 H -0.655183000 -2.966458000 1.261726000 H -2.369704000 -2.378695000 -1.267221000 H -0.655183000 -2.966458000 -1.261726000 C 2.109666000 -1.815970000 0.663573000 H 1.843362000 -0.928379000 1.227707000 C 2.109666000 -1.815970000 -0.663573000 H 2.375241000 -2.700953000 -1.231836000 H 2.375241000 -2.700953000 1.231836000 H 1.843362000 -0.928379000 -1.227707000 C -0.563779000 0.378794000 0.000000000 C -0.361168000 1.070653000 -1.204075000 C -0.361168000 1.070653000 1.204075000 C 0.035570000 2.402211000 -1.208074000 C 0.035570000 2.402211000 1.208074000 C 0.235411000 3.066109000 0.000000000 H -0.518554000 0.547289000 -2.141750000 H -0.518554000 0.547289000 2.141750000 H 0.189753000 2.923709000 -2.145419000 H 0.189753000 2.923709000 2.145419000 H 0.546791000 4.104730000 0.000000000	E(HF)=-412.334158495 ν1=37.0 C -1.265187000 -2.403332000 0.776779000 B -0.827446000 -1.158278000 0.000000000 C -1.265187000 -2.403332000 -0.776779000 H -2.230947000 -2.412831000 1.272924000 H -0.535687000 -3.051151000 1.250252000 H -2.230947000 -2.412831000 -1.272924000 H -0.535687000 -3.051151000 -1.250252000 C 2.140911000 -1.911937000 0.598815000 C 2.140911000 -1.911937000 -0.598815000 H 2.135581000 -1.902848000 -1.663365000 H 2.135581000 -1.902848000 1.663365000 C -0.474037000 0.334407000 0.000000000 C -0.303656000 1.034219000 -1.203459000 C -0.303656000 1.034219000 1.203459000 C 0.026981000 2.383764000 -1.207720000 C 0.026981000 2.383764000 1.207720000 C 0.193625000 3.057121000 0.000000000 H -0.435483000 0.504642000 -2.141439000 H -0.435483000 0.504642000 2.141439000 H 0.155665000 2.912007000 -2.145194000 H 0.155665000 2.912007000 2.145194000 H 0.452870000 4.109993000 0.000000000
NH_2-borirane + ethene	NH_2-borirane + ethyne
E(HF)=-237.967535888 ν1=34.0 C 0.615346000 -1.509403000 0.782411000 B -0.601560000 -1.016781000 0.000000000 C 0.615346000 -1.509403000 -0.782411000	E(HF)=-236.719107747 ν1=54.9 C 0.662955000 -1.318530000 0.782206000 B -0.586013000 -0.906556000 0.000000000 C 0.662955000 -1.318530000 -0.782206000

H 0.607079000 -2.481930000 1.263420000 H 1.285834000 -0.799556000 1.255388000 H 0.607079000 -2.481930000 -1.263420000 H 1.285834000 -0.799556000 -1.255388000 C 0.615346000 2.121730000 0.663210000 H -0.162077000 1.616670000 1.226169000 C 0.615346000 2.121730000 -0.663210000 H 1.392211000 2.620980000 -1.231851000 H 1.392211000 2.620980000 1.231851000 H -0.162077000 1.616670000 -1.226169000 N -1.886218000 -0.505549000 0.000000000 H -2.401536000 -0.318753000 0.845717000 H -2.401536000 -0.318753000 -0.845717000	H 0.714006000 -2.289311000 1.264548000 H 1.297194000 -0.572987000 1.249285000 H 0.714006000 -2.289311000 -1.264548000 H 1.297194000 -0.572987000 -1.249285000 C 0.662955000 2.192559000 0.598607000 C 0.662955000 2.192559000 -0.598607000 H 0.660038000 2.187655000 -1.662981000 H 0.660038000 2.187655000 1.662981000 N -1.919712000 -0.547641000 0.000000000 H -2.442678000 -0.386395000 0.845711000 H -2.442678000 -0.386395000 -0.845711000
R-borirene + ethyne	
H-borirene + ethyne	F-borirene + ethyne
E(HF)=-180.094292426 ν1=23.7 C -1.725692000 -0.664801000 -0.288335000 B -1.029106000 -0.097446000 0.878021000 H -0.476184000 -0.187439000 1.910674000 C -1.630237000 0.676912000 -0.221296000 H -2.135931000 -1.417137000 -0.946567000 H -1.926813000 1.540551000 -0.799912000 C 2.010975000 0.620131000 -0.077867000 C 2.250691000 -0.551396000 -0.136924000 H 2.459508000 -1.593902000 -0.186588000 H 1.790531000 1.660081000 -0.021183000	E(HF)=-279.399891512 ν1=34.7 C 0.594131000 -1.559680000 0.680030000 B -0.528118000 -0.908459000 0.000000000 F -1.696862000 -0.294403000 0.000000000 C 0.594131000 -1.559680000 -0.680030000 H 1.239164000 -1.935517000 1.462299000 H 1.239164000 -1.935517000 -1.462299000 C 0.594131000 2.127504000 -0.598569000 C 0.594131000 2.127504000 0.598569000 H 0.587442000 2.124540000 1.663025000 H 0.587442000 2.124540000 -1.663025000
Cl-borirene + ethyne	Me-borirene + ethyne
E(HF)=-639.745162291 ν1=28.2 C 0.207669000 1.527478000 0.208201000 B 1.101738000 0.387162000 0.014984000 Cl 1.413118000 -1.324788000 -0.008763000 C 1.490399000 1.786566000 -0.145734000 H -0.703282000 2.067211000 0.423577000 H 2.111477000 2.646556000 -0.352106000 C -3.455902000 0.003456000 -0.104893000 C -2.419515000 -0.575885000 0.052115000 H -1.494944000 -1.088447000 0.191037000 H -4.380858000 0.510581000 -0.246588000	E(HF)=-219.416658538 ν1=14.5 C -1.401182000 -1.153345000 -0.004251000 B -1.335474000 0.326546000 -0.000750000 C -2.569467000 -0.479723000 0.004862000 H -1.077002000 -2.186113000 -0.008998000 H -3.626030000 -0.708521000 0.010252000 C 3.400202000 -0.240790000 0.002073000 C 2.221440000 -0.453398000 -0.000180000 H 1.169670000 -0.637046000 -0.002152000 H 4.447694000 -0.052636000 0.004028000 C -0.535559000 1.659417000 -0.001720000 H 0.124598000 1.706514000 -0.872820000 H -1.174116000 2.542927000 -0.004177000 H 0.119963000 1.709179000 0.872916000
Ph-borirene + ethyne	NH_2-borirene + ethyne
E(HF)=-411.123071585 ν1=15.5 C 1.190917000 -2.787266000 0.000547000 B 0.563031000 -1.451775000 -0.006944000 C 2.012770000 -1.717463000 -0.018433000 H 1.273827000 -3.865285000 0.010791000 H 3.073028000 -1.507252000 -0.030454000 C 3.445174000 1.685093000 -0.581530000 C 3.428652000 1.674024000 0.615479000 H 3.409250000 1.661220000 1.679791000 H 3.454666000 1.691583000 -1.646014000 C -0.655850000 -0.508697000 -0.004381000 C -0.484165000 0.882518000 -0.019218000 C -1.961670000 -1.017072000 0.013069000 C -1.580528000 1.737857000 -0.016927000 C -3.061272000 -0.166791000 0.015380000 C -2.869504000 1.212158000 0.000364000 H 0.521687000 1.289367000 -0.032798000 H -2.110864000 -2.091542000 0.024672000 H -1.432636000 2.811505000 -0.028447000 H -4.065515000 -0.574067000 0.028946000 H -3.725741000 1.877178000 0.002129000	E(HF)=-235.500854710 ν1=50.8 C 1.484037000 -1.088280000 -0.000674000 B 1.211168000 0.375740000 -0.000131000 C 2.547997000 -0.266839000 0.001155000 H 1.310463000 -2.156523000 -0.001470000 H 3.625004000 -0.358327000 0.002503000 C -2.151688000 -0.629921000 -0.000358000 C -3.247691000 -0.146458000 0.000811000 H -4.225970000 0.272931000 0.002161000 H -1.165519000 -1.039469000 -0.002236000 N 0.362589000 1.480575000 -0.000683000 H 0.708389000 2.425033000 0.000515000 H -0.642266000 1.402615000 -0.001642000

Transition states TS1_2	
Transition states TS1_2a	**Transition states TS1_2b**
TS1_2a R = F	TS1_2b R = F
E(HF)=-281.860323688 ν1=190.0i C 0.513493000 -1.441076000 0.789448000 B -0.447700000 -0.558950000 0.000000000 F -1.691688000 -0.087219000 0.000000000 C 0.513493000 -1.441076000 -0.789448000 H 0.122615000 -2.332775000 1.270466000 H 1.417264000 -1.070680000 1.256431000 H 0.122615000 -2.332775000 -1.270466000 H 1.417264000 -1.070680000 -1.256431000 C 0.513493000 1.728038000 0.666391000 H -0.391422000 1.915687000 1.233242000 C 0.513493000 1.728038000 -0.666391000 H 1.421478000 1.555861000 -1.232606000 H 1.421478000 1.555861000 1.232606000 H -0.391422000 1.915687000 -1.233242000	E(HF)=-280.611954409 ν1=212.1i C 0.547480000 -1.308004000 0.788744000 B -0.433918000 -0.443092000 0.000000000 F -1.700022000 -0.038374000 0.000000000 C 0.547480000 -1.308004000 -0.788744000 H 0.172444000 -2.206701000 1.269163000 H 1.449308000 -0.923936000 1.249000000 H 0.172444000 -2.206701000 -1.269163000 H 1.449308000 -0.923936000 -1.249000000 C 0.547480000 1.749057000 0.600292000 C 0.547480000 1.749057000 -0.600292000 H 0.543385000 1.764734000 -1.665400000 H 0.543385000 1.764734000 1.665400000
TS1_2a R = Cl	TS1_2b R = Cl
E(HF)=-642.202276595 ν1=204.8i C 0.922054000 -1.421926000 0.781979000 B -0.085192000 -0.584331000 0.000000000 Cl -1.772067000 -0.107065000 0.000000000 C 0.922054000 -1.421926000 -0.781979000 H 0.558894000 -2.315387000 1.280608000 H 1.801892000 -0.999575000 1.249951000 H 0.558894000 -2.315387000 -1.280608000 H 1.801892000 -0.999575000 -1.249951000 C 0.922054000 1.775133000 0.666280000 H 0.024393000 1.987709000 1.235791000 C 0.922054000 1.775133000 -0.666280000 H 1.825718000 1.578891000 -1.231770000 H 1.825718000 1.578891000 1.231770000 H 0.024393000 1.987709000 -1.235791000	E(HF)=-640.954199148 ν1=222.3i C 0.968079000 -1.300336000 0.781213000 B -0.054088000 -0.475952000 0.000000000 Cl -1.753748000 -0.052081000 0.000000000 C 0.968079000 -1.300336000 -0.781213000 H 0.619016000 -2.199648000 1.279116000 H 1.845832000 -0.866000000 1.243074000 H 0.619016000 -2.199648000 -1.279116000 H 1.845832000 -0.866000000 -1.243074000 C 0.968079000 1.784064000 0.600151000 C 0.968079000 1.784064000 -0.600151000 H 0.960283000 1.795849000 -1.665360000 H 0.960283000 1.795849000 1.665360000
TS1_2a R = Me	TS1_2b R = Me
E(HF)=-221.870292979 ν1=205.4i C -1.309925000 -0.793946000 0.803491000 C -1.334009000 -0.819969000 -0.742005000 B -0.607216000 0.324568000 0.002509000 C -0.407512000 1.870418000 -0.044419000 C 1.758475000 -0.441165000 -0.663862000 C 1.819970000 -0.257418000 0.654686000 H -2.233575000 -0.549720000 1.320228000 H -0.766866000 -1.601871000 1.278270000 H -2.271765000 -0.571965000 -1.231646000 H -0.826038000 -1.651267000 -1.213623000 H 1.978322000 0.724152000 1.086064000 H 1.624480000 -1.427497000 -1.091998000 H 1.735770000 -1.086027000 1.347432000 H 1.862733000 0.381623000 -1.361475000 H 0.029117000 2.295995000 0.861155000 H 0.155917000 2.217462000 -0.913677000 H -1.414007000 2.298757000 -0.140619000	E(HF)=-220.623004090 ν1=215.7i C 0.636775000 -1.310859000 0.772641000 B -0.389090000 -0.448208000 0.000000000 C 0.636775000 -1.310859000 -0.772641000 H 0.271290000 -2.202630000 1.273614000 H 1.522517000 -0.898600000 1.240375000 H 0.271290000 -2.202630000 -1.273614000 H 1.522517000 -0.898600000 -1.240375000 C 0.636775000 1.731687000 0.600357000 C 0.636775000 1.731687000 -0.600357000 H 0.638179000 1.744317000 -1.665250000 H 0.638179000 1.744317000 1.665250000 C -1.891138000 -0.031950000 0.000000000 H -2.190276000 0.529470000 -0.887835000 H -2.473734000 -0.962312000 0.000000000 H -2.190276000 0.529470000 0.887835000
TS1_2a R = Ph	TS1_2b R = Ph
E(HF)=-413.580410790 ν1=212.9i C -1.332541000 -2.278129000 0.773968000 B -0.580850000 -1.175542000 0.000000000 C -1.332541000 -2.278129000 -0.773968000	E(HF)=-412.331529056 ν1=219.3i C -1.193438000 -2.354109000 0.773108000 B -0.470557000 -1.229217000 0.000000000 C -1.193438000 -2.354109000 -0.773108000

H -2.254909000 -1.998705000 1.274628000 H -0.834090000 -3.115563000 1.245220000 H -2.254909000 -1.998705000 -1.274628000 H -0.834090000 -3.115563000 -1.245220000 C 1.791242000 -1.920449000 0.666857000 H 1.934360000 -1.006816000 1.232369000 C 1.791242000 -1.920449000 -0.666857000 H 1.670366000 -2.836285000 -1.233269000 H 1.670366000 -2.836285000 1.233269000 H 1.934360000 -1.006816000 -1.232369000 C -0.310287000 0.351166000 0.000000000 C -0.203812000 1.066401000 1.200739000 C -0.203812000 1.066401000 -1.200739000 C 0.008987000 2.440652000 1.205795000 C 0.008987000 2.440652000 -1.205795000 C 0.117633000 3.128173000 0.000000000 H -0.296756000 0.530620000 2.140591000 H -0.296756000 0.530620000 -2.140591000 H 0.086456000 2.976976000 2.144569000 H 0.086456000 2.976976000 -2.144569000 H 0.282807000 4.199538000 0.000000000	H -2.124147000 -2.102516000 1.272719000 H -0.670344000 -3.180027000 1.239480000 H -2.124147000 -2.102516000 -1.272719000 H -0.670344000 -3.180027000 -1.239480000 C 1.814389000 -1.971981000 0.600470000 C 1.814389000 -1.971981000 -0.600470000 H 1.831453000 -1.967608000 -1.665123000 H 1.831453000 -1.967608000 1.665123000 C -0.259816000 0.306470000 0.000000000 C -0.172947000 1.024075000 -1.200278000 C -0.172947000 1.024075000 1.200278000 C 0.003140000 2.403470000 -1.205556000 C 0.003140000 2.403470000 1.205556000 C 0.093887000 3.093794000 0.000000000 H -0.251913000 0.487364000 -2.140837000 H -0.251913000 0.487364000 2.140837000 H 0.066598000 2.941761000 -2.144305000 H 0.066598000 2.941761000 2.144305000 H 0.231338000 4.169097000 0.000000000
TS1_2a R = NH_2	TS1_2b R = NH_2
E(HF)=-237.953457904 ν1=267.6i C 0.567857000 -1.341288000 0.767430000 B -0.387853000 -0.368951000 0.000000000 C 0.567857000 -1.341288000 -0.767430000 H 0.092931000 -2.186609000 1.255305000 H 1.488203000 -1.037006000 1.248217000 H 0.092931000 -2.186609000 -1.255305000 H 1.488203000 -1.037006000 -1.248217000 C 0.567857000 1.580312000 0.671054000 H -0.307179000 1.871098000 1.237959000 C 0.567857000 1.580312000 -0.671054000 H 1.463736000 1.353658000 -1.234345000 H 1.463736000 1.353658000 1.234345000 H -0.307179000 1.871098000 -1.237959000 N -1.785440000 -0.122779000 0.000000000 H -2.333302000 -0.083178000 0.842976000 H -2.333302000 -0.083178000 -0.842976000	E(HF)=-236.703611404 ν1=284.3i C 0.600704000 -1.216699000 0.763017000 B -0.369433000 -0.242703000 0.000000000 C 0.600704000 -1.216699000 -0.763017000 H 0.129528000 -2.064071000 1.249624000 H 1.515316000 -0.894860000 1.245439000 H 0.129528000 -2.064071000 -1.249624000 H 1.515316000 -0.894860000 -1.245439000 C 0.600704000 1.573575000 0.603880000 C 0.600704000 1.573575000 -0.603880000 H 0.629682000 1.661156000 -1.664862000 H 0.629682000 1.661156000 1.664862000 N -1.783995000 -0.086131000 0.000000000 H -2.315409000 0.064732000 0.840866000 H -2.315409000 0.064732000 -0.840866000
Transition states TS1_2c	
TS1_2c R = H	TS1_2c R = F
E(HF)=-180.075747610 ν1=285.9i C 0.163884000 -1.336800000 0.651718000 B -0.699842000 -0.228394000 0.000000000 H -1.858540000 0.027650000 0.000000000 C 0.163884000 -1.336800000 -0.651718000 H 0.508341000 -1.887740000 1.514223000 H 0.508341000 -1.887740000 -1.514223000 C 0.163884000 1.477707000 -0.605739000 C 0.163884000 1.477707000 0.605739000 H 0.203924000 1.599458000 1.663885000 H 0.203924000 1.599458000 -1.663885000	E(HF)=-279.382671057 ν1=270.2i C 0.543225000 -1.362501000 0.660082000 B -0.285562000 -0.265734000 0.000000000 F -1.614340000 0.070804000 0.000000000 C 0.543225000 -1.362501000 -0.660082000 H 0.900064000 -1.956336000 1.490237000 H 0.900064000 -1.956336000 -1.490237000 C 0.543225000 1.483135000 -0.604569000 C 0.543225000 1.483135000 0.604569000 H 0.559672000 1.578250000 1.666377000 H 0.559672000 1.578250000 -1.666377000
TS1_2c R = Cl	TS1_2c R = Me
E(HF)=-639.726860393 ν1=267.7i C 0.965594000 -1.389035000 0.661153000 B 0.097179000 -0.344085000 0.000000000 Cl -1.664483000 0.053522000 0.000000000 C 0.965594000 -1.389035000 -0.661153000 H 1.347668000 -1.955966000 1.497857000 H 1.347668000 -1.955966000 -1.497857000 C 0.965594000 1.519318000 -0.603015000 C 0.965594000 1.519318000 0.603015000 H 0.970366000 1.579544000 1.667362000	E(HF)=-219.390760397 ν1=282.0i C -0.638909000 1.335799000 0.649729000 B 0.235422000 0.212577000 0.000000000 C -0.638909000 1.335799000 -0.649729000 H -0.969056000 1.891096000 1.515517000 H -0.969056000 1.891096000 -1.515517000 C -0.638909000 -1.422197000 -0.607335000 C -0.638909000 -1.422197000 0.607335000 H -0.683051000 -1.574045000 1.662054000 H -0.683051000 -1.574045000 -1.662054000

H 0.970366000 1.579544000 -1.667362000	C 1.805636000 -0.054262000 0.000000000 H 2.140480000 -0.615611000 -0.879150000 H 2.346140000 0.896573000 0.000000000 H 2.140480000 -0.615611000 0.879150000
TS1_2c R = Ph	TS1_2c R = NH_2
E(HF)=-411.100482703 ν1=244.2i C 2.234777000 -1.389161000 0.655793000 B 1.331872000 -0.333216000 0.000000000 C 2.234777000 -1.389161000 -0.655793000 H 2.609654000 -1.942016000 1.505633000 H 2.609654000 -1.942016000 -1.505633000 C 2.234777000 1.470955000 -0.603789000 C 2.234777000 1.470955000 0.603789000 H 2.253151000 1.547046000 1.666919000 H 2.253151000 1.547046000 -1.666919000 C -0.224663000 -0.072071000 0.000000000 C -0.866633000 1.172055000 0.000000000 C -1.048568000 -1.211449000 0.000000000 C -2.256574000 1.277489000 0.000000000 C -2.433545000 -1.114417000 0.000000000 C -3.047226000 0.135920000 0.000000000 H -0.282679000 2.084753000 0.000000000 H -0.588294000 -2.194645000 0.000000000 H -2.720038000 2.257788000 0.000000000 H -3.037429000 -2.015165000 0.000000000 H -4.127927000 0.216590000 0.000000000	E(HF)=-235.457857444 ν1=289.3i C -1.383141000 -0.447861000 0.653419000 B -0.175119000 0.270300000 -0.022091000 C -1.339166000 -0.589322000 -0.640477000 H -2.004561000 -0.642736000 1.516202000 H -1.898358000 -0.976466000 -1.480821000 C 1.364357000 -0.746111000 -0.554525000 C 1.397209000 -0.642340000 0.656174000 H 1.550685000 -0.577808000 1.709143000 H 1.516625000 -0.907334000 -1.598007000 N 0.204332000 1.701002000 -0.023637000 H 0.558972000 2.083017000 -0.891145000 H -0.513644000 2.316612000 0.332989000
Intermediates 2	
Intermediates 2a	**Intermediates 2b**
2a R=H	2b R=H
E(HF)=-182.588056856 ν1=173.0 C 1.330919000 0.712222000 -0.131247000 B 0.000000000 0.000000000 0.619372000 H 0.000000000 0.000000000 1.806107000 C 1.330919000 -0.712222000 -0.131247000 H 1.898013000 1.251073000 0.616123000 H 1.155844000 1.246172000 -1.054381000 H 1.898013000 -1.251073000 0.616123000 H 1.155844000 -1.246172000 -1.054381000 C -1.330919000 0.712222000 -0.131247000 H -1.898013000 1.251073000 0.616123000 C -1.330919000 -0.712222000 -0.131247000 H -1.155844000 -1.246172000 -1.054381000 H -1.155844000 1.246172000 -1.054381000 H -1.898013000 -1.251073000 0.616123000	E(HF)=-181.336780235 ν1=164.0 C 0.147115000 -1.253462000 0.703585000 B -0.659714000 0.097621000 0.000000000 H -1.847826000 0.016915000 0.000000000 C 0.147115000 -1.253462000 -0.703585000 H -0.599550000 -1.814248000 1.249693000 H 1.050401000 -1.012543000 1.246531000 H -0.599550000 -1.814248000 -1.249693000 H 1.050401000 -1.012543000 -1.246531000 C 0.147115000 1.377438000 0.631870000 C 0.147115000 1.377438000 -0.631870000 H 0.356972000 1.830428000 -1.584176000 H 0.356972000 1.830428000 1.584176000
2a R=F	2b R=F
E(HF)=-281.890690305 ν1=143.7 C -0.714726000 1.332174000 -0.478575000 B 0.000000000 0.000000000 0.234454000 F 0.000000000 0.000000000 1.631664000 C 0.714726000 1.332174000 -0.478575000 H -1.244428000 1.853103000 0.309749000 H -1.257530000 1.195310000 -1.402613000 H 1.244428000 1.853103000 0.309749000 H 1.257530000 1.195310000 -1.402613000 C -0.714726000 -1.332174000 -0.478575000 H -1.244428000 -1.853103000 0.309749000 C 0.714726000 -1.332174000 -0.478575000 H 1.257530000 -1.195310000 -1.402613000 H -1.257530000 -1.195310000 -1.402613000 H 1.244428000 -1.853103000 0.309749000	E(HF)=-280.642945623 ν1=131.4 C 0.510330000 -1.265821000 0.702873000 B -0.242382000 0.115804000 0.000000000 F -1.635497000 -0.010099000 0.000000000 C 0.510330000 -1.265821000 -0.702873000 H -0.289249000 -1.756272000 1.243533000 H 1.421268000 -1.072401000 1.250723000 H -0.289249000 -1.756272000 -1.243533000 H 1.421268000 -1.072401000 -1.250723000 C 0.510330000 1.383907000 0.636781000 C 0.510330000 1.383907000 -0.636781000 H 0.709712000 1.876092000 -1.573679000 H 0.709712000 1.876092000 1.573679000
2a R=Cl	2b R=Cl

E(HF)=-642.239869801 ν1=168.7 C -0.713599000 1.332700000 -0.862190000 B 0.000000000 0.000000000 -0.142244000 Cl 0.000000000 0.000000000 1.701012000 C 0.713599000 1.332700000 -0.862190000 H -1.249313000 1.874747000 -0.093401000 H -1.252310000 1.169768000 -1.784952000 H 1.249313000 1.874747000 -0.093401000 H 1.252310000 1.169768000 -1.784952000 C -0.713599000 -1.332700000 -0.862190000 H -1.249313000 -1.874747000 -0.093401000 C 0.713599000 -1.332700000 -0.862190000 H 1.252310000 -1.169768000 -1.784952000 H -1.252310000 -1.169768000 -1.784952000 H 1.249313000 -1.874747000 -0.093401000	E(HF)=-640.990987010 ν1=151.9 C 0.912155000 -1.262202000 0.705006000 B 0.158400000 0.103936000 0.000000000 Cl -1.692975000 0.003227000 0.000000000 C 0.912155000 -1.262202000 -0.705006000 H 0.136214000 -1.787422000 1.246466000 H 1.821638000 -1.048784000 1.249071000 H 0.136214000 -1.787422000 -1.246466000 H 1.821638000 -1.048784000 -1.249071000 C 0.912155000 1.380274000 0.633778000 C 0.912155000 1.380274000 -0.633778000 H 1.090575000 1.840505000 -1.589678000 H 1.090575000 1.840505000 1.589678000
2a R=Me	2b R=Me
E(HF)=-221.900948319 ν1=54.6 C -1.336980000 -0.512693000 0.721606000 C -1.320593000 -0.578149000 -0.701246000 B 0.002452000 0.217649000 0.000395000 C 1.301017000 -0.611919000 -0.701793000 C 1.318811000 -0.547083000 0.722579000 C 0.028581000 1.819526000 -0.034118000 H -1.904942000 0.266041000 1.216041000 H -1.181913000 -1.411425000 1.301579000 H -1.873039000 0.150126000 -1.281262000 H -1.154150000 -1.526747000 -1.191375000 H 1.910473000 0.213693000 1.217170000 H 1.110477000 -1.556023000 -1.191710000 H 1.139815000 -1.441934000 1.301664000 H 1.875671000 0.099308000 -1.281475000 H 0.973131000 2.202954000 -0.435018000 H -0.763604000 2.240004000 -0.662448000 H -0.089201000 2.257659000 0.962691000	E(HF)=-220.649952076 ν1=65.0 C 0.603035000 -1.240185000 0.706511000 B -0.225548000 0.087174000 0.000000000 C 0.603035000 -1.240185000 -0.706511000 H -0.136387000 -1.814514000 1.249928000 H 1.509520000 -1.007350000 1.247375000 H -0.136387000 -1.814514000 -1.249928000 H 1.509520000 -1.007350000 -1.247375000 C 0.603035000 1.366581000 0.630943000 C 0.603035000 1.366581000 -0.630943000 H 0.796116000 1.816362000 -1.588525000 H 0.796116000 1.816362000 1.588525000 C -1.827419000 0.013044000 0.000000000 H -2.262387000 0.499768000 -0.879065000 H -2.194321000 -1.019418000 0.000000000 H -2.262387000 0.499768000 0.879065000
2a R=Ph	2b R=Ph
E(HF)=-413.612284659 ν1=14.2 C 1.324756000 0.712765000 -2.059827000 B 0.000000000 0.000000000 -1.294518000 C 1.324756000 -0.712765000 -2.059827000 H 1.895324000 1.245311000 -1.308983000 H 1.151592000 1.250193000 -2.981157000 H 1.895324000 -1.245311000 -1.308983000 H 1.151592000 -1.250193000 -2.981157000 C -1.324756000 0.712765000 -2.059827000 H -1.895324000 1.245311000 -1.308983000 C -1.324756000 -0.712765000 -2.059827000 H -1.151592000 -1.250193000 -2.981157000 H -1.151592000 1.250193000 -2.981157000 H -1.895324000 -1.245311000 -1.308983000 C 0.000000000 0.000000000 0.298493000 C 0.000000000 1.193763000 1.029927000 C 0.000000000 -1.193763000 1.029927000 C 0.000000000 1.201558000 2.421991000 C 0.000000000 -1.201558000 2.421991000 C 0.000000000 0.000000000 3.123010000 H 0.000000000 2.140035000 0.494945000 H 0.000000000 -2.140035000 0.494945000 H 0.000000000 2.142761000 2.960123000 H 0.000000000 -2.142761000 2.960123000 H 0.000000000 0.000000000 4.206841000	E(HF)=-412.359847319 ν1=11.0 C -2.116224000 0.146848000 -1.444636000 B -1.330435000 0.023142000 0.087152000 C -2.116996000 -1.151202000 -0.895800000 H -1.353096000 0.433198000 -2.157363000 H -3.024273000 0.733650000 -1.455367000 H -1.359880000 -1.863878000 -1.197828000 H -3.026923000 -1.565833000 -0.484763000 C -2.172412000 1.113829000 0.982223000 C -2.172601000 -0.041838000 1.493686000 H -2.389032000 -0.731914000 2.289477000 H -2.392861000 2.166235000 1.004347000 C 0.264255000 0.008621000 0.041425000 C 0.999210000 -1.148888000 0.324155000 C 0.992275000 1.165398000 -0.263762000 C 2.391365000 -1.157909000 0.304026000 C 2.383897000 1.171751000 -0.287817000 C 3.088742000 0.005926000 -0.003698000 H 0.469162000 -2.065082000 0.571973000 H 0.455616000 2.084272000 -0.486277000 H 2.932406000 -2.070211000 0.529709000 H 2.919551000 2.083650000 -0.527583000 H 4.172439000 0.004992000 -0.020900000
2a R=NH_2	2b R=NH_2
E(HF)=-237.968398226	E(HF)=-236.718253416

ν1=172.0 C -0.536178000 1.318569000 0.714928000 B 0.249358000 0.008115000 0.000000000 C -0.536178000 1.318569000 -0.714928000 H 0.205598000 1.900610000 1.247210000 H -1.459890000 1.148982000 1.249620000 H 0.205598000 1.900610000 -1.247210000 H -1.459890000 1.148982000 -1.249620000 C -0.536178000 -1.327438000 0.709383000 H 0.233983000 -1.870583000 1.241189000 C -0.536178000 -1.327438000 -0.709383000 H -1.455349000 -1.152281000 -1.249546000 H -1.455349000 -1.152281000 1.249546000 H 0.233983000 -1.870583000 -1.241189000 N 1.733786000 -0.070592000 0.000000000 H 2.218143000 0.253273000 0.824656000 H 2.218143000 0.253273000 -0.824656000	ν1=124.5 C 0.573530000 -1.259668000 0.700111000 B -0.259191000 0.112913000 0.000000000 C 0.573530000 -1.259668000 -0.700111000 H -0.201875000 -1.788549000 1.238133000 H 1.475475000 -1.024058000 1.247200000 H -0.201875000 -1.788549000 -1.238133000 H 1.475475000 -1.024058000 -1.247200000 C 0.573530000 1.366453000 0.634737000 C 0.573530000 1.366453000 -0.634737000 H 0.806746000 1.841581000 -1.572328000 H 0.806746000 1.841581000 1.572328000 N -1.740589000 -0.066112000 0.000000000 H -2.222668000 0.279422000 0.818865000 H -2.222668000 0.279422000 -0.818865000
Intermediates 2c	
2c R=H	2c R=F
E(HF)=-180.079968896 ν1=135.9 C 1.320953000 0.626067000 -0.158739000 B 0.000000000 0.000000000 0.655341000 H 0.000000000 0.000000000 1.848109000 C 1.320953000 -0.626067000 -0.158739000 H 1.730864000 1.603240000 -0.328771000 H 1.730864000 -1.603240000 -0.328771000 C -1.320953000 0.626067000 -0.158739000 C -1.320953000 -0.626067000 -0.158739000 H -1.730864000 -1.603240000 -0.328771000 H -1.730864000 1.603240000 -0.328771000	E(HF)=-279.387958250 ν1=83.9 C -0.628460000 1.320483000 -0.540140000 B 0.000000000 0.000000000 0.221434000 F 0.000000000 0.000000000 1.620639000 C 0.628460000 1.320483000 -0.540140000 H -1.601996000 1.751946000 -0.682392000 H 1.601996000 1.751946000 -0.682392000 C -0.628460000 -1.320483000 -0.540140000 C 0.628460000 -1.320483000 -0.540140000 H 1.601996000 -1.751946000 -0.682392000 H -1.601996000 -1.751946000 -0.682392000
2c R=Cl	2c R=Me
E(HF)=-639.736023673 ν1=119.2 C -0.627452000 1.323769000 -0.950305000 B 0.000000000 0.000000000 -0.203441000 Cl 0.000000000 0.000000000 1.655941000 C 0.627452000 1.323769000 -0.950305000 H -1.607391000 1.742451000 -1.081620000 H 1.607391000 1.742451000 -1.081620000 C -0.627452000 -1.323769000 -0.950305000 C 0.627452000 -1.323769000 -0.950305000 H 1.607391000 -1.742451000 -1.081620000 H -1.607391000 -1.742451000 -1.081620000	E(HF)=-219.393032930 ν1=72.8 C -1.262588000 -0.726059000 0.624724000 B 0.005396000 0.201548000 -0.001906000 C -1.264759000 -0.726547000 -0.624257000 H -1.648587000 -0.899331000 1.610836000 H -1.653267000 -0.899702000 -1.609383000 C 1.353142000 -0.543771000 0.628965000 C 1.355225000 -0.544155000 -0.628539000 H 1.806629000 -0.694910000 -1.592099000 H 1.801535000 -0.694652000 1.593938000 C -0.144445000 1.799416000 -0.000121000 H -0.588083000 2.173890000 0.929655000 H 0.821995000 2.299175000 -0.114337000 H -0.786652000 2.154487000 -0.813712000
2c R=Ph	
E(HF)=-411.107113863 ν1=46.1 C -0.626375000 1.317126000 -2.204697000 B 0.000000000 0.000000000 -1.388585000 C 0.626375000 1.317126000 -2.204697000 H -1.606209000 1.730292000 -2.353824000 H 1.606209000 1.730292000 -2.353824000 C -0.626375000 -1.317126000 -2.204697000 C 0.626375000 -1.317126000 -2.204697000 H 1.606209000 -1.730292000 -2.353824000 H -1.606209000 -1.730292000 -2.353824000 C 0.000000000 0.000000000 0.201906000 C 0.000000000 1.194615000 0.937308000 C 0.000000000 -1.194615000 0.937308000 C 0.000000000 1.200186000 2.328877000 C 0.000000000 -1.200186000 2.328877000 C 0.000000000 0.000000000 3.032476000	

H 0.000000000 2.144374000 0.411032000 H 0.000000000 -2.144374000 0.411032000 H 0.000000000 2.142240000 2.866104000 H 0.000000000 -2.142240000 2.866104000 H 0.000000000 0.000000000 4.116172000	
Transition states TS2_3	
Transition states TS2_3a	**Transition states TS2_3b**
TS2_3a R=H	TS2_3b R=H
E(HF)=-182.582234163 ν1=307.2i C 0.124665000 0.767866000 1.094847000 B -0.605566000 -0.417128000 0.000000000 H -1.788086000 -0.292626000 0.000000000 C 0.124665000 -0.655712000 1.409892000 H -0.675004000 1.391975000 1.472191000 H 1.072931000 1.275190000 1.011420000 H -0.573099000 -0.998336000 2.163375000 H 1.087146000 -1.152619000 1.421397000 C 0.124665000 0.767866000 -1.094847000 H -0.675004000 1.391975000 -1.472191000 C 0.124665000 -0.655712000 -1.409892000 H 1.087146000 -1.152619000 -1.421397000 H 1.072931000 1.275190000 -1.011420000 H -0.573099000 -0.998336000 -2.163375000	E(HF)=-181.332566994 ν1=287.9i C 0.999388000 0.788148000 -0.044641000 C 1.339434000 -0.600230000 -0.266088000 B -0.040210000 -0.467074000 0.588238000 C -1.447407000 -0.564854000 -0.187759000 C -1.180305000 0.668450000 -0.035973000 H 0.032632000 -0.586862000 1.771935000 H 1.414858000 1.315734000 0.805070000 H 0.772437000 1.419110000 -0.892750000 H 2.125854000 -1.027201000 0.342043000 H 1.274385000 -0.972867000 -1.280320000 H -2.221231000 -1.267672000 -0.439652000 H -1.464544000 1.706053000 -0.040751000
TS2_3a R=F	TS2_3b R=F
E(HF)=-281.888076538 ν1=248.1i C 0.471275000 0.808425000 1.145342000 B -0.228876000 -0.305108000 0.000000000 F -1.617389000 -0.221816000 0.000000000 C 0.471275000 -0.616705000 1.415636000 H -0.358748000 1.408131000 1.499353000 H 1.407387000 1.335539000 1.046665000 H -0.276103000 -1.001643000 2.098560000 H 1.422607000 -1.131408000 1.423467000 C 0.471275000 0.808425000 -1.145342000 H -0.358748000 1.408131000 -1.499353000 C 0.471275000 -0.616705000 -1.415636000 H 1.422607000 -1.131408000 -1.423467000 H 1.407387000 1.335539000 -1.046665000 H -0.276103000 -1.001643000 -2.098560000	E(HF)=-280.641289514 ν1=210.8i C 1.037551000 -0.809794000 -0.582067000 C 1.327942000 -0.335817000 0.739789000 B -0.063228000 0.314881000 0.156853000 C -1.470230000 -0.228703000 0.668266000 C -1.249852000 -0.656699000 -0.510347000 F 0.075725000 1.613356000 -0.325806000 H 1.442386000 -0.282825000 -1.438157000 H 0.788020000 -1.848030000 -0.748443000 H 2.046128000 0.466343000 0.848463000 H 1.245632000 -1.025844000 1.567722000 H -2.196260000 -0.091169000 1.450792000 H -1.563767000 -1.127006000 -1.426235000
TS2_3a R=Cl	TS2_3b R=Cl
E(HF)=-642.234960304 ν1=298.8i C -0.851439000 -0.564037000 1.413315000 B -0.147287000 -0.309269000 0.000000000 Cl 1.689090000 -0.220461000 0.000000000 C -0.851439000 0.861601000 1.110545000 H -0.133691000 -0.922076000 2.140402000 H -1.809911000 -1.067753000 1.422512000 H -0.033280000 1.474464000 1.468193000 H -1.794902000 1.377071000 1.018632000 C -0.851439000 -0.564037000 -1.413315000 H -0.133691000 -0.922076000 -2.140402000 C -0.851439000 0.861601000 -1.110545000 H -1.794902000 1.377071000 -1.018632000 H -1.809911000 -1.067753000 -1.422512000 H -0.033280000 1.474464000 -1.468193000	E(HF)=-640.987759438 ν1=267.4i C -1.063952000 1.043325000 0.672773000 B -0.107050000 -0.062836000 -0.276663000 Cl 1.699453000 -0.030847000 0.099708000 C -0.759036000 1.362439000 -0.702095000 H -0.416835000 1.408284000 1.461473000 H -2.087119000 0.852415000 0.965929000 H 0.021387000 2.087465000 -0.889825000 H -1.569547000 1.337485000 -1.418303000 C -1.052031000 -1.168304000 0.575792000 C -0.810176000 -1.438539000 -0.644896000 H -0.813579000 -2.199729000 -1.404687000 H -1.378588000 -1.440866000 1.564248000
TS2_3a R=Me	TS2_3b R=Me
E(HF)=-221.897308834 ν1=285.8i C -0.552527000 0.601407000 -1.399813000	E(HF)=-220.647443105 ν1=254.2i C -0.813558000 -1.011493000 0.639851000

C -0.552527000 -0.822978000 -1.115538000 B 0.206511000 0.320652000 0.000000000 C -0.552527000 -0.822978000 1.115538000 C -0.552527000 0.601407000 1.399813000 C 1.802991000 0.272579000 0.000000000 H 0.149070000 0.966119000 -2.140754000 H -1.509367000 1.108108000 -1.389910000 H 0.243543000 -1.444425000 -1.506738000 H -1.497678000 -1.333163000 -1.014037000 H 0.149070000 0.966119000 2.140754000 H -1.497678000 -1.333163000 1.014037000 H -1.509367000 1.108108000 1.389910000 H 0.243543000 -1.444425000 1.506738000 H 2.214695000 -0.231109000 0.881224000 H 2.214695000 -0.231109000 -0.881224000 H 2.209616000 1.289067000 0.000000000	C -1.183492000 -0.732159000 -0.725230000 B -0.008920000 0.290264000 -0.207296000 C 1.503218000 -0.081415000 -0.651694000 C 1.342058000 -0.464992000 0.547067000 C -0.433137000 1.775746000 0.206241000 H -1.362859000 -0.551993000 1.453316000 H -0.359116000 -1.960939000 0.886360000 H -2.099915000 -0.182964000 -0.900311000 H -0.926207000 -1.466295000 -1.477381000 H 2.219935000 0.127847000 -1.426102000 H 1.711213000 -0.805358000 1.498636000 H -0.433961000 2.438377000 -0.665603000 H -1.442803000 1.819739000 0.629128000 H 0.247781000 2.216138000 0.941029000
TS2_3a R=Ph	TS2_3b R=Ph
E(HF)=-413.605917986 ν1=308.8i C -2.048604000 -0.964380000 1.086497000 B -1.297641000 0.220300000 0.000000000 C -2.048604000 0.462083000 1.399988000 H -1.245920000 -1.580429000 1.473769000 H -2.994475000 -1.476985000 1.009604000 H -1.356222000 0.796792000 2.162904000 H -3.009440000 0.962214000 1.402543000 C -2.048604000 -0.964380000 -1.086497000 H -1.245920000 -1.580429000 -1.473769000 C -2.048604000 0.462083000 -1.399988000 H -3.009440000 0.962214000 -1.402543000 H -2.994475000 -1.476985000 -1.009604000 H -1.356222000 0.796792000 -2.162904000 C 0.293988000 0.157444000 0.000000000 C 1.005144000 1.365541000 0.000000000 C 1.044630000 -1.022813000 0.000000000 C 2.395336000 1.395878000 0.000000000 C 2.437656000 -1.006216000 0.000000000 C 3.117960000 0.205774000 0.000000000 H 0.453299000 2.301425000 0.000000000 H 0.535729000 -1.983622000 0.000000000 H 2.917250000 2.346270000 0.000000000 H 2.990702000 -1.938857000 0.000000000 H 4.201541000 0.224019000 0.000000000	E(HF)=-412.358186877 ν1=286.2i C 2.216905000 -1.041496000 0.713068000 B 1.311181000 0.062774000 -0.309932000 C 2.126823000 -1.290813000 -0.707291000 H 1.494044000 -1.490982000 1.385283000 H 3.181819000 -0.842926000 1.159796000 H 1.452557000 -2.065697000 -1.048068000 H 3.030478000 -1.175655000 -1.291334000 C 2.173410000 1.143755000 0.721463000 C 2.073505000 1.471816000 -0.502407000 H 2.170368000 2.279850000 -1.206213000 H 2.379080000 1.370171000 1.753351000 C -0.271551000 0.012743000 -0.153418000 C -0.987301000 -1.187578000 -0.048410000 C -1.017494000 1.198319000 -0.119834000 C -2.371762000 -1.207828000 0.087957000 C -2.403576000 1.191108000 0.005238000 C -3.087544000 -0.015010000 0.112375000 H -0.459622000 -2.137267000 -0.070479000 H -0.503223000 2.152252000 -0.192175000 H -2.892978000 -2.155030000 0.171829000 H -2.950372000 2.127387000 0.021535000 H -4.166547000 -0.026080000 0.213702000
TS2_3a R=NH_2	TS2_3b R=NH_2
E(HF)=-237.963155884 ν1=297.5i C 1.134979000 -0.702536000 -0.629663000 B 0.005430000 0.313151000 0.232994000 C 1.376379000 -0.368331000 0.767856000 H 1.559474000 -0.070661000 -1.402139000 H 1.047158000 -1.736453000 -0.923398000 H 2.116758000 0.391583000 0.985701000 H 1.327324000 -1.178879000 1.484592000 C -1.116033000 -0.758982000 -0.649331000 H -1.454874000 -0.168163000 -1.490265000 C -1.421726000 -0.309536000 0.689786000 H -1.434504000 -1.049345000 1.479247000 H -0.999306000 -1.815730000 -0.836277000 H -2.141496000 0.493076000 0.793960000 N -0.053761000 1.710385000 -0.282976000 H 0.766393000 2.039198000 -0.776587000 H -0.279348000 2.393231000 0.429138000	E(HF)=-236.716959603 ν1=197.3i C 1.037477000 0.844850000 0.639489000 C 1.327134000 0.445348000 -0.696169000 B -0.061105000 -0.297050000 -0.146974000 C -1.442049000 0.355188000 -0.696582000 C -1.274299000 0.631229000 0.533992000 N 0.131919000 -1.714445000 0.261991000 H 1.452821000 0.283392000 1.466405000 H 0.738726000 1.861889000 0.851890000 H 2.073240000 -0.323687000 -0.850147000 H 1.208167000 1.164337000 -1.494914000 H -2.128684000 0.324097000 -1.525061000 H -1.632508000 0.996832000 1.482086000 H -0.639482000 -2.136158000 0.761137000 H 0.420221000 -2.344037000 -0.474845000
Transition states TS2_3c	
TS2_3c R=H	TS2_3c R=F
E(HF)=-180.077742530 ν1=238.6i	E(HF)=-279.387661349 ν1=124.5i

C 0.159787000 0.668667000 1.128520000 C 0.159787000 -0.564329000 1.403030000 B -0.646933000 -0.328465000 0.000000000 C 0.159787000 -0.564329000 -1.403030000 C 0.159787000 0.668667000 -1.128520000 H -1.839335000 -0.372440000 0.000000000 H 0.290715000 1.712098000 1.352338000 H 0.328844000 -1.330743000 2.136753000 H 0.328844000 -1.330743000 -2.136753000 H 0.290715000 1.712098000 -1.352338000	C 0.538088000 0.709569000 1.206323000 C 0.538088000 -0.537701000 1.391243000 B -0.219075000 -0.164469000 0.000000000 C 0.538088000 -0.537701000 -1.391243000 C 0.538088000 0.709569000 -1.206323000 F -1.613674000 -0.214992000 0.000000000 H 0.672379000 1.739846000 1.481101000 H 0.679790000 -1.392417000 2.026709000 H 0.679790000 -1.392417000 -2.026709000 H 0.672379000 1.739846000 -1.481101000
TS2_3c R=Cl	TS2_3c R=Me
E(HF)=-639.734449254 ν1=196.5i C 0.945534000 0.810300000 1.140216000 B 0.203001000 -0.175781000 0.000000000 Cl -1.644482000 -0.295906000 0.000000000 C 0.945534000 -0.425911000 1.407728000 H 1.052121000 1.856696000 1.363438000 H 1.072066000 -1.208380000 2.133238000 C 0.945534000 0.810300000 -1.140216000 C 0.945534000 -0.425911000 -1.407728000 H 1.072066000 -1.208380000 -2.133238000 H 1.052121000 1.856696000 -1.363438000	E(HF)=-219.391915307 ν1=190.1i C 1.121958000 0.849134000 0.534324000 C 1.371311000 0.526670000 -0.658077000 B 0.004633000 -0.244447000 -0.154851000 C -1.408631000 0.427645000 -0.659008000 C -1.183338000 0.761194000 0.536891000 C 0.072243000 -1.802817000 0.212637000 H 1.345366000 1.262889000 1.501290000 H 2.065028000 0.486496000 -1.477468000 H -2.103485000 0.349005000 -1.474965000 H -1.446017000 1.157586000 1.501462000 H -0.846935000 -2.328992000 -0.061661000 H 0.897130000 -2.307135000 -0.300825000 H 0.224486000 -1.968568000 1.285810000
TS2_3c R=Ph	
E(HF)=-411.104790622 ν1=138.7i C 0.639347000 -2.298907000 1.122311000 B -0.249407000 -1.366271000 0.000000000 C -0.584024000 -2.140677000 1.399526000 H 1.661361000 -2.548739000 1.347268000 H -1.360428000 -2.194168000 2.140919000 C 0.639347000 -2.298907000 -1.122311000 C -0.584024000 -2.140677000 -1.399526000 H -1.360428000 -2.194168000 -2.140919000 H 1.661361000 -2.548739000 -1.347268000 C -0.109156000 0.216436000 0.000000000 C -0.055465000 0.947153000 1.195091000 C -0.055465000 0.947153000 -1.195091000 C 0.045748000 2.334872000 1.201121000 C 0.045748000 2.334872000 -1.201121000 C 0.097161000 3.035155000 0.000000000 H -0.090139000 0.420032000 2.144088000 H -0.090139000 0.420032000 -2.144088000 H 0.086127000 2.871143000 2.142758000 H 0.086127000 2.871143000 -2.142758000 H 0.177885000 4.115984000 0.000000000	
Products 3	
Products 3a	**Products 3b**
3a R=H	3b R=H
E(HF)=-182.638685304 ν1=209.1 C 0.000000000 0.768351000 -0.960519000 B 0.000000000 0.000000000 1.376393000 C 0.499619000 1.160573000 0.445831000 H -1.025855000 1.129247000 -1.093046000 H 0.598493000 1.189733000 -1.771004000 H 0.275488000 2.184689000 0.749907000 H 1.600327000 1.073910000 0.477734000 C 0.000000000 -0.768351000 -0.960519000 H -0.598493000 -1.189733000 -1.771004000 C -0.499619000 -1.160573000 0.445831000 H -0.275488000 -2.184689000 0.749907000 H 1.025855000 -1.129247000 -1.093046000	E(HF)=-181.422867192 ν1=122.7 C 1.180002000 0.268796000 0.000000000 B -0.983599000 -0.925477000 0.000000000 H -1.809708000 -1.781590000 0.000000000 C 0.576612000 -1.151032000 0.000000000 H 1.812525000 0.460541000 0.873508000 H 1.812525000 0.460541000 -0.873508000 H 0.894500000 -1.736404000 0.869688000 H 0.894500000 -1.736404000 -0.869688000 C 0.000000000 1.200349000 0.000000000 C -1.207932000 0.600335000 0.000000000 H -2.129323000 1.171452000 0.000000000 H 0.150877000 2.278559000 0.000000000

H -1.600327000 -1.073910000 0.477734000 H 0.000000000 0.000000000 2.567110000	
3a R=F	3b R=F
E(HF)=-281.961117093 ν1=119.0 C -0.310872000 0.705167000 -1.419885000 B 0.000000000 0.000000000 0.879443000 C 0.000000000 1.284150000 -0.023275000 H -1.395887000 0.617253000 -1.541510000 H 0.057050000 1.324373000 -2.239896000 H -0.656010000 2.096207000 0.295071000 H 1.023498000 1.687580000 -0.007319000 C 0.310872000 -0.705167000 -1.419885000 H -0.057050000 -1.324373000 -2.239896000 C 0.000000000 -1.284150000 -0.023275000 H 0.656010000 -2.096207000 0.295071000 H 1.395887000 -0.617253000 -1.541510000 H -1.023498000 -1.687580000 -0.007319000 F 0.000000000 0.000000000 2.212001000	E(HF)=-280.743928869 ν1=98.2 C -0.583156000 -1.530341000 0.000000000 B 0.000000000 0.841387000 0.000000000 F -0.078735000 2.173054000 0.000000000 C -1.236717000 -0.132408000 0.000000000 H -0.866345000 -2.125664000 0.873781000 H -0.866345000 -2.125664000 -0.873781000 H -1.875756000 0.027295000 0.873386000 H -1.875756000 0.027295000 -0.873386000 C 0.907206000 -1.290719000 0.000000000 C 1.290802000 -0.002113000 0.000000000 H 2.330840000 0.300880000 0.000000000 H 1.593166000 -2.135074000 0.000000000
3a R=F	3b R=Cl
E(HF)=-642.300836682 ν1=104.2 C 0.000000000 0.769532000 -1.886359000 B 0.000000000 0.000000000 0.417589000 C 0.515777000 1.169295000 -0.486737000 H -1.027016000 1.129229000 -2.009035000 H 0.591128000 1.189404000 -2.702265000 H 0.254841000 2.179354000 -0.166568000 H 1.615329000 1.112825000 -0.465536000 C 0.000000000 -0.769532000 -1.886359000 H -0.591128000 -1.189404000 -2.702265000 C -0.515777000 -1.169295000 -0.486737000 H -0.254841000 -2.179354000 -0.166568000 H 1.027016000 -1.129229000 -2.009035000 H -1.615329000 -1.112825000 -0.465536000 Cl 0.000000000 0.000000000 2.180942000	E(HF)=-641.084073857 ν1=82.9 C -0.456292000 -2.034507000 0.000000000 B 0.000000000 0.366060000 0.000000000 Cl -0.191685000 2.121109000 0.000000000 C -1.179949000 -0.670504000 0.000000000 H -0.709624000 -2.643228000 0.873932000 H -0.709624000 -2.643228000 -0.873932000 H -1.827038000 -0.542039000 0.872771000 H -1.827038000 -0.542039000 -0.872771000 C 1.015850000 -1.716105000 0.000000000 C 1.326547000 -0.405570000 0.000000000 H 2.345521000 -0.038895000 0.000000000 H 1.749508000 -2.519603000 0.000000000
3a R=Me	3b R=Me
E(HF)=-221.960874606 ν1=93.1 C 1.499313000 -0.734461000 0.253087000 B -0.838202000 0.005034000 -0.028687000 C 0.101491000 -1.257323000 -0.133797000 H 1.604628000 -0.754087000 1.343593000 H 2.320212000 -1.323910000 -0.161328000 H -0.217809000 -2.157746000 0.396438000 H 0.096231000 -1.522178000 -1.205082000 C 1.514704000 0.725160000 -0.228868000 H 2.324129000 1.307351000 0.217150000 C 0.107560000 1.262001000 0.103278000 H -0.184170000 2.157052000 -0.451154000 H 1.662652000 0.743200000 -1.314325000 H 0.067978000 1.542786000 1.169350000 C -2.402850000 0.002802000 0.001133000 H -2.855856000 0.916673000 -0.389251000 H -2.851523000 -0.863725000 -0.489844000 H -2.696760000 -0.059662000 1.058892000	E(HF)=-220.744307166 ν1=83.2 C -1.598979000 -0.634500000 0.017428000 B 0.792419000 0.030949000 -0.025660000 C -0.173630000 -1.223628000 -0.019417000 H -2.209828000 -0.945980000 -0.836643000 H -2.157829000 -0.937302000 0.909561000 H -0.009768000 -1.841797000 -0.909290000 H 0.025614000 -1.883826000 0.831525000 C -1.410790000 0.859038000 0.006794000 C -0.130880000 1.276094000 -0.016270000 H 0.126142000 2.330442000 -0.025208000 H -2.275076000 1.520950000 0.018444000 C 2.358318000 -0.005506000 0.005812000 H 2.666504000 0.057737000 1.058657000 H 2.786000000 -0.930266000 -0.387666000 H 2.821914000 0.846305000 -0.497158000
3a R=Ph	3b R=Ph
E(HF)=-413.671373967 ν1=57.8 C -0.308715000 0.703473000 -3.245052000 B 0.000000000 0.000000000 -0.905816000 C 0.007027000 1.268896000 -1.845204000 H -1.394579000 0.619042000 -3.365312000	E(HF)=-412.454846430 ν1=55.1 C -0.504798000 -3.381872000 0.000000000 B 0.085417000 -0.975345000 0.000000000 C -1.142834000 -1.976132000 0.000000000 H -0.793617000 -3.976180000 0.873532000

H	0.059395000	1.327182000	-4.062589000	H	-0.793617000	-3.976180000	-0.873532000
H	-0.620240000	2.112812000	-1.548449000	H	-1.787428000	-1.822623000	0.872246000
H	1.044575000	1.641976000	-1.831369000	H	-1.787428000	-1.822623000	-0.872246000
C	0.308715000	-0.703473000	-3.245052000	C	0.981099000	-3.146837000	0.000000000
H	-0.059395000	-1.327182000	-4.062589000	C	1.359434000	-1.854513000	0.000000000
C	-0.007027000	-1.268896000	-1.845204000	H	2.407532000	-1.573445000	0.000000000
H	0.620240000	-2.112812000	-1.548449000	H	1.670429000	-3.989233000	0.000000000
H	1.394579000	-0.619042000	-3.365312000	C	0.000000000	0.578081000	0.000000000
H	-1.044575000	-1.641976000	-1.831369000	C	1.156445000	1.373021000	0.000000000
C	0.000000000	0.000000000	0.649992000	C	-1.240170000	1.234571000	0.000000000
C	0.000000000	1.200673000	1.376599000	C	1.081620000	2.760922000	0.000000000
C	0.000000000	-1.200673000	1.376599000	C	-1.326519000	2.621360000	0.000000000
C	0.002640000	1.206396000	2.766343000	C	-0.162320000	3.385587000	0.000000000
C	-0.002640000	-1.206396000	2.766343000	H	2.129711000	0.893234000	0.000000000
C	0.000000000	0.000000000	3.461302000	H	-2.152078000	0.645260000	0.000000000
H	-0.000566000	2.144298000	0.840292000	H	1.987148000	3.356666000	0.000000000
H	0.000566000	-2.144298000	0.840292000	H	-2.294544000	3.108805000	0.000000000
H	0.004864000	2.144359000	3.309277000	H	-0.224942000	4.467912000	0.000000000
H	-0.004864000	-2.144359000	3.309277000				
H	0.000000000	0.000000000	4.545392000				

3a R=Ph	3b R=NH_2
E(HF)=-238.059349744 ν1=103.9	E(HF)=-236.840362193 ν1=60.6
C -0.321928000 0.698410000 -1.461074000 B 0.000000000 0.000000000 0.864539000 C 0.000000000 1.283680000 -0.069851000 H -1.407227000 0.589875000 -1.568305000 H 0.023884000 1.321702000 -2.288962000 H -0.662420000 2.099747000 0.228924000 H 1.019157000 1.694963000 -0.078387000 C 0.321928000 -0.698410000 -1.461074000 H -0.023884000 -1.321702000 -2.288962000 C 0.000000000 -1.283680000 -0.069851000 H 0.662420000 -2.099747000 0.228924000 H 1.407227000 -0.589875000 -1.568305000 H -1.019157000 -1.694963000 -0.078387000 N 0.000000000 0.000000000 2.262256000 H 0.029022000 -0.843096000 2.813033000 H -0.029022000 0.843096000 2.813033000	C -0.584632000 -1.578327000 0.000000000 B 0.000000000 0.825698000 0.000000000 C -1.236623000 -0.174484000 0.000000000 H -0.872618000 -2.172291000 0.873763000 H -0.872618000 -2.172291000 -0.873763000 H -1.878187000 -0.032157000 0.874626000 H -1.878187000 -0.032157000 -0.874626000 C 0.906160000 -1.341339000 0.000000000 C 1.284792000 -0.054099000 0.000000000 H 2.331362000 0.233875000 0.000000000 H 1.593349000 -2.185107000 0.000000000 N -0.065794000 2.224635000 0.000000000 H 0.752130000 2.812082000 0.000000000 H -0.932864000 2.736611000 0.000000000

Products 3c

3c R=H	3c R=F
E(HF)=-180.175879750 ν1=214.8	E(HF)=-279.499882371 ν1=151.1
C 0.000000000 0.758140000 -0.896612000 B 0.000000000 0.000000000 1.316268000 H 0.000000000 0.000000000 2.502981000 C 0.000000000 1.251891000 0.347791000 H 0.000000000 1.330887000 -1.818820000 H 0.000000000 2.310718000 0.569586000 C 0.000000000 -0.758140000 -0.896612000 C 0.000000000 -1.251891000 0.347791000 H 0.000000000 -2.310718000 0.569586000 H 0.000000000 -1.330887000 -1.818820000	C 0.000000000 1.263469000 -0.151948000 B 0.000000000 0.000000000 0.792388000 C 0.000000000 -1.263469000 -0.151948000 C 0.000000000 -0.757693000 -1.390579000 C 0.000000000 0.757693000 -1.390579000 F 0.000000000 0.000000000 2.114514000 H 0.000000000 1.325232000 -2.315174000 H 0.000000000 2.320726000 0.074050000 H 0.000000000 -2.320726000 0.074050000 H 0.000000000 -1.325232000 -2.315174000

3c R=Cl	3c R=Me
E(HF)=-639.838875864 ν1=117.0	E(HF)=-219.500044661 ν1=101.2
C 0.000000000 0.757467000 -1.875289000 B 0.000000000 0.000000000 0.308835000 Cl 0.000000000 0.000000000 2.055847000 C 0.000000000 1.258074000 -0.633522000 H 0.000000000 1.329314000 -2.797104000 H 0.000000000 2.312746000 -0.396810000 C 0.000000000 -0.757467000 -1.875289000 C 0.000000000 -1.258074000 -0.633522000 H 0.000000000 -2.312746000 -0.396810000 H 0.000000000 -1.329314000 -2.797104000	C 0.014015000 -1.484013000 0.756426000 B 0.019536000 0.740767000 0.000000000 C 0.014015000 -0.239775000 1.250481000 H 0.013770000 -2.406072000 1.329540000 H 0.014209000 -0.020310000 2.310864000 C 0.014015000 -1.484013000 -0.756426000 C 0.014015000 -0.239775000 -1.250481000 H 0.014209000 -0.020310000 -2.310864000 H 0.013770000 -2.406072000 -1.329540000 C -0.030677000 2.294797000 0.000000000

	H -1.099815000 2.559434000 0.000000000 H 0.396944000 2.753082000 0.893597000 H 0.396944000 2.753082000 -0.893597000
3c R=Ph	3c R=NH_2
E(HF)=-411.211809831 ν1=58.6 C 0.000000000 -0.754789000 -3.267497000 B 0.000000000 0.000000000 -1.047858000 C 0.000000000 -1.251206000 -2.023135000 H 0.000000000 -1.328166000 -4.189272000 H 0.000000000 -2.313632000 -1.814489000 C 0.000000000 0.754789000 -3.267497000 C 0.000000000 1.251206000 -2.023135000 H 0.000000000 2.313632000 -1.814489000 H 0.000000000 1.328166000 -4.189272000 C 0.000000000 0.000000000 0.493563000 C 0.000000000 -1.203511000 1.218926000 C 0.000000000 1.203511000 1.218926000 C 0.000000000 -1.208100000 2.607561000 C 0.000000000 1.208100000 2.607561000 C 0.000000000 0.000000000 3.300664000 H 0.000000000 -2.145675000 0.681176000 H 0.000000000 2.145675000 0.681176000 H 0.000000000 -2.144954000 3.152015000 H 0.000000000 2.144954000 3.152015000 H 0.000000000 0.000000000 4.384804000	E(HF)=-235.603132351 ν1=142.5 C 0.000000000 0.752079000 -1.441398000 B 0.000000000 0.000000000 0.769847000 C 0.000000000 1.254918000 -0.198853000 H 0.000000000 1.324564000 -2.363567000 H 0.000000000 2.317466000 0.010951000 C 0.000000000 -0.752079000 -1.441398000 C 0.000000000 -1.254918000 -0.198853000 H 0.000000000 -2.317466000 0.010951000 H 0.000000000 -1.324564000 -2.363567000 N 0.000000000 0.000000000 2.160087000 H 0.000000000 -0.844934000 2.709195000 H 0.000000000 0.844934000 2.709195000
Reactions of borylenes with 1,5-cyclooctadiene and dibenzo[*a*,*e*]cyclooctatetraene	
Olefins	
COD	DBCOT
E(HF)=-311.960569339 ν1=65.7 C 0.659971000 1.382459000 0.675896000 C 1.563998000 0.599268000 -0.244578000 C -0.659971000 1.799674000 0.007722000 C -1.554295000 0.706033000 -0.513304000 C 0.659971000 -1.799674000 0.007722000 C -0.659971000 -1.382459000 0.675896000 C -1.563998000 -0.599268000 -0.244578000 C 1.554295000 -0.706033000 -0.513304000 H -2.303336000 1.057279000 -1.220165000 H -2.305524000 -1.194147000 -0.772919000 H 2.305524000 1.194147000 -0.772919000 H 2.303336000 -1.057279000 -1.220165000 H -1.234985000 2.420608000 0.706014000 H -0.422535000 2.455871000 -0.837578000 H 1.182211000 2.297523000 0.967613000 H 0.468953000 0.845294000 1.602621000 H -0.468953000 -0.845294000 1.602621000 H -1.182211000 -2.297523000 0.967613000 H 1.234985000 -2.420608000 0.706014000 H 0.422535000 -2.455871000 -0.837578000	E(HF)=-616.785101971 ν1=48.7 C 3.372286000 0.696233000 -1.211982000 C 3.372286000 -0.696233000 -1.211982000 C 2.480504000 1.380056000 -0.400479000 H 4.070693000 -1.244644000 -1.832711000 H 2.488001000 2.464694000 -0.382394000 C 2.480504000 -1.380056000 -0.400479000 C 1.554404000 0.700796000 0.400287000 H 2.488001000 -2.464694000 -0.382394000 C 0.666206000 1.513966000 1.264262000 C 1.554404000 -0.700796000 0.400287000 C 0.666206000 -1.513966000 1.264262000 H 4.070693000 1.244644000 -1.832711000 C -1.554404000 0.700796000 0.400287000 C -1.554404000 -0.700796000 0.400287000 C -2.480504000 1.380056000 -0.400479000 C -0.666206000 -1.513966000 1.264262000 H -2.488001000 2.464694000 -0.382394000 C -2.480504000 -1.380056000 -0.400479000 C -3.372286000 0.696233000 -1.211982000 H -2.488001000 -2.464694000 -0.382394000 H -4.070693000 1.244644000 -1.832711000 C -3.372286000 -0.696233000 -1.211982000 H -4.070693000 -1.244644000 -1.832711000 C -0.666206000 1.513966000 1.264262000 H 1.172925000 -2.234034000 1.902583000 H -1.172925000 -2.234034000 1.902583000 H 1.172925000 2.234034000 1.902583000 H -1.172925000 2.234034000 1.902583000
Borylenes	
BH	BCl
E(HF)=-25.2804987331 ν1=2477.6 B 0.000000000 0.000000000 0.205109000	E(HF)=-484.975872642 ν1=821.8 B 0.000000000 0.000000000 -1.334447000

H 0.000000000 0.000000000 -1.025543000	Cl 0.000000000 0.000000000 0.392484000
BMe	BNH_2
E(HF)=-64.6200612489 ν1=556.0 B 0.000000000 0.000000000 -1.068658000 C 0.000000000 0.000000000 0.468326000 H 0.000000000 1.030434000 0.844444000 H 0.892382000 -0.515217000 0.844444000 H -0.892382000 -0.515217000 0.844444000	E(HF)=-80.7288821899 ν1=439.2 B 0.000000000 0.000000000 -0.962635000 N 0.000000000 0.000000000 0.413434000 H 0.000000000 -0.853464000 0.959569000 H 0.000000000 0.853464000 0.959569000
Transition states TS4_5	
Transition states TS4_5a	**Transition states TS4_5b**
TS4_5a R=Cl	TS4_5b R=Cl
E(HF)=-796.935734462 ν1=308.9i C -0.505601000 1.028400000 1.563139000 C -2.198359000 -0.217413000 -0.651087000 C -1.690380000 -1.518799000 0.002528000 C -0.062641000 1.943611000 0.404483000 C -1.147346000 0.515186000 -1.443590000 C -0.372821000 -1.418455000 0.739898000 C -0.280607000 1.428700000 -0.995306000 C 0.057540000 -0.367683000 1.505617000 H -0.156146000 1.488409000 2.490736000 H -3.015941000 -0.485113000 -1.324521000 H -1.571771000 -2.283956000 -0.767411000 H 1.010101000 2.131781000 0.513889000 H -1.094093000 0.269623000 -2.500478000 H 0.046823000 -2.389915000 0.996556000 H 0.387714000 1.865270000 -1.734682000 H 0.940139000 -0.544258000 2.112728000 H -0.545747000 2.922893000 0.511964000 H -2.633616000 0.440731000 0.098414000 H -1.592250000 1.000597000 1.637543000 H -2.448608000 -1.878740000 0.706790000 B 0.987988000 -1.168060000 -0.687414000 Cl 2.525573000 -0.297547000 -0.356385000	E(HF)=-1101.75676074 ν1=312.9i C 3.711788000 -1.015303000 -0.947083000 C 3.762312000 -1.319599000 0.409833000 C 2.673824000 -0.236859000 -1.438594000 H 4.572941000 -1.918875000 0.806470000 H 2.640905000 0.015080000 -2.493323000 C 2.772555000 -0.842150000 1.256366000 C 1.662530000 0.233028000 -0.596841000 H 2.812045000 -1.063393000 2.317448000 C 0.588214000 1.059019000 -1.223542000 C 1.709759000 -0.078777000 0.766008000 C 0.698233000 0.428518000 1.718739000 H 4.483154000 -1.373793000 -1.617993000 C -1.421858000 -0.423416000 -0.671422000 C -1.334653000 -0.688175000 0.704894000 C -2.259765000 -1.226271000 -1.460111000 C -0.612099000 0.183766000 1.670069000 H -2.352447000 -1.000106000 -2.517017000 C -2.048913000 -1.764686000 1.236317000 C -2.947662000 -2.303031000 -0.923182000 H -1.989472000 -1.950863000 2.303414000 H -3.575855000 -2.915728000 -1.558711000 C -2.834568000 -2.581896000 0.435040000 H -3.371202000 -3.415241000 0.872163000 C -0.716280000 0.663892000 -1.362464000 H 1.079622000 1.021220000 2.546370000 H -1.235290000 0.605473000 2.455532000 H 0.958856000 1.714638000 -2.008064000 H -1.307280000 1.191874000 -2.106265000 B 0.225340000 2.629327000 0.011350000 Cl -1.427246000 3.259690000 0.205827000
TS4_5a R=Me	TS4_5b R=Me
E(HF)=-376.586937583 ν1=171.9i C -0.137485000 1.077237000 1.516300000 C -1.941709000 -0.056144000 -0.657942000 C -1.603387000 -1.369471000 0.076896000 C 0.369062000 1.918749000 0.328242000 C -0.803143000 0.509437000 -1.467900000 C -0.316504000 -1.391577000 0.861821000 C 0.142508000 1.356088000 -1.051810000 C 0.293042000 -0.369162000 1.491976000 H 0.255219000 1.532439000 2.429442000 H -2.772122000 -0.267656000 -1.336327000 H -1.537330000 -2.173326000 -0.658877000 H 1.447043000 2.071187000 0.450531000 H -0.764837000 0.201160000 -2.508569000 H 0.064273000 -2.390198000 1.059337000 H 0.862051000 1.689605000 -1.797465000 H 1.187748000 -0.606246000 2.062983000 H -0.067396000 2.923595000 0.390775000 H -2.315101000 0.691212000 0.040481000 H -1.221312000 1.144833000 1.597446000	E(HF)=-681.409805615 ν1=178.3i C 3.593984000 -1.196414000 -0.884584000 C 3.597630000 -1.437340000 0.486032000 C 2.628618000 -0.364056000 -1.431158000 H 4.352582000 -2.076300000 0.928196000 H 2.634338000 -0.157025000 -2.496010000 C 2.636621000 -0.840106000 1.287799000 C 1.638470000 0.221035000 -0.635490000 H 2.647060000 -1.005134000 2.359874000 C 0.660874000 1.101243000 -1.322454000 C 1.642640000 -0.021315000 0.742271000 C 0.682345000 0.612155000 1.673488000 H 4.346806000 -1.644248000 -1.522107000 C -1.499104000 -0.077355000 -0.678487000 C -1.478098000 -0.289285000 0.708981000 C -2.402551000 -0.810878000 -1.459634000 C -0.646990000 0.496142000 1.655600000 H -2.432325000 -0.626982000 -2.528396000 C -2.349538000 -1.233683000 1.263981000 C -3.241386000 -1.761821000 -0.900155000

H -2.432640000 -1.618025000 0.750415000 B 1.281634000 -1.413909000 -0.912327000 C 2.642553000 -0.724498000 -0.528162000 H 2.622378000 0.297249000 -0.149349000 H 3.112437000 -1.364944000 0.231802000 H 3.281803000 -0.765303000 -1.417517000	H -2.341106000 -1.377978000 2.339169000 H -3.920579000 -2.323755000 -1.529976000 C -3.213393000 -1.977469000 0.474436000 H -3.871000000 -2.708914000 0.928544000 C -0.672937000 0.926617000 -1.383290000 H 1.132396000 1.164346000 2.494550000 H -1.200988000 0.969022000 2.464110000 H 1.103594000 1.796963000 -2.028757000 H -1.220374000 1.546552000 -2.090217000 B 0.285950000 3.013777000 0.162753000 C -1.229040000 3.422847000 0.250840000 H -1.466169000 3.948952000 -0.685065000 H -1.974455000 2.641250000 0.406777000 H -1.308391000 4.162465000 1.056475000
TS4_5a R=NH_2	TS4_5b R=NH_2
E(HF)=-392.687825123 ν1=290.6i C 0.106680000 0.926999000 1.567723000 C 0.287725000 1.892734000 0.381808000 C -0.347883000 1.524450000 -0.932276000 C -1.303291000 0.637540000 -1.207036000 C -2.051937000 -0.258385000 -0.253736000 C -1.327849000 -1.579832000 0.054236000 C 0.069127000 -1.485800000 0.619383000 C 0.619618000 -0.475987000 1.345574000 B 1.367072000 -1.175596000 -1.053554000 N 2.529412000 -0.419768000 -0.863225000 H 0.658486000 1.349175000 2.411939000 H -3.012103000 -0.514622000 -0.709080000 H -1.268992000 -2.180651000 -0.856174000 H 1.360951000 2.018279000 0.195052000 H -1.559071000 0.513915000 -2.255966000 H 0.541876000 -2.458402000 0.729439000 H 0.068161000 2.063785000 -1.780878000 H 1.573138000 -0.701035000 1.819281000 H -0.066280000 2.886371000 0.684221000 H -2.295083000 0.264750000 0.669061000 H -0.936556000 0.914858000 1.881393000 H -1.932668000 -2.143785000 0.774787000 H 3.178674000 -0.405738000 -1.637576000 H 2.835099000 0.119141000 -0.069212000	E(HF)=-697.511625921 ν1=268.2i C 3.538209000 -1.187547000 -1.047960000 C 3.528924000 -1.645483000 0.266036000 C 2.603880000 -0.245684000 -1.451287000 H 4.260119000 -2.371946000 0.599940000 H 2.621543000 0.127473000 -2.469708000 C 2.585325000 -1.151254000 1.153771000 C 1.630982000 0.240413000 -0.570964000 H 2.584883000 -1.486233000 2.185608000 C 0.678819000 1.238395000 -1.127789000 C 1.621021000 -0.222428000 0.749255000 C 0.686209000 0.289090000 1.774209000 H 4.277166000 -1.553060000 -1.751037000 C -1.555129000 0.078590000 -0.636577000 C -1.521549000 -0.346843000 0.703189000 C -2.539213000 -0.457215000 -1.483920000 C -0.643542000 0.243948000 1.744829000 H -2.582573000 -0.108663000 -2.510435000 C -2.444021000 -1.307448000 1.132864000 C -3.432690000 -1.422227000 -1.048834000 H -2.420450000 -1.616335000 2.172816000 H -4.169929000 -1.825337000 -1.732928000 C -3.380618000 -1.859278000 0.271670000 H -4.075475000 -2.608211000 0.632173000 C -0.668038000 1.088358000 -1.237185000 H 1.157387000 0.706356000 2.660648000 H -1.173945000 0.626075000 2.614462000 H 1.136886000 1.911146000 -1.845033000 H -1.165564000 1.764280000 -1.930121000 B 0.556149000 2.952311000 0.257536000 N -0.713053000 3.469235000 0.510372000 H -0.754294000 4.318356000 1.057608000 H -1.616548000 3.069583000 0.307876000
Intermediates 5	
Intermediates 5a	**Intermediates 5b**
5a R=H	5b R=H
E(HF)=-337.408267586 ν1=182.1 C 1.208141000 -0.947985000 -0.827371000 C -1.208141000 0.947985000 -0.827371000 C 0.000000000 1.858696000 -0.567444000 C 0.000000000 -1.858696000 -0.567444000 C -1.400908000 0.097309000 0.425840000 C 0.828092000 1.210976000 0.533327000 C -0.828092000 -1.210976000 0.533327000 C 1.400908000 -0.097309000 0.425840000 H 2.109568000 -1.527704000 -1.035429000 H -2.109568000 1.527704000 -1.035429000 H -0.346042000 2.826295000 -0.196963000 H 0.346042000 -2.826295000 -0.196963000 H -2.265084000 0.309220000 1.044930000 H 1.298402000 1.883399000 1.243288000 H -1.298402000 -1.883399000 1.243288000	E(HF)=-642.230513456 ν1=50.5 C -0.696427000 2.768209000 -1.672941000 C 0.696427000 2.768209000 -1.672941000 C -1.404779000 2.114538000 -0.665909000 H 1.232941000 3.281467000 -2.462355000 H -2.489094000 2.110537000 -0.667201000 C 1.404779000 2.114538000 -0.665909000 C -0.695239000 1.480129000 0.345719000 H 2.489094000 2.110537000 -0.667201000 C -1.252656000 0.720453000 1.505973000 C 0.695239000 1.480129000 0.345719000 C 1.252656000 0.720453000 1.505973000 H -1.232941000 3.281467000 -2.462355000 C -0.695239000 -1.480129000 0.345719000 C 0.695239000 -1.480129000 0.345719000 C -1.404779000 -2.114538000 -0.665909000

H 2.265084000 -0.309220000 1.044930000 H -0.591884000 -2.056641000 -1.468875000 H -1.051409000 0.305164000 -1.697194000 H 1.051409000 -0.305164000 -1.697194000 H 0.591884000 2.056641000 -1.468875000 B 0.000000000 0.000000000 1.377252000 H 0.000000000 0.000000000 2.561992000	C 1.252656000 -0.720453000 1.505973000 H -2.489094000 -2.110537000 -0.667201000 C 1.404779000 -2.114538000 -0.665909000 C -0.696427000 -2.768209000 -1.672941000 H 2.489094000 -2.110537000 -0.667201000 H -1.232941000 -3.281467000 -2.462355000 C 0.696427000 -2.768209000 -1.672941000 H 1.232941000 -3.281467000 -2.462355000 C -1.252656000 -0.720453000 1.505973000 H 1.964345000 1.222255000 2.153409000 H 1.964345000 -1.222255000 2.153409000 H -1.964345000 1.222255000 2.153409000 H -1.964345000 -1.222255000 2.153409000 B 0.000000000 0.000000000 2.402297000 H 0.000000000 0.000000000 3.584902000
5a R=Cl	5b R=Cl
E(HF)=-797.059962023 ν1=161.2 C 0.866531000 1.283797000 -1.450504000 C -0.866531000 -1.283797000 -1.450504000 C -1.854481000 -0.134526000 -1.197798000 C 1.854481000 0.134526000 -1.197798000 C 0.000000000 -1.407201000 -0.198656000 C -1.264866000 0.735335000 -0.096942000 C 1.264866000 -0.735335000 -0.096942000 C 0.000000000 1.407201000 -0.198656000 H 1.385212000 2.223606000 -1.646830000 H -1.385212000 -2.223606000 -1.646830000 H -2.800222000 -0.537937000 -0.830032000 H 2.800222000 0.537937000 -0.830032000 H -0.148523000 -2.269195000 0.442433000 H -1.958578000 1.140399000 0.633172000 H 1.958578000 -1.140399000 0.633172000 H 0.148523000 2.269195000 0.442433000 H 2.083388000 -0.441012000 -2.101449000 H -0.236472000 -1.092036000 -2.322696000 H 0.236472000 1.092036000 -2.322696000 H -2.083388000 0.441012000 -2.101449000 B 0.000000000 0.000000000 0.725404000 Cl 0.000000000 0.000000000 2.550034000	E(HF)=-1101.88110700 ν1=50.0 C -0.696583000 2.788380000 -2.186503000 C 0.696583000 2.788380000 -2.186503000 C -1.405817000 2.129981000 -1.183808000 H 1.232635000 3.306243000 -2.973083000 H -2.489954000 2.127573000 -1.184366000 C 1.405817000 2.129981000 -1.183808000 C -0.695315000 1.487927000 -0.177770000 H 2.489954000 2.127573000 -1.184366000 C -1.250143000 0.722332000 0.979319000 C 0.695315000 1.487927000 -0.177770000 C 1.250143000 0.722332000 0.979319000 H -1.232635000 3.306243000 -2.973083000 C -0.695315000 -1.487927000 -0.177770000 C 0.695315000 -1.487927000 -0.177770000 C -1.405817000 -2.129981000 -1.183808000 C 1.250143000 -0.722332000 0.979319000 H -2.489954000 -2.127573000 -1.184366000 C 1.405817000 -2.129981000 -1.183808000 C -0.696583000 -2.788380000 -2.186503000 H 2.489954000 -2.127573000 -1.184366000 H -1.232635000 -3.306243000 -2.973083000 C 0.696583000 -2.788380000 -2.186503000 H 1.232635000 -3.306243000 -2.973083000 C -1.250143000 -0.722332000 0.979319000 H 1.947338000 1.217868000 1.648353000 H 1.947338000 -1.217868000 1.648353000 H -1.947338000 1.217868000 1.648353000 H -1.947338000 -1.217868000 1.648353000 B 0.000000000 0.000000000 1.854820000 Cl 0.000000000 0.000000000 3.671328000
5a R=Me	5b R=Me
E(HF)=-376.721555824 ν1=63.2 C 1.162252000 1.196441000 -0.986146000 C 1.179599000 -1.161477000 1.004339000 C 0.956306000 -1.798274000 -0.375075000 C 0.889489000 1.826288000 0.387111000 C -0.092453000 -0.388200000 1.344705000 C -0.157274000 -1.016163000 -1.055709000 C -0.214157000 1.009956000 1.043415000 C -0.075433000 0.380327000 -1.350410000 H 1.352123000 1.957113000 -1.746067000 H 1.379690000 -1.917895000 1.765823000 H 0.613094000 -2.827992000 -0.252361000 H 0.518112000 2.845251000 0.256533000 H -0.713351000 -0.773953000 2.146176000 H -0.859762000 -1.591694000 -1.651223000 H -0.936990000 1.564574000 1.634437000 H -0.706633000 0.753443000 -2.150063000 H 1.786077000 1.892612000 1.014453000 H 2.043122000 -0.490996000 1.005770000 H 2.046171000 0.553574000 -0.969410000	C 2.761147000 -1.967826000 -0.690071000 C 2.110011000 -0.962472000 -1.402911000 C 1.479961000 0.054571000 -0.697049000 C 1.481634000 0.062843000 0.693519000 C 2.114724000 -0.947049000 1.407189000 C 2.763500000 -1.960005000 0.702943000 C 0.728195000 1.231250000 1.239319000 B 0.012924000 2.142071000 -0.002972000 C 0.724284000 1.216549000 -1.254253000 C -0.713344000 1.224796000 -1.253314000 C -1.481651000 0.070888000 -0.696939000 C -2.122335000 -0.939412000 -1.402932000 C -2.783667000 -1.937996000 -0.689968000 C -2.785736000 -1.930243000 0.703083000 C -2.126488000 -0.924108000 1.407360000 C -1.483092000 0.079093000 0.693472000 C -0.717016000 1.239432000 1.238388000 H -3.301181000 -2.727155000 -1.222778000 H -2.124206000 -0.919921000 2.491662000

H 1.866865000 -1.836916000 -0.984360000 B -1.048350000 -0.018848000 -0.006422000 C -2.644134000 -0.035888000 -0.015766000 H -3.059690000 -0.973053000 -0.399430000 H -3.041841000 0.086246000 0.997555000 H -3.070402000 0.775870000 -0.614508000	H -2.116692000 -0.946612000 -2.487207000 H -3.304935000 -2.713648000 1.242715000 H 2.112857000 -0.942646000 2.491496000 H 2.104313000 -0.969528000 -2.487195000 H 3.275090000 -2.748433000 1.242542000 H 3.270799000 -2.762069000 -1.222920000 H -1.211550000 1.883983000 -1.958405000 H 1.229224000 1.869283000 -1.960676000 H -1.211498000 1.890528000 1.953447000 H 1.229140000 1.875929000 1.955814000 C 0.030728000 3.733736000 -0.005615000 H 0.965446000 4.145564000 -0.398487000 H -0.788147000 4.164786000 -0.589952000 H -0.078417000 4.125311000 1.011485000
5a R=NH_2	5b R=NH_2
E(HF)=-392.788830870 ν1=176.0 C 1.176471000 1.172890000 -0.980390000 C 1.130312000 -1.200787000 0.998123000 C 0.889469000 -1.814736000 -0.389759000 C 0.922007000 1.799126000 0.399607000 C -0.117535000 -0.395284000 1.350267000 C -0.201938000 -0.998022000 -1.064571000 C -0.204047000 1.009303000 1.050619000 C -0.079326000 0.391727000 -1.351535000 H 1.383673000 1.935133000 -1.734126000 H 1.309750000 -1.972615000 1.749296000 H 0.521710000 -2.837533000 -0.280450000 H 0.580598000 2.829779000 0.277517000 H -0.743892000 -0.761496000 2.156362000 H -0.939277000 -1.542059000 -1.645750000 H -0.906130000 1.577137000 1.654031000 H -0.724473000 0.794587000 -2.123782000 H 1.821450000 1.834966000 1.025096000 H 2.013610000 -0.556600000 1.006865000 H 2.045465000 0.509936000 -0.968825000 H 1.799479000 -1.867769000 -0.998286000 B -1.072204000 0.011595000 0.005563000 N -2.544973000 0.017004000 -0.091358000 H -3.032148000 0.870096000 0.138718000 H -3.046468000 -0.775863000 0.280859000	E(HF)=-697.613103471 ν1=50.6 C -1.935250000 -0.690101000 2.791425000 C -1.924415000 0.703180000 2.799357000 C -0.940483000 -1.401940000 2.123944000 H -2.704937000 1.242465000 3.323250000 H -0.948936000 -2.486167000 2.114999000 C -0.919432000 1.407536000 2.139304000 C 0.068893000 -0.696020000 1.481038000 H -0.912468000 2.491863000 2.141811000 C 1.221240000 -1.256528000 0.715665000 C 0.079605000 0.695034000 1.486946000 C 1.239493000 1.242411000 0.724334000 H -2.723784000 -1.223545000 3.309227000 C 0.068893000 -0.696020000 -1.481038000 C 0.079605000 0.695034000 -1.486946000 C -0.940483000 -1.401940000 -2.123944000 C 1.239493000 1.242411000 -0.724334000 H -0.948936000 -2.486167000 -2.114999000 C -0.919432000 1.407536000 -2.139304000 C -1.935250000 -0.690101000 -2.791425000 H -0.912468000 2.491863000 -2.141811000 H -2.723784000 -1.223545000 -3.309227000 C -1.924415000 0.703180000 -2.799357000 H -2.704937000 1.242465000 -3.323250000 C 1.221240000 -1.256528000 -0.715665000 H 1.880888000 1.969451000 1.213803000 H 1.880888000 1.969451000 -1.213803000 H 1.897022000 -1.944556000 1.214293000 H 1.897022000 -1.944556000 -1.214293000 B 2.154030000 0.008484000 0.000000000 N 3.619198000 -0.082049000 0.000000000 H 4.122041000 0.195023000 0.829251000 H 4.122041000 0.195023000 -0.829251000
Transition states TS5_6	
Transition states TS5_6a	**Transition states TS5_6b**
TS5_6a R=H	TS5_6b R=H
E(HF)=-337.386271833 ν1=362.5i C 1.155533000 0.861496000 -0.965456000 C -1.361088000 -0.983782000 -0.684568000 C -1.847621000 0.458369000 -0.545623000 C 1.617889000 -0.607858000 -0.727067000 C -0.527985000 -1.026083000 0.601794000 C -0.890404000 0.877247000 0.571912000 C 0.962920000 -1.086510000 0.569076000 C 0.503279000 1.368006000 0.330549000 H 2.011015000 1.491458000 -1.215203000 H -2.150239000 -1.737400000 -0.694424000 H -2.876647000 0.505414000 -0.185225000 H 2.700505000 -0.630609000 -0.580566000 H -0.986010000 -1.555357000 1.431446000 H -1.368554000 1.359126000 1.420326000 H 1.411814000 -1.929784000 1.082728000	E(HF)=-337.386271833 ν1=362.5i

H 0.688379000 2.396543000 0.620434000 H 1.406712000 -1.248809000 -1.589337000 H -0.740472000 -1.141913000 -1.566700000 H 0.471865000 0.928221000 -1.818724000 H -1.775749000 1.078511000 -1.442069000 B 0.609930000 0.207439000 1.409409000 H 0.482586000 0.282093000 2.586565000	
TS5_6a R=Cl	TS5_6b R=H
E(HF)=-797.039888507 ν1=378.6i C -1.169128000 1.396955000 0.981931000 C -1.750138000 -1.052566000 -0.899619000 C -1.582718000 -1.605591000 0.514699000 C -0.982340000 1.832917000 -0.503937000 C -0.312088000 -0.565816000 -1.102994000 C -0.224232000 -0.977869000 0.827161000 C 0.033442000 0.882604000 -1.139594000 C -0.040854000 0.415229000 1.337004000 H -1.119639000 2.265762000 1.639758000 H -2.045284000 -1.789283000 -1.648172000 H -1.491005000 -2.692709000 0.516499000 H -0.559677000 2.839523000 -0.538208000 H 0.323008000 -1.199873000 -1.714790000 H 0.529948000 -1.667324000 1.198149000 H 0.579544000 1.220101000 -2.013576000 H 0.430065000 0.501812000 2.309835000 H -1.934684000 1.874721000 -1.041241000 H -2.457747000 -0.224803000 -0.951691000 H -2.155731000 0.950115000 1.142346000 H -2.362437000 -1.331507000 1.228764000 B 0.868017000 0.273944000 0.050982000 Cl 2.593641000 -0.239496000 -0.027676000	
TS5_6a R=Me	TS5_6b R=H
E(HF)=-376.703624786 ν1=372.8i C -0.586210000 1.509613000 0.992607000 C -1.657761000 -0.753463000 -0.894576000 C -1.596384000 -1.336281000 0.515981000 C -0.324044000 1.911099000 -0.489427000 C -0.152754000 -0.565533000 -1.109132000 C -0.135496000 -1.001944000 0.821556000 C 0.474594000 0.779013000 -1.134174000 C 0.327336000 0.321866000 1.326817000 H -0.360053000 2.345533000 1.656944000 H -2.101933000 -1.412797000 -1.642288000 H -1.731266000 -2.419324000 0.511011000 H 0.293763000 2.812159000 -0.518642000 H 0.323454000 -1.308121000 -1.742429000 H 0.450915000 -1.835675000 1.199693000 H 1.065288000 1.011473000 -2.014915000 H 0.803536000 0.307165000 2.301960000 H -1.251289000 2.152681000 -1.019651000 H -2.185812000 0.199440000 -0.939024000 H -1.642227000 1.270214000 1.158328000 H -2.300119000 -0.913907000 1.237365000 B 1.205892000 -0.015743000 0.037536000 C 2.600739000 -0.756292000 -0.053436000 H 2.743712000 -1.273127000 -1.007661000 H 3.406253000 -0.019083000 0.027813000 H 2.756204000 -1.486393000 0.746513000	
TS5_6a R=Me	TS5_6b R=H
E(HF)=-392.770861092 ν1=391.1i C -0.475758000 1.516290000 1.024997000 C -1.676356000 -0.592914000 -0.920818000 C -1.658624000 -1.265209000 0.449313000	

C -0.129900000 1.948956000 -0.427183000 C -0.175738000 -0.495911000 -1.188764000 C -0.205584000 -1.027526000 0.856621000 C 0.560252000 0.769113000 -1.108525000 C 0.333977000 0.254581000 1.346876000 H -0.218981000 2.310557000 1.727897000 H -2.192014000 -1.164682000 -1.694998000 H -1.834690000 -2.339243000 0.360334000 H 0.582547000 2.776686000 -0.397545000 H 0.244180000 -1.247408000 -1.850946000 H 0.301940000 -1.896925000 1.270712000 H 1.244767000 0.986293000 -1.923858000 H 0.867515000 0.217492000 2.291405000 H -1.008640000 2.309913000 -0.972501000 H -2.129278000 0.399072000 -0.893518000 H -1.550383000 1.342914000 1.145490000 H -2.376789000 -0.870909000 1.174868000 B 1.173653000 -0.173001000 0.041714000 N 2.464356000 -0.852673000 -0.033153000 H 2.625744000 -1.673241000 0.531545000 H 2.891708000 -0.961083000 -0.940489000	
Products 6	
Products 6a	**Products 6b**
6a R=H	6b R=H
E(HF)=-337.394991966 ν1=104.4 C -1.408525000 -0.850245000 -0.796088000 C 1.894967000 0.527570000 -0.459337000 C 1.561513000 -0.985572000 -0.390538000 C -1.047879000 0.612290000 -1.198642000 C 0.783005000 0.835631000 0.570581000 C 0.589165000 -0.733333000 0.793716000 C -0.616983000 1.320030000 0.104199000 C -0.937705000 -0.999721000 0.659939000 H -2.491689000 -0.996770000 -0.836118000 H 2.882269000 0.760381000 -0.057719000 H 2.401397000 -1.641473000 -0.158863000 H -1.913581000 1.119409000 -1.629091000 H 1.118884000 1.412023000 1.434292000 H 0.970765000 -1.100973000 1.746048000 H -0.711109000 2.403399000 0.092659000 H -1.268152000 -1.909188000 1.156285000 H -0.264857000 0.637637000 -1.961949000 H 1.801652000 1.006076000 -1.434964000 H -0.972313000 -1.590669000 -1.470701000 H 1.074723000 -1.362957000 -1.289289000 B -1.212968000 0.431555000 1.264838000 H -1.468495000 0.745431000 2.382233000	E(HF)=-642.214931022 ν1=42.7 C 1.785788000 -2.718273000 0.704707000 C 1.785788000 -2.718273000 -0.704707000 C 0.798005000 -2.068377000 1.410022000 H 2.571910000 -3.243193000 -1.234960000 H 0.785020000 -2.081129000 2.493751000 C 0.798005000 -2.068377000 -1.410022000 C -0.193926000 -1.356510000 0.708152000 H 0.785020000 -2.081129000 -2.493751000 C -1.466829000 -0.759327000 1.219392000 C -0.193926000 -1.356510000 -0.708152000 C -1.466829000 -0.759327000 -1.219392000 H 2.571910000 -3.243193000 1.234960000 C -0.458080000 1.630775000 0.694888000 C -0.458080000 1.630775000 -0.694888000 C 0.477775000 2.332284000 1.434339000 C -1.663849000 0.702513000 -0.787674000 H 0.489385000 2.343495000 2.518281000 C 0.477775000 2.332284000 -1.434339000 C 1.432298000 3.043540000 0.698559000 H 0.489385000 2.343495000 -2.518281000 H 2.195031000 3.609483000 1.221420000 C 1.432298000 3.043540000 -0.698559000 H 2.195031000 3.609483000 -1.221420000 C -1.663849000 0.702513000 0.787674000 H -1.675785000 -0.997911000 -2.258088000 H -2.552186000 1.131660000 -1.255352000 H -1.675785000 -0.997911000 2.258088000 H -2.552186000 1.131660000 1.255352000 B -1.959027000 -1.682209000 0.000000000 H -2.365793000 -2.793278000 0.000000000
6a R=Cl	6b R=Cl
E(HF)=-797.056733639 ν1=42.7 C -0.564953000 1.448057000 1.062948000 C -2.310414000 -0.410086000 -0.817076000 C -2.249845000 -1.034514000 0.602373000 C -0.377836000 1.854372000 -0.434888000 C -0.776171000 -0.605441000 -0.976787000 C -0.703320000 -1.046603000 0.539443000 C 0.195765000 0.599908000 -1.124573000 C 0.129080000 0.072782000 1.220692000 H -0.098360000 2.181636000 1.722767000 H -2.917375000 -0.953733000 -1.541402000	E(HF)=-1101.86869758 ν1=33.1 C 2.985404000 -0.836706000 0.699827000 C 2.985404000 -0.836706000 -0.699827000 C 1.793781000 -0.836608000 1.410222000 H 3.928881000 -0.843108000 -1.232830000 H 1.792803000 -0.855031000 2.494022000 C 1.793781000 -0.836608000 -1.410222000 C 0.590632000 -0.800926000 0.705683000 H 1.792803000 -0.855031000 -2.494022000 C -0.829973000 -0.900884000 1.212252000 C 0.590632000 -0.800926000 -0.705683000

H -2.655708000 -2.046353000 0.636038000 H 0.342076000 2.673404000 -0.518288000 H -0.520568000 -1.396738000 -1.682163000 H -0.248869000 -2.020862000 0.732439000 H 0.561265000 0.765886000 -2.135259000 H 0.442102000 -0.166274000 2.234460000 H -1.303583000 2.205787000 -0.893840000 H -2.633354000 0.630824000 -0.821060000 H -1.620862000 1.405426000 1.340269000 H -2.704004000 -0.459973000 1.410613000 B 1.154824000 0.103459000 0.023724000 Cl 2.795840000 -0.506305000 -0.060940000	C -0.829973000 -0.900884000 -1.212252000 H 3.928881000 -0.843108000 1.232830000 C -0.953075000 1.698592000 0.694874000 C -0.953075000 1.698592000 -0.694874000 C -0.402023000 2.730252000 1.434890000 C -1.643813000 0.346372000 -0.791531000 H -0.392990000 2.743187000 2.518705000 C -0.402023000 2.730252000 -1.434890000 C 0.156819000 3.779789000 0.698847000 H -0.392990000 2.743187000 -2.518705000 H 0.606086000 4.617038000 1.220796000 C 0.156819000 3.779789000 -0.698847000 H 0.606086000 4.617038000 -1.220796000 C -1.643813000 0.346372000 0.791531000 H -0.917731000 -1.210624000 -2.249724000 H -2.629687000 0.347742000 -1.260224000 H -0.917731000 -1.210624000 2.249724000 H -2.629687000 0.347742000 1.260224000 B -1.047363000 -1.908670000 0.000000000 Cl -1.171232000 -3.659625000 0.000000000
6a R=Me	6b R=Me
E(HF)=-376.718314461 ν1=56.6 C -0.105100000 1.824352000 -0.445537000 C 2.018185000 -0.879624000 0.610947000 C 2.023398000 -0.260247000 -0.811655000 C 0.117730000 1.448270000 1.051848000 C 0.479017000 -1.029024000 0.551375000 C 0.513433000 -0.593574000 -0.973549000 C -0.449882000 0.021720000 1.216547000 C -0.559278000 0.520956000 -1.122930000 H -0.899888000 2.571133000 -0.533916000 H 2.512853000 -1.851334000 0.649914000 H 2.680110000 -0.747404000 -1.533279000 H -0.414182000 2.140369000 1.708018000 H 0.117142000 -2.039303000 0.756904000 H 0.332575000 -1.408183000 -1.676000000 H -0.729846000 -0.240430000 2.235906000 H -0.925052000 0.645905000 -2.141035000 H 1.173513000 1.509982000 1.330225000 H 2.418563000 -0.261324000 1.415409000 H 0.783173000 2.265164000 -0.903923000 H 2.245970000 0.806606000 -0.818662000 B -1.463790000 -0.135929000 0.005163000 C -2.789681000 -0.948811000 -0.101297000 H -3.608462000 -0.226361000 0.027067000 H -2.941645000 -1.410190000 -1.079779000 H -2.912808000 -1.699098000 0.682841000	E(HF)=-681.534923605 ν1=41.7 C -0.820021000 3.497288000 0.698579000 C -0.047880000 2.591472000 1.434064000 C 0.710594000 1.700546000 0.694996000 C 0.710594000 1.700546000 -0.694996000 C -0.047880000 2.591472000 -1.434064000 C -0.820021000 3.497288000 -0.698579000 C 1.669176000 0.519875000 -0.788972000 B 1.461182000 -1.867626000 0.000000000 C 1.669176000 0.519875000 0.788972000 C 1.137155000 -0.861281000 1.212790000 C -0.255248000 -1.109403000 0.706742000 C -1.400988000 -1.507922000 1.409244000 C -2.535709000 -1.859117000 0.702254000 C -2.535709000 -1.859117000 -0.702254000 C -1.400988000 -1.507922000 -1.409244000 C -0.255248000 -1.109403000 -0.706742000 C 1.137155000 -0.861281000 -1.212790000 H -3.436102000 -2.142988000 1.234547000 H -1.393521000 -1.524922000 -2.493200000 H -1.393521000 -1.524922000 2.493200000 H -3.436102000 -2.142988000 -1.234547000 H -0.059018000 2.602955000 -2.518029000 H -0.059018000 2.602955000 2.518029000 H -1.436773000 4.219304000 -1.221627000 H -1.436773000 4.219304000 1.221627000 H 1.281182000 -1.139248000 2.253879000 H 2.632166000 0.730655000 1.258718000 H 1.281182000 -1.139248000 -2.253879000 H 2.632166000 0.730655000 -1.258718000 C 1.748224000 -3.406063000 0.000000000 H 2.833578000 -3.560044000 0.000000000 H 1.355184000 -3.907229000 0.887435000 H 1.355184000 -3.907229000 -0.887435000
6a R=NH_2	6b R=NH_2
E(HF)=-392.817877985 ν1=80.4 C -0.355975000 1.752974000 -0.179001000 C 2.148884000 -0.728297000 0.539253000 C 2.096380000 0.127798000 -0.754210000 C -0.122070000 1.160749000 1.248977000 C 0.654630000 -1.094961000 0.359905000 C 0.663553000 -0.405687000 -1.051276000 C -0.455206000 -0.349158000 1.136549000 C -0.577616000 0.522900000 -1.085971000 H -1.254140000 2.377839000 -0.187063000 H 2.794038000 -1.602489000 0.438279000 H 2.846063000 -0.116163000 -1.507903000	E(HF)=-697.629811574 ν1=38.1 C 3.020418000 -0.535369000 0.695925000 C 3.020418000 -0.535369000 -0.695925000 C 1.845799000 -0.788093000 1.406628000 H 3.940984000 -0.335448000 -1.231932000 H 1.846968000 -0.783204000 2.491366000 C 1.845799000 -0.788093000 -1.406628000 C 0.679567000 -1.048453000 0.703856000 H 1.846968000 -0.783204000 -2.491366000 C -0.718219000 -1.340393000 1.200579000 C 0.679567000 -1.048453000 -0.703856000 C -0.718219000 -1.340393000 -1.200579000

H -0.780690000 1.638790000 1.977203000 H 0.451821000 -2.169017000 0.362002000 H 0.646400000 -1.106736000 -1.887623000 H -0.705087000 -0.811681000 2.091694000 H -0.918468000 0.780091000 -2.088901000 H 0.900981000 1.332152000 1.593972000 H 2.422922000 -0.209605000 1.459234000 H 0.468091000 2.388941000 -0.508810000 H 2.144392000 1.200272000 -0.565598000 B -1.490973000 -0.307949000 -0.076620000 N -2.763487000 -0.850352000 -0.218600000 H -3.301112000 -0.775236000 -1.067529000 H -3.231424000 -1.352860000 0.518989000	H 3.940984000 -0.335448000 1.231932000 C -1.065451000 1.257537000 0.695020000 C -1.065451000 1.257537000 -0.695020000 C -0.592734000 2.327862000 1.434454000 C -1.639809000 -0.145768000 -0.795743000 H -0.578316000 2.337945000 2.518286000 C -0.592734000 2.327862000 -1.434454000 C -0.117417000 3.417748000 0.698952000 H -0.578316000 2.337945000 -2.518286000 H 0.267004000 4.286590000 1.221113000 C -0.117417000 3.417748000 -0.698952000 H 0.267004000 4.286590000 -1.221113000 C -1.639809000 -0.145768000 0.795743000 H -0.785291000 -1.625148000 -2.249367000 H -2.621746000 -0.226680000 -1.266241000 H -0.785291000 -1.625148000 2.249367000 H -2.621746000 -0.226680000 1.266241000 B -1.124353000 -2.325969000 0.000000000 N -1.674224000 -3.599545000 0.000000000 H -1.871857000 -4.111146000 -0.845378000 H -1.871857000 -4.111146000 0.845378000
Borirane-COD R=NH_2	Borirane-DBCOT R=NH_2
E(HF)=-392.787703684 ν1=63.3 C -0.117110000 1.122121000 1.476992000 C -0.456005000 1.981645000 0.245675000 C -0.718281000 1.276810000 -1.064714000 C -1.287689000 0.088957000 -1.269079000 C -1.822285000 -0.831779000 -0.212128000 C -0.801956000 -1.892797000 0.239996000 C 0.586654000 -1.381447000 0.604674000 C 0.918031000 0.020673000 1.243833000 B 1.498549000 -0.387483000 -0.125134000 N 2.386510000 -0.115959000 -1.153680000 H 0.293200000 1.806155000 2.226150000 H -2.699592000 -1.353349000 -0.605857000 H -0.690064000 -2.634057000 -0.559701000 H 0.390504000 2.654909000 0.074921000 H -1.349380000 -0.269179000 -2.294730000 H 1.152012000 -2.157541000 1.120675000 H -0.379505000 1.816907000 -1.946025000 H 1.583454000 -0.095803000 2.095897000 H -1.306280000 2.634224000 0.481740000 H -2.169670000 -0.257031000 0.644848000 H -1.019338000 0.710779000 1.934074000 H -1.234899000 -2.426734000 1.093241000 H 2.518936000 -0.731273000 -1.940200000 H 2.904139000 0.746020000 -1.215086000	E(HF)=-697.619586066 ν1=43.8 C 1.951306000 0.299883000 3.093575000 C 1.550639000 -1.031553000 3.138594000 C 1.260274000 1.190539000 2.283550000 H 2.078263000 -1.739508000 3.766953000 H 1.562857000 2.231606000 2.239656000 C 0.469598000 -1.454104000 2.377698000 C 0.176916000 0.770267000 1.508922000 H 0.155972000 -2.491844000 2.419756000 C -0.527506000 1.770852000 0.667284000 C -0.240127000 -0.569613000 1.557504000 C -1.417048000 -1.070914000 0.800054000 H 2.793035000 0.640723000 3.684372000 C 0.176916000 0.770267000 -1.508922000 C -0.240127000 -0.569613000 -1.557504000 C 1.260274000 1.190539000 -2.283550000 C -1.417048000 -1.070914000 -0.800054000 H 1.562857000 2.231606000 -2.239656000 C 0.469598000 -1.454104000 -2.377698000 C 1.951306000 0.299883000 -3.093575000 H 0.155972000 -2.491844000 -2.419756000 H 2.793035000 0.640723000 -3.684372000 C 1.550639000 -1.031553000 -3.138594000 H 2.078263000 -1.739508000 -3.766953000 C -0.527506000 1.770852000 -0.667284000 H -1.773277000 -2.025025000 1.181911000 H -1.773277000 -2.025025000 -1.181911000 H -1.035723000 2.580042000 1.188134000 H -1.035723000 2.580042000 -1.188134000 B -2.452790000 -0.261876000 0.000000000 N -3.672441000 0.387569000 0.000000000 H -4.139924000 0.670061000 0.846644000 H -4.139924000 0.670061000 -0.846644000
TS-BORIRANE_5a R=NH_2	TS-BORIRANE_5b R=NH_2
E(HF)=-392.782201251 ν1=188.4i C -1.393010000 1.069642000 0.849700000 C -0.900277000 -1.161132000 -1.199100000 C -0.896427000 -1.851033000 0.182996000 C -0.850430000 1.831879000 -0.381225000 C 0.370531000 -0.332833000 -1.366421000 C -0.076904000 -1.053023000 1.171622000 C 0.383944000 1.142832000 -0.935349000 C -0.288491000 0.251763000 1.465304000 H -1.789241000 1.767287000 1.591068000 H -0.963408000 -1.920607000 -1.981896000 H -0.440929000 -2.838841000 0.089586000	E(HF)=-697.609974798 ν1=232.1i C 1.974747000 0.599415000 2.819281000 C 1.847978000 -0.786804000 2.867199000 C 1.047624000 1.361570000 2.113520000 H 2.571592000 -1.373378000 3.421199000 H 1.140837000 2.441293000 2.071949000 C 0.800249000 -1.424063000 2.208116000 C -0.002490000 0.720235000 1.467087000 H 0.704454000 -2.503888000 2.244188000 C -1.066571000 1.406661000 0.682959000 C -0.135289000 -0.669133000 1.505536000 C -1.315193000 -1.191058000 0.770628000

H -0.559453000 2.841108000 -0.075005000 H 0.923282000 -0.520240000 -2.281798000 H 0.697180000 -1.576535000 1.723199000 H 0.976735000 1.773219000 -1.594047000 H 0.335154000 0.720323000 2.220778000 H -1.640646000 1.951390000 -1.132047000 H -1.791641000 -0.538179000 -1.321053000 H -2.216486000 0.410976000 0.569423000 H -1.912390000 -2.005888000 0.564083000 B 1.223183000 0.100766000 -0.109904000 N 2.567349000 0.009557000 0.353728000 H 3.081277000 0.805031000 0.692250000 H 3.119587000 -0.828354000 0.283728000	H 2.794912000 1.087051000 3.332598000 C -0.002490000 0.720235000 -1.467087000 C -0.135289000 -0.669133000 -1.505536000 C 1.047624000 1.361570000 -2.113520000 C -1.315193000 -1.191058000 -0.770628000 H 1.140837000 2.441293000 -2.071949000 C 0.800249000 -1.424063000 -2.208116000 C 1.974747000 0.599415000 -2.819281000 H 0.704454000 -2.503888000 -2.244188000 H 2.794912000 1.087051000 -3.332598000 C 1.847978000 -0.786804000 -2.867199000 H 2.571592000 -1.373378000 -3.421199000 C -1.066571000 1.406661000 -0.682959000 H -1.807864000 -2.056094000 1.204478000 H -1.807864000 -2.056094000 -1.204478000 H -1.805303000 2.004339000 1.210432000 H -1.805303000 2.004339000 -1.210432000 B -2.235047000 -0.143091000 0.000000000 N -3.636632000 0.155062000 0.000000000 H -4.189128000 0.114753000 0.840107000 H -4.189128000 0.114753000 -0.840107000

Dimerization of borirenes and boriranes

Dimerization of borirenes

Transition states TS7_8(I)	**Transition states TS7_8(II)**
TS7_8(I) R=H	TS7_8(II) R=H
E(HF)=-205.528943322 ν1=335.4i B 0.852659000 0.810359000 -0.341043000 B -0.602112000 -0.472086000 0.514380000 C 2.097011000 0.213087000 0.175984000 C -1.885335000 -0.469806000 -0.309762000 C 1.193256000 -0.688600000 -0.258956000 C -1.593277000 0.681373000 0.255508000 H 0.378474000 1.691547000 -0.956300000 H -0.217749000 -1.018590000 1.498987000 H 3.144891000 0.201227000 0.433803000 H -2.675729000 -0.932805000 -0.881017000 H 1.215053000 -1.732870000 -0.542171000 H -1.967609000 1.683802000 0.403374000	E(HF)=-205.537602923 ν1=348.8i C 1.450184000 0.713094000 0.259860000 C 1.657345000 -0.585707000 0.426697000 B 0.874071000 -0.209165000 -0.808214000 H 1.735157000 1.664030000 0.687759000 H 2.212763000 -1.255639000 1.066850000 H 0.818838000 -0.397533000 -1.971846000 B -1.019799000 0.785342000 -0.418376000 C -1.773681000 0.099072000 0.658114000 C -1.234400000 -0.710918000 -0.258324000 H -0.914454000 1.732163000 -1.105537000 H -2.457725000 0.033766000 1.490541000 H -1.262620000 -1.750912000 -0.552904000
TS7_8(I) R=Cl	TS7_8(II) R=Cl
E(HF)=-1124.82455119 ν1=347.6i B 1.010254000 0.703077000 0.011831000 B -0.838397000 -0.512403000 0.159638000 C 0.481939000 2.056182000 0.144423000 C -0.665424000 -1.811877000 0.906996000 C -0.131441000 1.149676000 0.941887000 C -0.089481000 -1.758218000 -0.279624000 Cl 2.454616000 -0.205633000 -0.300000000 Cl -2.325136000 0.308457000 -0.510374000 H 0.534523000 3.133119000 0.108494000 H -0.864592000 -2.512995000 1.703863000 H -0.757771000 1.217382000 1.822764000 H 0.453852000 -2.353457000 -0.998202000	E(HF)=-1124.83354646 ν1=360.8i C -0.867875000 0.736722000 1.589778000 C -1.691594000 1.420403000 0.799811000 B -1.043398000 0.207949000 0.190310000 H -0.538202000 0.702870000 2.618786000 H -2.395338000 2.239019000 0.850546000 Cl -1.541127000 -1.299855000 -0.629501000 B 1.191378000 0.392491000 -0.230387000 C 1.430376000 1.685968000 -0.869665000 C 0.282267000 1.082552000 -1.233818000 Cl 1.877796000 -1.007391000 0.525001000 H 2.017731000 2.527730000 -1.202547000 H -0.466514000 1.197485000 -2.006544000
TS7_8(I) R=F	TS7_8(II) R=H
E(HF)=-404.142150783 ν1=400.9i B 1.075885000 0.036225000 0.102883000 B -1.075885000 -0.036225000 -0.102883000 C 1.348753000 -1.130204000 0.977982000 C -1.348753000 1.130204000 -0.977982000 C 0.690394000 -1.410921000 -0.160567000 C -0.690394000 1.410921000 0.160567000	E(HF)=-404.148402412 ν1=355.6i C 1.258700000 -0.087949000 1.217120000 C 1.793423000 -0.977561000 0.372795000 B 0.984036000 0.119938000 -0.252829000 H 1.300430000 0.151532000 2.271322000 H 2.487170000 -1.805954000 0.414379000 F 1.063121000 1.056022000 -1.219945000

F 1.713233000 1.081454000 -0.443667000 F -1.713233000 -1.081454000 0.443667000 H 1.840966000 -1.695620000 1.755792000 H -1.840966000 1.695620000 -1.755792000 H 0.378069000 -2.292146000 -0.704650000 H -0.378069000 2.292146000 0.704650000	B -1.198116000 0.151173000 0.208977000 C -1.789837000 -1.170047000 -0.003126000 C -0.822421000 -0.832279000 -0.884121000 F -1.329139000 1.376816000 0.670639000 H -2.517721000 -1.962779000 0.080130000 H -0.444505000 -1.226876000 -1.818826000
Transition states TS7_9	
TS7_9 R=H	TS7_9 R=Cl
E(HF)=-205.535934339 ν1=373.7i B -1.231369000 0.885400000 0.014432000 B 0.738555000 0.364102000 -0.453575000 C -2.167066000 -0.260029000 -0.244550000 C 1.765202000 -0.704411000 -0.340205000 C -1.164983000 -0.525296000 0.583944000 C 1.987543000 0.423971000 0.346024000 H -1.166414000 2.038568000 0.245314000 H 0.006322000 0.924042000 -1.234758000 H -3.076647000 -0.712652000 -0.608816000 H 2.239715000 -1.656973000 -0.527942000 H -0.796433000 -1.294108000 1.248234000 H 2.733351000 0.848206000 1.002406000	E(HF)=-1124.82612449 ν1=342.2i B -0.973564000 0.496016000 0.029766000 B 1.162878000 -0.077945000 -0.066516000 C -1.094778000 1.839760000 0.637125000 C 2.483216000 0.369581000 -0.600199000 C -0.053739000 1.705110000 -0.188281000 C 1.803488000 -0.510147000 -1.339084000 Cl -1.911779000 -0.752760000 -0.759120000 Cl 0.492410000 -0.853104000 1.439461000 H -1.639162000 2.638741000 1.116222000 H 3.428888000 0.893080000 -0.594820000 H 0.652681000 2.333449000 -0.711417000 H 1.911189000 -1.081771000 -2.249390000
TS7_9 R=F	
E(HF)=-404.140756697 ν1=352.6i B -1.260612000 -0.102825000 -0.120477000 B 0.879839000 -0.109037000 0.218260000 C -1.693248000 1.261096000 0.207101000 C 2.211264000 0.569775000 0.136818000 C -0.503335000 1.210606000 -0.425476000 C 2.012509000 -0.467082000 -0.685895000 F -1.604357000 -1.294881000 -0.553301000 F 0.103139000 -0.767934000 1.185370000 H -2.426482000 2.027993000 0.404018000 H 3.000800000 1.261041000 0.397834000 H 0.104831000 1.926836000 -0.961397000 H 2.572524000 -1.037606000 -1.413286000	
Products 8 and 9	
Products 8	Products 9
8 R=H	9 R=H
E(HF)=-205.635987169 ν1=96.1 C 0.000000000 1.354031000 0.673780000 C 0.000000000 1.354031000 -0.673780000 B 0.000000000 0.000000000 -1.466062000 H 0.000000000 2.304292000 1.205897000 H 0.000000000 2.304292000 -1.205897000 H 0.000000000 0.000000000 -2.657192000 B 0.000000000 0.000000000 1.466062000 C 0.000000000 -1.354031000 0.673780000 C 0.000000000 -1.354031000 -0.673780000 H 0.000000000 0.000000000 2.657192000 H 0.000000000 -2.304292000 1.205897000 H 0.000000000 -2.304292000 -1.205897000	E(HF)=-205.595708958 ν1=38.5 B 1.960590000 1.159684000 0.000250000 B -0.732139000 -0.304231000 0.000015000 C 1.851525000 -0.373110000 -0.000088000 C -1.942238000 0.206753000 0.671830000 C 0.648701000 -0.989834000 -0.000146000 C -1.941944000 0.207397000 -0.671857000 H 3.011145000 1.720089000 0.000472000 H 0.956227000 1.806523000 0.000304000 H 2.739587000 -1.001972000 -0.000223000 H -2.585988000 0.486002000 1.493995000 H 0.625910000 -2.082554000 -0.000314000 H -2.585398000 0.487409000 -1.493995000
8 R=Cl	9 R=Cl
E(HF)=-1124.96470128 ν1=52.5 C 0.000000000 1.359969000 0.672873000 C 0.000000000 1.359969000 -0.672873000 B 0.000000000 0.000000000 -1.435219000 H 0.000000000 2.299228000 1.222293000 H 0.000000000 2.299228000 -1.222293000	E(HF)=-1124.91493951 ν1=32.6 B -0.032904000 1.131400000 0.000000000 B -0.713110000 -2.019165000 0.000000000 C -1.430723000 0.505925000 0.000000000 C -0.032904000 -3.144453000 0.670310000 C -1.675729000 -0.819097000 0.000000000

Cl 0.000000000 0.000000000 -3.197026000 B 0.000000000 0.000000000 1.435219000 C 0.000000000 -1.359969000 0.672873000 C 0.000000000 -1.359969000 -0.672873000 Cl 0.000000000 0.000000000 3.197026000 H 0.000000000 -2.299228000 1.222293000 H 0.000000000 -2.299228000 -1.222293000	C -0.032904000 -3.144453000 -0.670310000 Cl 0.165185000 2.880030000 0.000000000 Cl 1.429610000 0.146938000 0.000000000 H -2.279529000 1.185368000 0.000000000 H 0.329120000 -3.736446000 1.498565000 H -2.726595000 -1.119645000 0.000000000 H 0.329120000 -3.736446000 -1.498565000
8 R=F	9 R=F
E(HF)=-404.285653593 ν1=64.6 C 0.000000000 1.365259000 0.671965000 C 0.000000000 1.365259000 -0.671965000 B 0.000000000 0.000000000 -1.434004000 H 0.000000000 2.302888000 1.225169000 H 0.000000000 2.302888000 -1.225169000 F 0.000000000 0.000000000 -2.768330000 B 0.000000000 0.000000000 1.434004000 C 0.000000000 -1.365259000 0.671965000 C 0.000000000 -1.365259000 -0.671965000 F 0.000000000 0.000000000 2.768330000 H 0.000000000 -2.302888000 1.225169000 H 0.000000000 -2.302888000 -1.225169000	E(HF)=-404.244549328 ν1=30.1 B -1.520515000 -0.181531000 -0.000123000 B 1.497194000 0.406911000 0.000141000 C -0.952904000 1.244902000 -0.000160000 C 2.512913000 -0.423571000 -0.671397000 C 0.374127000 1.463489000 0.000003000 C 2.512633000 -0.423878000 0.671714000 F -2.820390000 -0.444100000 0.000406000 F -0.706774000 -1.237316000 -0.000552000 H -1.633502000 2.090879000 -0.000215000 H 3.048992000 -0.874837000 -1.494094000 H 0.716791000 2.499925000 0.000168000 H 3.048185000 -0.875779000 1.494406000
Dimerization of boriranes	
Van der Waals complexes for path IV	
VDW(IV) R=Cl	VDW(IV) R=F
E(HF)=-1127.27422461 ν1=32.4 C -1.190438000 1.310184000 0.977812000 C -0.057324000 2.209225000 1.582761000 B 0.057324000 1.647181000 0.179049000 H -2.124030000 1.799200000 0.715815000 H -0.277660000 3.261795000 1.730115000 Cl 0.895297000 1.622254000 -1.327085000 B -0.057324000 -1.647181000 0.179049000 C 0.057324000 -2.209225000 1.582761000 C 1.190438000 -1.310184000 0.977812000 Cl -0.895297000 -1.622254000 -1.327085000 H 0.277660000 -3.261795000 1.730115000 H 2.124030000 -1.799200000 0.715815000 H 0.505249000 1.774806000 2.402898000 H -1.345591000 0.346475000 1.452930000 H -0.505249000 -1.774806000 2.402898000 H 1.345591000 -0.346475000 1.452930000	E(HF)=-406.588257423 ν1=36.7 C 1.010507000 1.341638000 -0.576286000 C -0.252042000 2.179861000 -1.052243000 B -0.252042000 1.439568000 0.266411000 H 1.883691000 1.912828000 -0.273657000 H -0.141790000 3.259577000 -1.074914000 F -0.818149000 1.264367000 1.435595000 B 0.252042000 -1.439568000 0.266411000 C 0.252042000 -2.179861000 -1.052243000 C -1.010507000 -1.341638000 -0.576286000 F 0.818149000 -1.264367000 1.435595000 H 0.141790000 -3.259577000 -1.074914000 H -1.883691000 -1.912828000 -0.273657000 H -0.759857000 1.790037000 -1.927507000 H 1.271253000 0.496517000 -1.205160000 H 0.759857000 -1.790037000 -1.927507000 H -1.271253000 -0.496517000 -1.205160000
Van der Waals complexes for path V	
VDW(V) R=H	VDW(V) R=F
E(HF)=-207.964787347 ν1=63.7 B 1.491165000 0.868849000 0.108720000 B -1.300930000 0.317331000 0.802517000 C 2.665142000 -0.077450000 -0.089566000 C -2.037275000 -0.793350000 0.048225000 C 1.224626000 -0.635102000 -0.089034000 C -1.967719000 0.637024000 -0.538378000 H 1.077872000 1.960798000 0.248598000 H -0.860622000 0.708296000 1.822769000 H 3.289264000 -0.343540000 0.757598000 H -2.996826000 -1.130563000 0.429383000 H 0.822483000 -0.976818000 -1.039280000 H -1.362597000 0.762021000 -1.429919000 H 3.205612000 -0.071684000 -1.030877000 H 0.945788000 -1.277600000 0.740122000 H -2.881910000 1.222008000 -0.559516000 H -1.498884000 -1.570544000 -0.482540000	E(HF)=-406.589282535 ν1=40.1 B 1.508638000 0.384001000 -0.198804000 B -1.393669000 -0.056809000 0.496559000 C 2.462802000 -0.703377000 0.223287000 C -2.379273000 -0.846698000 -0.333533000 C 1.261298000 -1.001315000 -0.775309000 C -2.091600000 0.692710000 -0.608898000 F 1.199940000 1.658576000 -0.215574000 F -0.543607000 -0.029892000 1.508987000 H 2.358108000 -1.158714000 1.202695000 H -3.367165000 -1.080741000 0.050269000 H 1.540153000 -1.194643000 -1.807521000 H -1.561233000 0.924916000 -1.526722000 H 3.467798000 -0.771753000 -0.179644000 H 0.512778000 -1.694391000 -0.406481000 H -2.908967000 1.374876000 -0.399340000 H -2.042671000 -1.541586000 -1.096029000
VDW(V) R=Cl	

E(HF)=-1127.27589246
ν1=39.8

B	-1.596259000	-0.095214000	0.271203000
B	1.694855000	0.028714000	-0.057621000
C	-2.132066000	-1.486577000	0.520654000
C	2.472879000	0.189095000	1.232695000
C	-1.045650000	-0.862330000	1.465739000
C	1.769525000	1.412235000	0.546657000
Cl	-1.719191000	1.393946000	-0.591260000
Cl	1.163902000	-1.001861000	-1.348004000
H	-1.789796000	-2.312207000	-0.094826000
H	3.558103000	0.176532000	1.212673000
H	-1.370060000	-0.568112000	2.460044000
H	0.900372000	1.820086000	1.052837000
H	-3.130175000	-1.630270000	0.921705000
H	-0.080691000	-1.357371000	1.463942000
H	2.413741000	2.169300000	0.111217000
H	2.057306000	-0.145436000	2.177528000

Transition states TS10_11

TS10_11 R=Cl

E(HF)=-1127.27269503
ν1=189.7i

C	-1.220687000	1.089275000	0.919575000
C	-0.118362000	1.983837000	1.585278000
B	0.118362000	1.357001000	0.223971000
H	-2.081550000	1.582068000	0.474465000
H	-0.290415000	3.053802000	1.646906000
Cl	0.889917000	1.582643000	-1.308943000
B	-0.118362000	-1.357001000	0.223971000
C	0.118362000	-1.983837000	1.585278000
C	1.220687000	-1.089275000	0.919575000
Cl	-0.889917000	-1.582643000	-1.308943000
H	0.290415000	-3.053802000	1.646906000
H	2.081550000	-1.582068000	0.474465000
H	0.300989000	1.566258000	2.493659000
H	-1.504667000	0.211021000	1.488020000
H	-0.300989000	-1.566258000	2.493659000
H	1.504667000	-0.211021000	1.488020000

TS10_11 R=F

E(HF)=-406.588127817
ν1=110.3i

C	0.147653000	1.623650000	-0.562010000
C	-1.361437000	1.623518000	-1.054828000
B	-0.966132000	0.959914000	0.245322000
H	0.540335000	2.566419000	-0.190154000
H	-1.886559000	2.573463000	-1.036757000
F	-1.361437000	0.564168000	1.432464000
B	0.966132000	-0.959914000	0.245322000
C	1.361437000	-1.623518000	-1.054828000
C	-0.147653000	-1.623650000	-0.562010000
F	1.361437000	-0.564168000	1.432464000
H	1.886559000	-2.573463000	-1.036757000
H	-0.540335000	-2.566419000	-0.190154000
H	-1.538803000	1.061136000	-1.964092000
H	0.844799000	1.125814000	-1.226763000
H	1.538803000	-1.061136000	-1.964092000
H	-0.844799000	-1.125814000	-1.226763000

Transition states TS10_12

TS10_12 R=H

E(HF)=-207.964339055
ν1=141.3i

B	1.390914000	0.871441000	0.064057000
B	-1.093114000	0.248316000	0.758766000
C	2.580659000	-0.068469000	0.005604000
C	-1.979919000	-0.791539000	0.058363000
C	1.160019000	-0.635337000	-0.221153000
C	-1.946462000	0.672924000	-0.442691000
H	0.977573000	1.970703000	0.074809000
H	-0.604786000	0.577485000	1.783419000
H	3.063083000	-0.396541000	0.920030000
H	-2.881969000	-1.130471000	0.558621000
H	0.868807000	-0.912611000	-1.231731000
H	-1.490743000	0.832194000	-1.413842000
H	3.260901000	-0.003059000	-0.838083000
H	0.821318000	-1.348805000	0.520497000
H	-2.829146000	1.283779000	-0.280799000
H	-1.559820000	-1.536937000	-0.607783000

TS10_12 R=Cl

E(HF)=-1127.27162707
ν1=226.4i

B	-1.293811000	-0.202894000	0.234926000
B	1.304106000	0.048167000	0.015081000
C	-1.787641000	-1.534148000	0.729714000
C	2.372582000	0.295505000	1.072943000
C	-0.555663000	-0.857090000	1.431647000
C	1.556048000	1.480362000	0.454920000
Cl	-1.762802000	1.284353000	-0.497880000
Cl	0.969446000	-0.938259000	-1.414845000
H	-1.525051000	-2.448197000	0.210825000
H	3.416843000	0.205758000	0.790386000
H	-0.716544000	-0.358233000	2.385378000
H	0.877456000	1.982942000	1.134266000
H	-2.729569000	-1.584690000	1.265975000
H	0.329274000	-1.479144000	1.435345000
H	2.076384000	2.155605000	-0.216954000
H	2.194826000	0.108222000	2.125723000

TS10_12 R=Cl

E(HF)=-406.585404182
ν1=202.2i

B	1.340329000	0.331197000	-0.144447000
B	-1.047850000	-0.035103000	0.381061000
C	2.312038000	-0.786532000	0.067567000
C	-2.215307000	-0.825622000	-0.196043000

	C 0.861894000 -1.099529000 -0.509339000 C -1.851979000 0.616832000 -0.732688000 F 1.171826000 1.607102000 -0.354592000 F -0.458236000 0.260852000 1.560774000 H 2.465454000 -1.206781000 1.054481000 H -3.134706000 -0.911198000 0.374997000 H 0.789028000 -1.310088000 -1.574279000 H -1.492755000 0.653809000 -1.754548000 H 3.158014000 -0.911025000 -0.600266000 H 0.321758000 -1.821483000 0.088579000 H -2.548342000 1.414950000 -0.495026000 H -2.083040000 -1.631139000 -0.909629000
Products 11 and 12	
Products 11	**Products 12**
11 R=H	12 R=H
E(HF)=-208.081791360 ν1=130.5 C 1.328487000 0.248206000 0.729447000 C 1.328487000 -0.248206000 -0.729447000 B 0.000000000 0.000000000 -1.518310000 H 1.401334000 1.352076000 0.732172000 H 2.216343000 0.076659000 -1.279492000 H 0.000000000 0.000000000 -2.713715000 B 0.000000000 0.000000000 1.518310000 C -1.328487000 -0.248206000 0.729447000 C -1.328487000 0.248206000 -0.729447000 H 0.000000000 0.000000000 2.713715000 H -2.216343000 0.076659000 1.279492000 H -1.401334000 1.352076000 -0.732172000 H 1.401334000 -1.352076000 -0.732172000 H 2.216343000 -0.076659000 1.279492000 H -1.401334000 -1.352076000 0.732172000 H -2.216343000 -0.076659000 -1.279492000	E(HF)=-208.020210764 ν1=60.5 B 2.069395000 0.932808000 -0.565735000 B -0.713688000 -0.293931000 -0.050090000 C 1.851293000 -0.135173000 0.543040000 C -1.671244000 0.692647000 0.620984000 C 0.679741000 -0.966945000 -0.072293000 C -2.153572000 -0.199775000 -0.553936000 H 2.893937000 0.789914000 -1.414869000 H 1.309268000 1.851078000 -0.650601000 H 1.501124000 0.282794000 1.489421000 H -1.575054000 1.756169000 0.425523000 H 0.931782000 -1.365339000 -1.061167000 H -2.868651000 -0.981748000 -0.318189000 H 2.711515000 -0.780691000 0.726575000 H 0.529418000 -1.866303000 0.547922000 H -2.367661000 0.296737000 -1.495333000 H -2.081524000 0.478482000 1.603074000
11 R=Cl	12 R=Cl
E(HF)=-1127.40926478 ν1=44.7 C -0.276477000 1.333534000 0.720718000 C 0.276477000 1.333534000 -0.720718000 B 0.000000000 0.000000000 -1.487342000 H -1.375658000 1.411243000 0.685461000 H -0.047948000 2.209214000 -1.288347000 Cl 0.000000000 0.000000000 -3.262071000 B 0.000000000 0.000000000 1.487342000 C 0.276477000 -1.333534000 0.720718000 C -0.276477000 -1.333534000 -0.720718000 Cl 0.000000000 0.000000000 3.262071000 H -0.047948000 -2.209214000 1.288347000 H -1.375658000 -1.411243000 -0.685461000 H 1.375658000 1.411243000 -0.685461000 H 0.047948000 2.209214000 1.288347000 H 1.375658000 -1.411243000 0.685461000 H 0.047948000 -2.209214000 -1.288347000	E(HF)=-1127.34605552 ν1=28.3 B 1.173446000 0.137985000 -0.101123000 B -1.995018000 0.427200000 -0.065179000 C 0.377438000 1.472397000 -0.194775000 C -3.269030000 -0.412899000 -0.015011000 C -1.019152000 1.364065000 -0.823088000 C -2.444176000 -0.164885000 1.276157000 Cl 2.833185000 0.111980000 0.474397000 Cl 0.444585000 -1.404211000 -0.550970000 H 1.007246000 2.207593000 -0.710323000 H -3.257843000 -1.423018000 -0.412376000 H -1.508834000 2.349583000 -0.809194000 H -2.891453000 0.482210000 2.025006000 H 0.300155000 1.844259000 0.836696000 H -0.954762000 1.092622000 -1.880860000 H -1.934186000 -1.020627000 1.706171000 H -4.245040000 0.057311000 -0.081571000
11 R=F	12 R=F
E(HF)=-406.730746513 ν1=43.9 C -0.278335000 1.340494000 0.719683000 C 0.278335000 1.340494000 -0.719683000 B 0.000000000 0.000000000 -1.481113000 H -1.375590000 1.430504000 0.683025000 H -0.056333000 2.205702000 -1.298645000 F 0.000000000 0.000000000 -2.821849000 B 0.000000000 0.000000000 1.481113000 C 0.278335000 -1.340494000 0.719683000 C -0.278335000 -1.340494000 -0.719683000 F 0.000000000 0.000000000 2.821849000 H -0.056333000 -2.205702000 1.298645000	E(HF)=-406.675525766 ν1=30.1 B -1.579868000 -0.128136000 0.064280000 B 1.481322000 0.331549000 0.000442000 C -0.931520000 1.223127000 -0.353659000 C 2.868617000 -0.275707000 0.188406000 C 0.447479000 1.449798000 0.284369000 C 1.820724000 -0.978519000 -0.717359000 F -2.663789000 -0.612480000 -0.527185000 F -1.089237000 -0.858732000 1.061611000 H -1.633388000 2.029005000 -0.103670000 H 3.122360000 -0.771270000 1.120126000 H 0.884026000 2.402297000 -0.042120000

H	-1.375590000	-1.430504000	-0.683025000	H	2.020402000	-0.985629000	-1.784568000
H	1.375590000	1.430504000	-0.683025000	H	-0.860524000	1.237403000	-1.446443000
H	0.056333000	2.205702000	1.298645000	H	0.362552000	1.554194000	1.373474000
H	1.375590000	-1.430504000	0.683025000	H	1.412658000	-1.917726000	-0.355866000
H	0.056333000	-2.205702000	-1.298645000	H	3.730084000	0.163381000	-0.304912000

Intermediates and transition states

Path IV				**Path V**			
Intermediate IV R=H				Intermediate V R=H			
E(HF)=-208.066460074 ν1=117.7				E(HF)=-208.034859225 ν1=130.0			
C	0.470503000	1.321399000	0.114575000	B	-1.087851000	0.837702000	-0.489079000
C	-0.964495000	1.274673000	-0.548715000	B	0.460260000	0.117598000	-0.074050000
B	-0.964495000	0.198164000	0.543813000	C	-2.119150000	-0.270649000	-0.283486000
H	0.532830000	2.048585000	0.917381000	C	1.693557000	-0.784187000	-0.362284000
H	-1.529869000	2.190912000	-0.421994000	C	-0.966308000	-0.291103000	0.787225000
H	-1.338715000	0.439576000	1.645543000	C	1.883752000	0.604782000	0.273545000
B	0.964495000	-0.198164000	0.543813000	H	-1.197271000	1.974449000	-0.186230000
C	0.964495000	-1.274673000	-0.548715000	H	-0.104539000	0.531122000	-1.253196000
C	-0.470503000	-1.321399000	0.114575000	H	-2.098385000	-1.175382000	-0.879428000
H	1.338715000	-0.439576000	1.645543000	H	2.070200000	-0.910228000	-1.370750000
H	1.529869000	-2.190912000	-0.421994000	H	-1.168713000	0.235038000	1.712731000
H	-0.532830000	-2.048585000	0.917381000	H	2.188703000	0.628238000	1.314396000
H	-0.888001000	0.980731000	-1.592625000	H	-3.102475000	-0.009399000	0.087188000
H	1.198448000	1.557525000	-0.662527000	H	-0.658229000	-1.316392000	0.959549000
H	0.888001000	-0.980731000	-1.592625000	H	2.376249000	1.355761000	-0.333235000
H	-1.198448000	-1.557525000	-0.662527000	H	1.881306000	-1.642765000	0.274620000
TS R=H				TS R=H			
E(HF)=-208.066086049 ν1=139.5i				E(HF)=-208.017673064 ν1=224.4i			
C	0.302647000	1.393605000	0.146579000	B	-1.415802000	1.139517000	-0.283691000
C	-1.086567000	1.087970000	-0.553980000	B	0.559509000	-0.156918000	0.216699000
B	-1.086567000	-0.026178000	0.506237000	C	-2.013071000	-0.266488000	-0.358872000
H	0.177392000	2.067303000	0.990733000	C	1.716016000	-0.414633000	-0.758759000
H	-1.780879000	1.919007000	-0.477605000	C	-0.860745000	-0.628378000	0.684291000
H	-1.555730000	0.158734000	1.584750000	C	1.930971000	0.453580000	0.507811000
B	1.086567000	0.026178000	0.506237000	H	-1.745238000	1.931762000	0.539320000
C	1.086567000	-1.087970000	-0.553980000	H	-0.462694000	1.375472000	-0.977453000
C	-0.302647000	-1.393605000	0.146579000	H	-1.838013000	-0.834737000	-1.269581000
H	1.555730000	-0.158734000	1.584750000	H	1.771767000	0.094562000	-1.714093000
H	1.780879000	-1.919007000	-0.477605000	H	-1.133480000	-0.310815000	1.689980000
H	-0.177392000	-2.067303000	0.990733000	H	2.546829000	0.039619000	1.300132000
H	-0.918822000	0.808994000	-1.592468000	H	-2.991947000	-0.470490000	0.066346000
H	0.951073000	1.876586000	-0.592187000	H	-0.794516000	-1.722806000	0.675805000
H	0.918822000	-0.808994000	-1.592468000	H	2.101734000	1.512525000	0.347309000
H	-0.951073000	-1.876586000	-0.592187000	H	2.187997000	-1.392578000	-0.769633000

Boration reactions

R-borirane + ethene

Transition states TS2_13a				**Products 13a**			
TS2_13a R=H				13a R=H			
E(HF)=-182.551263483 ν1=458.2i				E(HF)=-182.602666261 ν1=47.6			
C	-1.436098000	0.580511000	-0.473547000	C	1.492739000	0.768688000	0.000000000
B	-0.081875000	-0.173358000	-0.256735000	B	0.000000000	0.431299000	0.000000000
H	0.290282000	-0.840882000	-1.218795000	H	-0.100327000	-2.317542000	0.878927000
C	-1.360375000	-0.616945000	0.508707000	C	0.429912000	1.900050000	0.000000000
H	-2.009109000	0.427347000	-1.380184000	H	2.080462000	0.643361000	-0.904227000
H	-1.589137000	1.557049000	-0.027755000	H	2.080462000	0.643361000	0.904227000
H	-1.911431000	-1.501863000	0.209513000	H	0.344761000	2.494794000	-0.904292000
H	-1.495780000	-0.365308000	1.555795000	H	0.344761000	2.494794000	0.904292000
C	1.212493000	0.621884000	0.521078000	C	-1.136361000	-0.618885000	0.000000000
H	1.323264000	1.647928000	0.199266000	H	-1.780735000	-0.398833000	0.862250000
C	1.689589000	-0.406610000	-0.303447000	C	-0.706689000	-2.089266000	0.000000000
H	1.890787000	-1.391374000	0.099348000	H	-0.100327000	-2.317542000	-0.878927000
H	1.118188000	0.441919000	1.582797000	H	-1.780735000	-0.398833000	-0.862250000
H	2.158659000	-0.181059000	-1.253060000	H	-1.565930000	-2.763575000	0.000000000

TS2_13a R=Cl

E(HF)=-642.175390336
ν1=384.3i

C	-1.838596000	-0.140281000	-0.697903000
B	-0.469547000	0.197147000	-0.063485000
Cl	0.929412000	-1.202362000	-0.056777000
C	-1.695023000	-0.052052000	0.846682000
H	-2.000385000	-1.130181000	-1.110983000
H	-2.431274000	0.631711000	-1.176520000
H	-1.796405000	-0.985673000	1.388036000
H	-2.203939000	0.779980000	1.323318000
C	0.387231000	1.625400000	-0.220098000
H	0.397623000	1.995038000	-1.240204000
C	1.557228000	0.940641000	0.202859000
H	1.767944000	0.841662000	1.261140000
H	-0.045854000	2.300616000	0.512062000
H	2.394974000	0.779018000	-0.463447000

13a R=Cl

E(HF)=-642.205757683
ν1=40.3

C	-2.571433000	-0.111711000	-0.539406000
B	-1.192451000	0.343996000	-0.071368000
Cl	1.869289000	-0.719886000	-0.233135000
C	-1.895632000	-0.780752000	0.686965000
H	-2.661790000	-0.706477000	-1.443203000
H	-3.448551000	0.497119000	-0.343996000
H	-1.544694000	-1.801085000	0.568153000
H	-2.347793000	-0.596966000	1.656619000
C	0.028795000	1.292952000	-0.194830000
H	0.252437000	1.534729000	-1.237826000
C	1.278818000	0.809567000	0.520704000
H	1.077729000	0.573258000	1.563780000
H	-0.291664000	2.243027000	0.262244000
H	2.105387000	1.514136000	0.453762000

TS2_13a R=Me

E(HF)=-221.838116974
ν1=496.1i

C	-1.561197000	-0.025165000	0.726199000
B	-0.174817000	-0.147232000	0.027922000
C	-1.481890000	-0.180009000	-0.816614000
H	-1.952146000	-0.873101000	1.277148000
H	-1.838101000	-1.123952000	-1.215854000
C	1.631399000	-0.142494000	-0.177443000
C	0.902104000	-1.337676000	0.188277000
H	0.808739000	-2.093811000	-0.580916000
H	2.355024000	0.266469000	0.517318000
C	0.598949000	1.516706000	0.066565000
H	1.330521000	1.984606000	-0.590017000
H	-0.367860000	1.912753000	-0.244454000
H	0.794161000	1.799230000	1.098555000
H	1.895823000	-0.018061000	-1.219595000
H	1.054533000	-1.709537000	1.194529000
H	-1.922984000	0.929107000	1.096266000
H	-1.819815000	0.674290000	-1.394492000

13a R=Me

E(HF)=-221.906989245
ν1=48.4

C	2.322742000	-0.212369000	-0.411617000
B	0.843895000	-0.303503000	-0.029560000
C	1.673184000	0.881571000	0.476202000
H	3.052688000	-0.863607000	0.059042000
H	1.984505000	0.924353000	1.515541000
C	-1.721287000	-0.335806000	0.474793000
C	-0.491351000	-1.085624000	-0.049194000
H	-0.292879000	-1.980980000	0.561644000
H	-2.573786000	-1.017577000	0.550254000
C	-2.087268000	0.841982000	-0.425141000
H	-2.962387000	1.378436000	-0.053201000
H	-1.257670000	1.552425000	-0.483552000
H	-2.308855000	0.500233000	-1.440219000
H	-1.516355000	0.029020000	1.485757000
H	-0.677351000	-1.487221000	-1.053390000
H	2.606098000	0.078159000	-1.418642000
H	1.550395000	1.865748000	0.034305000

TS2_13a R=NH_2

E(HF)=-237.917228652
ν1=502.4i

C	1.626323000	-0.209720000	-0.698256000
B	0.229708000	0.111387000	-0.076151000
C	1.472975000	-0.115793000	0.838343000
H	2.170430000	0.596290000	-1.183374000
H	1.872798000	-1.189889000	-1.090733000
H	1.946305000	0.734503000	1.321119000
H	1.627922000	-1.044549000	1.377116000
C	-0.966845000	-1.237357000	-0.157307000
H	-1.031286000	-1.632364000	-1.162880000
C	-1.801465000	-0.187244000	0.200587000
H	-1.966636000	0.058707000	1.242123000
H	-0.607512000	-1.908280000	0.610791000
H	-2.506818000	0.244170000	-0.497021000
N	-0.531446000	1.439465000	-0.130466000
H	-0.603663000	1.907019000	-1.025123000
H	-0.315878000	2.101889000	0.601784000

13a R=NH_2

E(HF)=-237.949437077
ν1=57.4

C	1.947793000	0.215555000	-0.675012000
B	0.671515000	-0.403060000	-0.103615000
C	1.705046000	0.195001000	0.857984000
H	1.898139000	1.183385000	-1.162896000
H	2.742085000	-0.417255000	-1.058603000
H	1.511280000	1.150169000	1.333655000
H	2.344117000	-0.456780000	1.445990000
C	-0.675706000	-1.177868000	-0.251164000
H	-0.927081000	-1.403186000	-1.292242000
C	-1.713232000	-0.223499000	0.348356000
H	-1.569076000	-0.170598000	1.429706000
H	-0.664438000	-2.123452000	0.299550000
H	-2.739580000	-0.561791000	0.158802000
N	-1.419587000	1.111143000	-0.197434000
H	-1.634663000	1.145223000	-1.188957000
H	-1.964666000	1.836455000	0.254127000

Intermediate R=NH_2

E(HF)=-237.966507110
ν1=100.2

C	-1.780619000	0.023432000	-0.681445000
B	-0.337630000	0.152889000	-0.102218000
C	-1.573892000	0.009228000	0.848038000
H	-2.132040000	-0.907471000	-1.117384000

TS-INT_13a R=NH_2

E(HF)=-237.949392198
ν1=91.7i

C	-1.909930000	-0.196838000	-0.677043000
B	-0.619740000	0.392799000	-0.100924000
C	-1.690066000	-0.145749000	0.858528000
H	-1.895793000	-1.179603000	-1.135405000

H -2.276327000 0.893580000 -1.098426000 H -1.806087000 -0.928269000 1.345997000 H -1.934518000 0.874044000 1.395116000 C 0.923263000 1.169718000 -0.151879000 H 1.171361000 1.552799000 -1.144545000 C 1.787861000 -0.042803000 0.217554000 H 1.943328000 -0.124534000 1.292337000 H 0.970710000 1.984494000 0.568655000 H 2.736088000 -0.197685000 -0.300463000 N 0.758405000 -1.081131000 -0.168759000 H 0.904661000 -1.434494000 -1.110394000 H 0.662465000 -1.866442000 0.467906000	H -2.670990000 0.458165000 -1.090048000 H -1.544330000 -1.096941000 1.357868000 H -2.311553000 0.544524000 1.420764000 C 0.720824000 1.188412000 -0.246142000 H 0.967591000 1.423491000 -1.285951000 C 1.727531000 0.185907000 0.326375000 H 1.630313000 0.158729000 1.413554000 H 0.728270000 2.123020000 0.320936000 H 2.766667000 0.436339000 0.082196000 N 1.297424000 -1.129776000 -0.180922000 H 1.496266000 -1.214641000 -1.172710000 H 1.760133000 -1.899041000 0.289560000
R-borirane + ethyne	
Van der Waals complexes	
VDW R=Cl	VDW R=Me
E(HF)=-640.955425527 ν1=54.2 C -1.236891000 1.090085000 0.785085000 B 0.037449000 0.861769000 0.000000000 C -1.236891000 1.090085000 -0.785085000 H -1.411854000 2.044764000 1.270946000 H -1.725536000 0.256821000 -1.278113000 C -0.040209000 -2.392354000 0.000000000 C -1.236891000 -2.343878000 0.000000000 H -2.301143000 -2.306870000 0.000000000 H 1.023762000 -2.437410000 0.000000000 Cl 1.757071000 0.656979000 0.000000000 H -1.411854000 2.044764000 -1.270946000 H -1.725536000 0.256821000 1.278113000	E(HF)=-220.623208641 ν1=70.1 C -1.030731000 -1.171579000 0.776140000 B -0.958587000 0.147260000 0.000000000 C -1.030731000 -1.171579000 -0.776140000 H -1.954134000 -1.463363000 1.267098000 H -0.148671000 -1.557224000 -1.276518000 C 2.179513000 0.809877000 0.000000000 C 2.229146000 -0.386599000 0.000000000 H 2.275345000 -1.450511000 0.000000000 H 2.138400000 1.873670000 0.000000000 C -1.030731000 1.692904000 0.000000000 H -0.606321000 2.150270000 -0.895554000 H -2.101361000 1.943037000 0.000000000 H -0.606321000 2.150270000 0.895554000 H -1.954134000 -1.463363000 -1.267098000 H -0.148671000 -1.557224000 1.276518000
VDW R=NH_2	
E(HF)=-236.719757963 ν1=55.9 C -1.154158000 -0.859718000 0.782732000 B -1.154158000 0.451514000 0.000000000 C -1.154158000 -0.859718000 -0.782732000 H -2.058944000 -1.217035000 1.263324000 H -0.243215000 -1.209520000 1.257258000 H -2.058944000 -1.217035000 -1.263324000 H -0.243215000 -1.209520000 -1.257258000 C 2.781471000 -0.838274000 0.000000000 H 3.359465000 -1.732204000 0.000000000 C 2.131424000 0.167676000 0.000000000 H 1.540460000 1.055471000 0.000000000 N -1.120427000 1.835454000 0.000000000 H -1.154656000 2.382148000 0.846398000 H -1.154656000 2.382148000 -0.846398000	
Transition states TS1_13b	**Products 13b**
TS1_13b R=H	13b R=H
E(HF)=-181.294376595 ν1=451.5i C 0.161331000 1.310475000 0.783871000 B 0.325456000 -0.023044000 0.000000000 H 1.413493000 -0.592825000 0.000000000 C 0.161331000 1.310475000 -0.783871000 H 1.011476000 1.789147000 1.257198000 H -0.783273000 1.580856000 1.244850000 H 1.011476000 1.789147000 -1.257198000 H -0.783273000 1.580856000 -1.244850000 C -0.890350000 -1.178950000 0.000000000 H -1.954765000 -1.063378000 0.000000000 C 0.161331000 -1.834696000 0.000000000 H 0.895732000 -2.612406000 0.000000000	E(HF)=-181.377538101 ν1=68.5 C 0.696225000 1.702626000 0.000000000 B 0.000000000 0.344184000 0.000000000 H -0.182140000 -2.336781000 0.000000000 C 1.530361000 0.392199000 0.000000000 H 0.722439000 2.302269000 0.904574000 H 0.722439000 2.302269000 -0.904574000 H 2.084926000 0.164498000 0.904905000 H 2.084926000 0.164498000 -0.904905000 C -1.261481000 -0.523470000 0.000000000 H -2.255230000 -0.082274000 0.000000000 C -1.157229000 -1.858406000 0.000000000 H -2.024623000 -2.513094000 0.000000000

TS1_13b R=Cl	13b R=Cl
E(HF)=-640.931143148 ν1=385.3i	E(HF)=-640.979523529 ν1=55.4
C 0.700409000 1.574139000 0.774138000 B -0.001924000 0.427005000 0.000000000 C 0.700409000 1.574139000 -0.774138000 H 1.645450000 1.364073000 1.262652000 H 0.133547000 2.364142000 -1.253864000 C -1.646482000 -1.001374000 0.000000000 C -1.638086000 0.249724000 0.000000000 H -2.340773000 1.065683000 0.000000000 H -1.812057000 -2.057294000 0.000000000 Cl 0.700409000 -1.351742000 0.000000000 H 1.645450000 1.364073000 -1.262652000 H 0.133547000 2.364142000 1.253864000	C -1.521699000 1.295109000 0.000000000 B 0.000000000 1.219011000 0.000000000 C -0.671169000 2.591334000 0.000000000 H -2.073130000 1.060057000 0.905123000 H -0.684223000 3.191207000 -0.904741000 C 1.312590000 -0.958955000 0.000000000 C 1.277324000 0.376518000 0.000000000 H 2.255609000 0.851383000 0.000000000 H 2.229300000 -1.537282000 0.000000000 Cl -0.079557000 -1.984454000 0.000000000 H -0.684223000 3.191207000 0.904741000 H -2.073130000 1.060057000 -0.905123000
TS1_13b R=Me	13b R=Me
E(HF)=-220.592333344 ν1=474.7i	E(HF)=-220.686790671 ν1=71.8
C -0.109426000 1.476624000 0.781892000 B -0.109426000 0.128876000 0.000000000 C -0.109426000 1.476624000 -0.781892000 H 0.789849000 1.853026000 1.259278000 H -1.016262000 1.846405000 -1.247891000 C -0.301484000 -1.697042000 0.000000000 C -1.307087000 -0.935003000 0.000000000 H -2.380686000 -0.932444000 0.000000000 H 0.212222000 -2.639146000 0.000000000 C 1.442407000 -0.700629000 0.000000000 H 1.764009000 -1.230568000 -0.896262000 H 1.950490000 0.266037000 0.000000000 H 1.764009000 -1.230568000 0.896262000 H 0.789849000 1.853026000 -1.259278000 H -1.016262000 1.846405000 1.247891000	C 0.609712000 2.250111000 0.000000000 B 0.000000000 0.846733000 0.000000000 C 1.525555000 0.999821000 0.000000000 H 0.596913000 2.850451000 0.904371000 H 2.094196000 0.805970000 -0.904732000 C -1.212707000 -1.384840000 0.000000000 C -1.243356000 -0.039058000 0.000000000 H -2.226761000 0.425251000 0.000000000 H -2.160384000 -1.924729000 0.000000000 C 0.003424000 -2.253386000 0.000000000 H -0.005471000 -2.907995000 -0.876749000 H 0.920108000 -1.666929000 0.000000000 H -0.005471000 -2.907995000 0.876749000 H 2.094196000 0.805970000 0.904732000 H 0.596913000 2.850451000 -0.904371000
TS1_13b R=NH_2	13b R=NH_2
E(HF)=-236.669914813 ν1=548.1i	E(HF)=-236.749427555 ν1=100.2
C -0.737477000 1.305770000 0.775569000 B 0.052973000 0.205308000 0.000000000 C -0.737477000 1.305770000 -0.775569000 H -0.178141000 2.097854000 1.265545000 H -1.699570000 1.122434000 1.241509000 H -0.178141000 2.097854000 -1.265545000 H -1.699570000 1.122434000 -1.241509000 C -0.737477000 -1.366328000 0.000000000 H -1.803050000 -1.470653000 0.000000000 C 0.385013000 -1.881203000 0.000000000 H 1.282444000 -2.456998000 0.000000000 N 1.553870000 -0.035672000 0.000000000 H 2.049288000 0.263091000 0.829209000 H 2.049288000 0.263091000 -0.829209000	C 0.767205000 2.158767000 0.000000000 B 0.000000000 0.834908000 0.000000000 C 1.548386000 0.818540000 0.000000000 H 0.825046000 2.755207000 0.904776000 H 0.825046000 2.755207000 -0.904776000 H 2.102202000 0.584163000 0.905000000 H 2.102202000 0.584163000 -0.905000000 C -1.261938000 0.032828000 0.000000000 H -2.245319000 0.487818000 0.000000000 C -1.238467000 -1.333763000 0.000000000 H -2.164691000 -1.904807000 0.000000000 N -0.131718000 -2.104256000 0.000000000 H 0.774241000 -1.658992000 0.000000000 H -0.187811000 -3.105735000 0.000000000
Intermediate R=NH_2	TS-INT_13a R=NH_2
E(HF)=-236.737708216 ν1=187.5	E(HF)=-236.722760980 ν1=143.9i
C 0.615465000 1.513401000 0.767858000 B -0.044911000 0.319669000 0.000000000 C 0.615465000 1.513401000 -0.767858000 H 1.584199000 1.399818000 1.245153000 H -0.014146000 2.246150000 1.260076000 H 1.584199000 1.399818000 -1.245153000 H -0.014146000 2.246150000 -1.260076000 C -1.420975000 -0.465960000 0.000000000 H -2.487661000 -0.290508000 0.000000000 C -0.800855000 -1.643660000 0.000000000	C 0.640765000 1.656623000 0.771597000 B -0.203996000 0.629600000 0.000000000 C 0.640765000 1.656623000 -0.771597000 H 1.556077000 1.339498000 1.258443000 H 0.148704000 2.483451000 1.274375000 H 1.556077000 1.339498000 -1.258443000 H 0.148704000 2.483451000 -1.274375000 C -1.337463000 -0.420561000 0.000000000 H -2.407493000 -0.247412000 0.000000000 C -0.807661000 -1.638384000 0.000000000

H -1.072556000 -2.692094000 0.000000000 N 0.615465000 -1.210520000 0.000000000 H 1.140907000 -1.468564000 0.831765000 H 1.140907000 -1.468564000 -0.831765000	H -1.347944000 -2.581615000 0.000000000 N 0.640765000 -1.620042000 0.000000000 H 1.031031000 -2.075194000 0.819226000 H 1.031031000 -2.075194000 -0.819226000
R-borirene + ethyne	
Van der Waals complexes	
VDW R=H	VDW R=Cl
E(HF)=-180.094340519 ν1=38.4 C -1.555931000 0.608216000 0.405261000 B -1.099035000 0.055654000 -0.880915000 C -1.847950000 -0.681654000 0.148200000 H -1.706799000 1.332057000 1.193692000 H -2.349457000 -1.511045000 0.625957000 C 2.390623000 -0.543463000 0.151193000 C 1.975140000 0.571793000 0.020051000 H 1.596283000 1.559639000 -0.099982000 H 2.760199000 -1.534927000 0.266290000 H -0.576340000 0.146655000 -1.929606000	E(HF)=-639.745162317 ν1=28.0 C -1.490989000 1.786242000 -0.145695000 B -1.101531000 0.387052000 0.015009000 Cl -1.412450000 -1.324999000 -0.008511000 C -0.208037000 1.527849000 0.207927000 H -2.112562000 2.645878000 -0.352049000 H 0.702744000 2.067950000 0.423084000 C 2.419266000 -0.576063000 0.050993000 C 3.455429000 0.004187000 -0.104127000 H 4.380204000 0.512123000 -0.244080000 H 1.494917000 -1.089521000 0.188090000
VDW R=Me	VDW R=NH_2
E(HF)=-219.415446825 ν1=43.9 C 1.630047000 -0.800219000 -0.637384000 B 1.035184000 0.392924000 0.001243000 C 1.592119000 -0.777586000 0.710621000 H 1.969507000 -1.465032000 -1.420383000 H 1.884891000 -1.413922000 1.534855000 C -2.526727000 0.025103000 0.078544000 C -1.991232000 -1.032744000 -0.088457000 H -1.511596000 -1.971393000 -0.236408000 H -2.999566000 0.967217000 0.227280000 C 0.407375000 1.814278000 -0.048227000 H -0.145579000 2.057928000 0.860289000 H 1.208787000 2.553459000 -0.152474000 H -0.251857000 1.934137000 -0.909952000	E(HF)=-235.499511203 ν1=11.8 C -1.871136000 -0.906936000 0.672909000 B -1.382910000 0.316703000 -0.002268000 C -1.845275000 -0.919435000 -0.672945000 H -2.144880000 -1.577876000 1.474882000 H -2.088902000 -1.605227000 -1.472065000 C 2.369553000 0.050292000 0.002453000 C 3.447086000 -0.473020000 0.004632000 H 4.403616000 -0.939109000 0.007879000 H 1.409054000 0.518821000 0.000805000 N -0.830759000 1.604244000 -0.004097000 H -0.739142000 2.149504000 0.837177000 H -0.711252000 2.135259000 -0.850952000
Transition states TS1_13c	**Products 13c**
TS1_13c R=H	13c R=H
E(HF)=-180.042995822 ν1=674.6i C 0.173921000 1.431245000 0.663614000 B 0.339202000 0.052366000 0.000000000 H 1.408073000 -0.590558000 0.000000000 C 0.173921000 1.431245000 -0.663614000 H 0.102229000 2.149713000 1.469458000 H 0.102229000 2.149713000 -1.469458000 C 0.173921000 -1.772207000 0.000000000 C -0.897956000 -1.153717000 0.000000000 H -1.961206000 -1.039189000 0.000000000 H 0.909831000 -2.550909000 0.000000000	E(HF)=-180.169630211 ν1=90.5 C 1.407532000 0.853616000 0.000000000 B 0.000000000 0.408481000 0.000000000 H 0.311662000 -2.300106000 0.000000000 C 0.456501000 1.810258000 0.000000000 H 2.486959000 0.794171000 0.000000000 H 0.402227000 2.890042000 0.000000000 C -0.730388000 -1.994062000 0.000000000 C -1.067807000 -0.701768000 0.000000000 H -2.124759000 -0.446284000 0.000000000 H -1.471118000 -2.788494000 0.000000000
TS1_13c R=Cl	13c R=Cl
E(HF)=-639.694987632 ν1=475.8i C 0.729503000 1.694198000 0.664332000 B 0.053543000 0.513785000 0.000000000 Cl 0.729503000 -1.303133000 0.000000000 C 0.729503000 1.694198000 -0.664332000 H 1.112684000 2.275518000 1.490967000 H 1.112684000 2.275518000 -1.490967000 C -1.633327000 -0.984973000 0.000000000 C -1.623452000 0.262322000 0.000000000 H -2.321047000 1.081553000 0.000000000 H -1.786967000 -2.042735000 0.000000000	E(HF)=-639.772742163 ν1=43.4 C -0.661152000 2.613348000 0.000000000 B 0.000000000 1.297583000 0.000000000 Cl -0.197386000 -1.903410000 0.000000000 C -1.453317000 1.520988000 0.000000000 H -0.768170000 3.689096000 0.000000000 H -2.506420000 1.278374000 0.000000000 C 1.240941000 -0.932290000 0.000000000 C 1.249521000 0.398624000 0.000000000 H 2.240864000 0.844327000 0.000000000 H 2.133338000 -1.545758000 0.000000000

TS1_13c R=Me	13c R=Me
E(HF)=-219.34268688 ν1=588.9i	E(HF)=-219.478342423 ν1=61.3
C -0.227918000 1.578007000 0.662469000 B -0.086067000 0.190070000 0.000000000 C -0.227918000 1.578007000 -0.662469000 H -0.320533000 2.286172000 1.475560000 H -0.320533000 2.286172000 -1.475560000 C -0.227918000 -1.664219000 0.000000000 C -1.263067000 -0.959245000 0.000000000 H -2.335422000 -0.944164000 0.000000000 H 0.371441000 -2.554839000 0.000000000 C 1.507815000 -0.572385000 0.000000000 H 1.845177000 -1.098495000 -0.894194000 H 1.979059000 0.412300000 0.000000000 H 1.845177000 -1.098495000 0.894194000	C -1.438280000 1.267800000 0.000000000 B 0.000000000 0.926502000 0.000000000 C -0.562840000 2.292510000 0.000000000 H -2.510605000 1.126620000 0.000000000 H -0.590374000 3.373204000 0.000000000 C 1.079301000 -1.386500000 0.000000000 C 1.187918000 -0.050300000 0.000000000 H 2.195024000 0.359162000 0.000000000 H 1.991808000 -1.982617000 0.000000000 C -0.191875000 -2.176774000 0.000000000 H -0.230994000 -2.828762000 0.877665000 H -1.069210000 -1.531775000 0.000000000 H -0.230994000 -2.828762000 -0.877665000
TS1_13c R=NH_2	13c R=NH_2
E(HF)=-235.434363949 ν1=601.4i	E(HF)=-235.535740303 ν1=117.8
C -0.769821000 1.446862000 0.665396000 B 0.027042000 0.331842000 0.000000000 C -0.769821000 1.446862000 -0.665396000 H -1.166885000 2.045408000 1.474791000 H -1.166885000 2.045408000 -1.474791000 C 0.351541000 -1.861468000 0.000000000 C -0.769821000 -1.342291000 0.000000000 H -1.832551000 -1.467556000 0.000000000 H 1.222028000 -2.478777000 0.000000000 N 1.503181000 -0.058949000 0.000000000 H 2.017177000 0.234578000 0.823347000 H 2.017177000 0.234578000 -0.823347000	C -2.307023000 0.264165000 0.008788000 B -0.830385000 0.362240000 -0.000726000 C -1.627886000 -0.896706000 -0.015022000 H -3.336813000 0.592577000 0.025833000 H -1.863686000 -1.953009000 -0.026398000 C 1.681656000 0.448440000 -0.007115000 C 0.494514000 1.099154000 -0.007384000 H 0.540549000 2.181170000 -0.013645000 H 2.617970000 1.001192000 -0.025049000 N 1.853238000 -0.904730000 0.060968000 H 1.037323000 -1.486551000 -0.055736000 H 2.736351000 -1.303786000 -0.203754000
Intermediate R=NH_2	TS-INT_13c R=NH_2
E(HF)=-235.502720015 ν1=117.8	E(HF)=-235.502578591 ν1=188.7i
C 0.651115000 1.631745000 0.662656000 B -0.038420000 0.444243000 0.000000000 C 0.651115000 1.631745000 -0.662656000 H 0.963741000 2.268040000 1.480181000 H 0.963741000 2.268040000 -1.480181000 C -0.769808000 -1.587661000 0.000000000 C -1.381159000 -0.407917000 0.000000000 H -2.448720000 -0.232351000 0.000000000 H -1.088002000 -2.623293000 0.000000000 N 0.651115000 -1.216809000 0.000000000 H 1.167980000 -1.495729000 0.829818000 H 1.167980000 -1.495729000 -0.829818000	C 0.655714000 1.653783000 0.664572000 B -0.066690000 0.502094000 0.000000000 C 0.655714000 1.653783000 -0.664572000 H 0.998992000 2.275258000 1.480925000 H 0.998992000 2.275258000 -1.480925000 C -0.774914000 -1.583268000 0.000000000 C -1.366437000 -0.394756000 0.000000000 H -2.432847000 -0.209784000 0.000000000 H -1.146790000 -2.601579000 0.000000000 N 0.655714000 -1.288398000 0.000000000 H 1.152325000 -1.604044000 0.828253000 H 1.152325000 -1.604044000 -0.828253000

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Electronically Excited States of Borylenes

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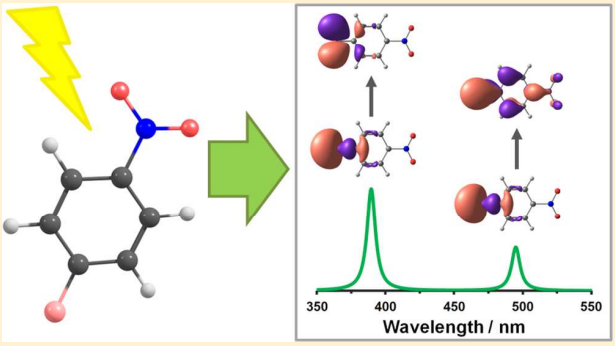
Supporting Information

ABSTRACT: Borylenes, RB, are elusive reactive intermediates. Still not much is known about their excited states from spectroscopic experiments, and existing knowledge is limited to diatomic borylenes only. The electronic structure and geometry of borylenes with diverse substituents on boron (where R = H, F, Cl, CH_3, CF_3, *t*Bu, NH_2, Ph, and $SiMe_3$) were studied by means of computational chemistry. For this purpose, geometries of borylenes in their lowest singlet and triplet states were optimized at the B3LYP/def2-TZVP level of theory. Additionally, the influence of substitution on the energies of frontier molecular orbitals, HOMO−LUMO energy gaps, singlet−triplet energy splittings, and excitation energies was investigated. Two lowest vertical singlet−singlet excitations were computed using EOM-CCSD and TD-DFT (using hybrid B3LYP, and long-range separated CAM-B3LYP and ωB97X functionals) in combination with the aug-cc-pVTZ basis set. The electronic transitions involve excitations from nonbonding sp boron orbital (HOMO) mainly to empty p(B) orbitals and partially to the orbitals of the substituent, and are of n → π^* type. The results can facilitate prospective identification of borylenes, e.g., in UV−vis matrix isolation or time-resolved spectroscopy experiments.



INTRODUCTION

Boron prefers the coordination numbers three, four, or even higher in its molecular compounds. Thus, monovalent boron compounds, borylenes BR, are exceptional and fascinating. The low coordination number makes borylenes, which may be considered the boron analogues of carbenes CR_2, highly reactive and rather rare. There are a number of instances where borylenes were invoked as transient reactive intermediates.[1−14]

Direct spectroscopic investigation of borylenes is scarce. Besides the diatomic borylenes (BH, BF, BCl, BBr, and BI) that were investigated by microwave spectroscopy,[15−21] only a few larger borylenes were identified by direct spectroscopic techniques. These include aminoborylene, H_2NB,[5] and ethynylborylene,[6] which formed during co-condensation of boron atoms with ammonia and acetylene, respectively, and phenylborylene.[7] This was obtained by exhaustive denitrogenation of diazidophenylborane. These borylenes were observed by infrared spectroscopy under inert gas matrix isolation conditions and identified by comparison with computed vibrational spectra.

Optical spectroscopy, which probes the manifold of electronically excited states, is another important technique for identification of reactive intermediates. Particularly transient absorption and UV/vis matrix isolation spectroscopy demonstrated their usefulness in studying reactive species like carbenes[22−33] and nitrenes.[34−42] Existing knowledge, of either experimental or computational nature, on the excited states is only available for diatomic borylenes (BH, BF, BCl, BBr, and BI). Most investigations have been performed on the excited states of parent borylene (BH),[20,43−68] including the experimental determination of the singlet−triplet energy splitting[62] that was confirmed by sophisticated computations.[52,57,66] A number of studies concerning the electronically excited states of chloroborylene (BCl),[69−81] fluoroborylene (BF),[61,82−93] and bromoborylene (BBr)[80,94−99] are available. Iodoborylene (BI) is the least studied haloborylene.[100−105] Investigations on diatomic borylenes until 1975 are summarized in the book authored by Huber and Herzberg.[106] The singlet−triplet energy separation of methylborylene (CH_3B) was previously calculated by Schleyer et al.[107]

Knowledge of the energies of energetically low-lying electronically excited states of larger borylenes with respect to the ground state will be extremely important in identifying borylenes as reactive intermediates in future matrix isolation or time-resolved spectroscopy experiments. We here investigate by computational means the lowest energy excited states of borylenes using equation of motion (EOM) coupled cluster theory with single and double excitations (CCSD).[108−111] In addition, computationally economic time-dependent density functional (TD-DFT)[112−116] methods are employed and their performance in comparison to that of EOM-CCSD is evaluated.

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COMPUTATIONAL DETAILS

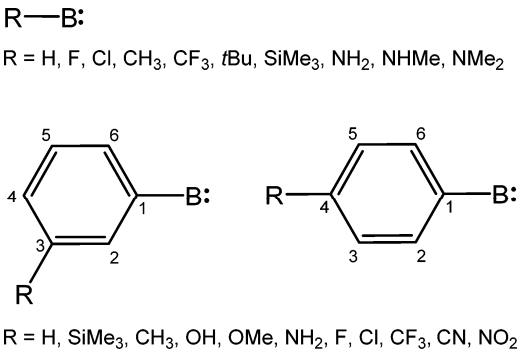
Ground state geometries of singlet borylenes were optimized using density functional theory using the hybrid GGA B3LYP functional[117,118] in combination with the def2-TZVP[119,120] basis set. All optimized singlet and triplet structures are minima as confirmed by subsequent analytical harmonic frequency calculations. Computations of singlet vertical excitation energies employed equation-of-motion coupled cluster singles and doubles (EOM-CCSD)[108−111] and time-dependent density functional theory (TD-DFT), both methods in combination with the aug-cc-pVTZ[121,122] basis set. Excited state calculations were performed using the B3LYP/def2-TZVP optimized ground state geometries of singlet borylenes. Functionals used in time-dependent computations were B3LYP, range-separated[123] hybrid CAM-B3LYP,[124] and ωB97X.[125] The choice of functional for TDDFT computations is not straightforward. Many benchmark studies have been carried out to estimate the accuracy of the TDDFT method and the performance of various functionals.[126−131] Long-range corrected functionals have demonstrated to be efficient in the case of charge transfer (CT) and through-space CT excitations, in calculating Rydberg states, or excitations in large π-systems where functionals without the long-range correction often fail.[132−136] Natural transition orbital (NTO)[137] analysis was carried out using the TD-ωB97X results to estimate the main contribution to the electronic excitation and to visualize the pairs of orbitals taking part in particular transitions. The frozen core approximation was applied during EOM-CCSD calculations. All calculations were performed using the Gaussian09 program.[138] The discussion in the main part of the article focuses on B3LYP/def2-TZVP optimized singlet ground state and triplet state structures. All calculations were carried out for isolated molecules. Figures of molecular structures and orbitals were prepared using the CYLView[139] and Chemcraft[140] programs, respectively.

RESULTS AND DISCUSSION

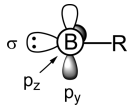
To allow a comprehensive study of substituent effects on electronic structure and vertical excitation energies of borylenes, a larger number of substituents R varying in electronic nature as electron donating or electron withdrawing were chosen: R = CH_3, *t*Bu, Ph, $SiMe_3$, NR_2, F, Cl, CF_3. Parent borylene, HB, is the reference molecule. The effect of substitution by electron-donating or electron-withdrawing groups in meta and para positions (relative to boron) on structure and excitation energies in arylborylenes was also investigated, R = CH_3, OH, OMe, NH_2, $SiMe_3$, F, Cl, CF_3, CN, NO_2 (Scheme 1). Substitution in ortho position was not studied due to expected interference of steric effects.

1. Electronic Structure Description of Parent and Substituted Borylenes. Similar to carbenes, borylenes are reactive intermediates possessing one lone electron pair. This nonbonding n_σ type orbital is of sp character and the highest occupied molecular orbital (HOMO) of borylene (Scheme 2). Unlike carbenes, borylenes have only one substituent and two empty p orbitals. These p_π type orbitals constitute the two lowest unoccupied molecular orbitals (LUMO and LUMO+1), and are degenerate in linear ($C_{\infty v}$ symmetry) and C_{3v} symmetrical borylenes (like CH_3B). The electronic configuration of the singlet ground state of borylenes is σ^2. The lowest energy excited states can be characterized as σ^1p^1, giving rise to $^1\Pi$ and $^3\Pi$ states in the case of linear or C_{3v} symmetry

Scheme 1. Molecules Studied in the Present Work



Scheme 2. Orbitals of the Lowest Singlet State of Borylenes



borylenes. In borylenes of lower symmetry p orbitals are no longer degenerate because of disparate interaction with substituents. The two orbitals transform according to b_1 and b_2 (states $^{1,3}B_1$ and $^{1,3}B_2$) in C_{2v}, to a′ and a″ (states ^{1,3}A′ and ^{1,3}A″) in C_s, and a (states ^{1,3}A) in C_1 point groups.

2. Geometries of Singlet and Triplet Borylenes. Geometries of singlet substituted borylenes were optimized within the highest possible symmetry (Figure S1). The resulting structures are the energetically most stable conformers. Most of the triplet borylenes have the same molecular symmetry as singlet species. In the case of CH_3B, *t*BuB, $SiMe_3B$, and CF_3B symmetry is reduced to C_s in the triplet state. Shortening of the R−B bond in triplet borylenes is observed in nearly all cases, apart from FB, CH_3B, and *t*BuB in which this bond is notably elongated (Table S1). In the series of singlet borylenes with carbon substituents (CH_3B, *t*BuB, PhB, and CF_3B) the longest C−B bond was found for CF_3B (1.650 Å) and shortest ones for PhB and CH_3B (~1.53 Å). In the aminoborylene series the N−B bond length is approximately invariant (~1.37 Å) to methyl substitution on the nitrogen atom. The Si−B bond in $SiMe_3B$ (2.115 Å) is longer than in H_2BSiMe_3 (2.019 Å) calculated at the same level of theory. Substitution of one hydrogen atom by boron in phenylborylene causes structural changes of the phenyl ring. Bonds C1C2 and C1C6 are elongated from 1.391 (as calculated in benzene at B3LYP/def2-TZVP) to 1.405 Å, while the remaining CC bonds hardly change.

Substitution of the phenyl ring of PhB in meta or para positions results in minor structural changes (Figure S2). Most noteworthy is the influence of electron-donating groups (EDG) at the para position. As expected, EDG favor the quinoidal distortion with shorter C−B bonds and significant bond length alternation in the phenyl ring (Scheme 3). Electron-withdrawing groups (EWG), on the contrary, result in longer C−B bonds.

3. Effect of Substitution on Frontier Molecular Orbital Energies, HOMO−LUMO Gaps, and Singlet−Triplet Energy Splittings. HOMO and LUMO energies of parent borylene (BH) are −6.52 and −2.60 eV as computed at B3LYP/def2-TZVP, respectively. Upon substitution, these energy values shift, depending on the nature of the substituent

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Scheme 3. Contribution of the Quinoidal Resonance Structure to the Ground State of *p*-EDG Substituted Arylborylenes

(Figure 1). In the case of σ-electron-withdrawing substituents (F, Cl, CF_3), the HOMO energy drops compared to that for

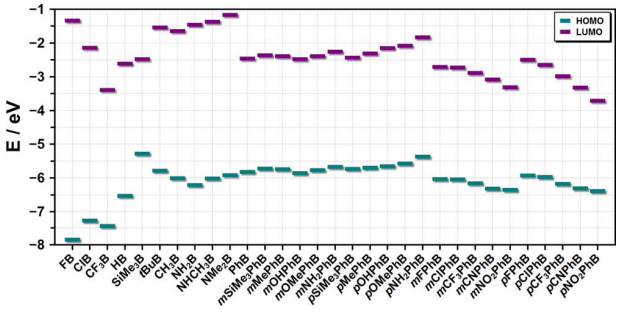

Figure 1. Energies of HOMO and LUMO of borylenes given in eV computed at the B3LYP/def2-TZVP level of theory.

HB. This is reminiscent of the situation in carbenes[141,142] and can similarly be explained in the spirit of Bent's rule[143] by rehybridization of the B atom that results in increased s-character of the lone electron pair. Halogen substituents tend to shift the LUMO energies upward due to π-electron donation into empty p(B) orbitals from halogen lone electron pairs. Therefore, the energy of the LUMO level in the FB molecule is elevated to −1.33 eV. The electron-withdrawing CF_3 group lowers both HOMO and LUMO energies. On the contrary, introduction of electron-donating groups (CH_3, *t*Bu, $SiMe_3$) results in a HOMO energy increase, while the LUMO levels are shifted to higher energies. The $SiMe_3$ group elevates the energy of HOMO to −5.27 eV, which is the highest HOMO energy among all studied borylenes. The aminoborylenes are special. The lp(N)−p_z(B) interaction produces a BN double bond whose π^* orbital becomes LUMO+1. The σ and p_y(B) orbital energies are increased compared to those of BH. Aryl substituents increase the HOMO and decrease the LUMO energies. There is a good correlation between energy of HOMO of substituted phenylborylenes and σ_m (Figure 2A) and σ_p (Figure 2B) substituent parameters.[144] Correlations with σ^+ were poor. Electron-donating substituents tend to increase HOMO energy, whereas electron-withdrawing groups decrease its energy with respect to unsubstituted PhB.

The alterations of HOMO and LUMO energy levels by change of substituents have an influence on the size of the energy gap between highest occupied and lowest unoccupied molecular orbitals. Most substituents increase the HOMO−LUMO gap compared to that of BH (3.92 eV, Table S1). The largest gaps were obtained for haloborylenes (6.51 eV for BF), followed by aminoborylenes (4.65−4.76 eV) and alkylborylenes (>4 eV). Exceptions are phenylborylene and (trimethylsilyl)-borylene that have smaller H−L gaps than parent borylene, 3.36 and 2.80 eV, respectively. The HOMO−LUMO gaps of arylborylenes are most strongly influenced by EDG and EWG substitution in the para position. The former substitution pattern increases, and the latter decreases, the gap.

The singlet−triplet energy splittings were computed at the B3LYP/def2-TZVP+ZPVE level of theory that only slightly

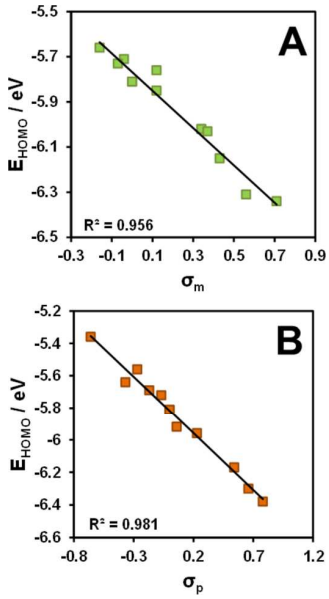

Figure 2. HOMO energies (eV) of *m*-arylborylenes plotted against σ_m substituent parameter (A), HOMO energies (eV) of *p*-arylborylenes plotted against σ_p substituent parameter (B).

underestimates this energy difference for BH (exp 29.8 kcal/mol; calc 26.4 kcal/mol).[62] The S−T splittings correlate well with the HOMO−LUMO energy gaps discussed above (Figure 3). Most borylenes studied here have larger S−T gaps than the

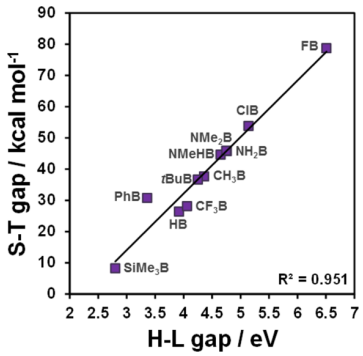

Figure 3. Correlation between HOMO−LUMO gap and singlet−triplet energy splitting of substituted borylenes computed at the B3LYP/def2-TZVP level of theory.

parent borylene. The smallest S−T gap was computed for (trimethylsilyl)borylene (8.2 kcal/mol). Among the arylborylenes there is a fair correlation of the singlet−triplet splitting with the substituent parameter σ_m (Figure 4A) or σ_p (Figure 4B). The effect of the substitution on the S−T separation is more pronounced in para position. Electron releasing groups at the aryl ring tend to increase and electron-withdrawing substituents decrease the S−T gaps. Similar trends were obtained from the computational and experimental investigations on the influence of substitution on singlet−triplet energy splitting in phenylcarbenes[145,146] and phenyl(carbomethoxy)carbenes.[147] The S−T gap in the arylborylene series increases with increasing energy of the HOMO of meta-substituted (Figure 4C) and para-substituted arylborylenes (Figure 4D).

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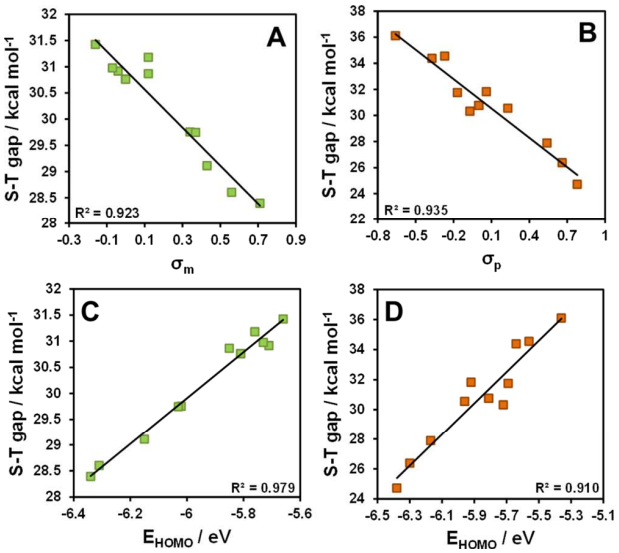

Figure 4. Singlet−triplet gap (kcal/mol) of meta-substituted arylborylenes plotted against σ_m substituent parameter (A), singlet−triplet gap (kcal/mol) of para-substituted arylborylenes plotted against σ_p substituent parameter (B), singlet−triplet gap (kcal/mol) of meta-substituted arylborylenes plotted against energies of HOMO (C), and singlet−triplet gap (kcal/mol) of para-substituted arylborylenes plotted against energies of HOMO (D). HOMO energies and singlet−triplet gaps were computed at the B3LYP/def2-TZVP level of theory.

4. Electronic Transitions in Substituted Borylenes. To investigate the influence of substitution on the experimentally observable electronic transition energies in borylenes, we employed geometries computed at the B3LYP/def2-TZVP level of theory and calculated vertical singlet−singlet transition energies from the singlet ground state. For the purpose of this study, we focus on the lowest (for $C_{\infty v}$ and C_{3v} symmetric borylenes) and the two lowest singlet excitations (for borylenes of lower symmetry) computed with time-dependent density functional theory (TDDFT) and equation-of-motion coupled cluster singles and doubles (EOM-CCSD). Time-dependent methods are computationally efficient and give reasonably good results for the prediction of electronic energies and properties of excited states.[148−152] EOM-CCSD, which is an accurate and reliable method for computation of excited states,[153,154] was used to provide reference values to TD-DFT results where experimental excitation energies of borylenes are not available. To display the orbital pairs involved in particular transition, natural transition orbitals (NTO)[137] were calculated. The method is especially useful when a transition is complex and the evaluation of the main contribution is troublesome.

4.1. Excitation Energies of Two Lowest Singlet Electronic Transitions. The two lowest singlet electronic transitions are of n → π^* type. These comprise the excitations from the nonbonding HOMO (sp orbital located on boron), which holds a lone pair of electrons, to LUMO and LUMO+1, which mainly involve empty p_y and p_z orbitals of boron and partially orbitals of substituent (Scheme 2, Figure 5, and Figure S3 for comparison). In this section we will refer to the excitation energies obtained from the EOM-CCSD computations. Despite the differences between TD-DFT (and between functionals used in TD calculations) and EOM-CCSD in detail, all methods used here give similar trends of excitation energy changes with the nature of the substituent (Tables S2, S3, Figure 5, and Figure S3).

4.2. S_1 State. The lowest energy electronic transition in diatomic borylenes is $X^1\Sigma^+ \rightarrow A^1\Pi$. The vertical excitation energies of HB (2.93 eV), FB (6.47 eV), and ClB (4.66 eV) calculated at the EOM-CCSD level are about 0.1 eV higher than the experimentally obtained adiabatic energies of the S_1 states, 2.86, 6.34, 4.56 eV, respectively.[106] The transition energies of diatomic borylenes increase with increasing electronegativity of the substituent, which is consistent with the increasing HOMO−LUMO gap in the series (Table S1 and Figure 6). There is a good correlation between the HOMO−LUMO gap and the S_1 energy (Figure 7). The excitation energies of CH_3B, *t*BuB, and CF_3B are higher than 3 eV and the transitions have moderate oscillator strengths (f = 0.028−0.045). Excitation energies of aminoborylenes are over 4 eV (f = 0.077−0.091). A very low transition energy of 1.63 eV, which lies almost in the near-infrared region (758.9 nm), was obtained for (trimethylsilyl)borylene. The absorption band should be of low intensity as the computed oscillator strength is small (f = 0.003).

The first excited state ($^1B_1$) of phenylborylene is largely due to a HOMO−LUMO excitation and is 2.85 eV in energy above the ground state. Excitation energies rise with the strength of the electron-donating properties of the substituents and drop when electron-withdrawing groups are introduced. The effects are stronger in the para position (Figure 8). The HOMO of phenylborylene is similar to HOMO orbitals of other borylenes. Substituents in the para or meta position have no effect on its

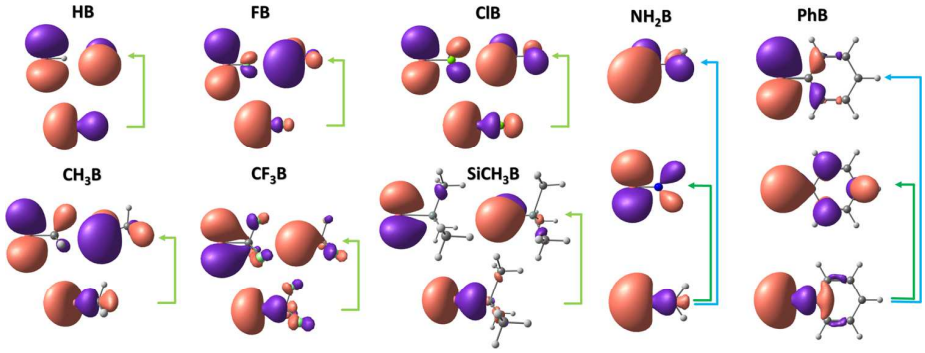

Figure 5. Natural transition orbitals of borylenes computed at the ωB97X/aug-cc-pVTZ level of theory. Green arrows indicate the first, blue ones the second excitation.

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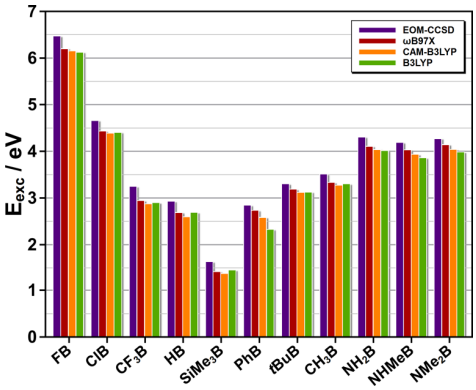

Figure 6. Vertical excitation energies to the S_1 state of borylenes calculated at the TD-DFT and EOM-CCSD levels of theory in combination with aug-cc-pVTZ basis set.

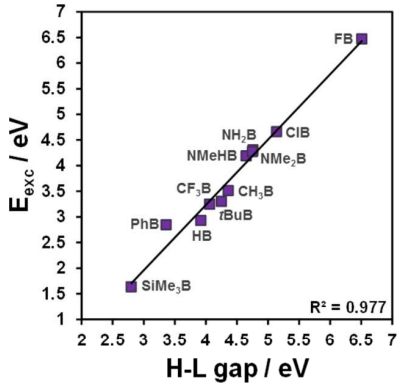

Figure 7. Correlation between HOMO−LUMO gaps obtained from the B3LYP/def2-TZVP computations and vertical excitation energies of the first excited state computed at the EOM-CCSD/aug-cc-pVTZ level of theory.

shape. The LUMO consists of p orbitals of boron and three p orbitals placed on C2, C4, and C6 atoms in the phenyl ring. Substitutions in the meta position have a small or no effect on the spatial distribution of the LUMO. Substitution in the para position changes the shape of LUMO: orbital lobes are partially distributed on the substituent (except *p*SiMe3PhB). This can be one explanation for more pronounced changes in excitation energies in para-substituted phenylborylenes.

4.3. S_2 State of Lower Symmetry Borylenes. The second electronic transition is also of n → π^* type and involves excitation from nonbonding HOMO mainly to the empty boron p_y orbital and can involve an orbital of the substituent depending on its type (see Figures 5 and S3). Excitation energies in aminoborylenes vary from 5.80 eV in NH_2B to 5.51 eV in NMe_2B. Oscillator strengths decrease with substitution by methyl groups from 0.175 to 0.144 (Table S3).

The excitation energy to S_2 of unsubstituted phenylborylene amounts to 3.35 eV (Figure 8 and Table S3). The excitation energies (3.32−3.38 eV) and oscillator strengths remain approximately constant with substitution of the phenyl ring (Table S3) because the virtual orbital to which the electron is promoted is mainly located on the boron atom (empty p orbital) (Figure S3).

5. Performance of TD-DFT vs EOM-CCSD Methods in Prediction of Electronic Spectra of Borylenes. In our present study, TD-DFT methods tend to underestimate excitation energies of borylenes compared to EOM-CCSD results. Functionals with long-range correction, like CAM-B3LYP and *ω*B97X perform better than B3LYP, especially when spatial overlap of orbitals participating in the electronic transition is poor, like in the case of substituted phenylborylenes. To estimate the overall performance of TD-DFT, the mean absolute deviation (MAD) was calculated (Figure S6 and Table S5). TD-B3LYP underestimates excitation energies of the first transition in the range 0.18−0.85 eV compared to EOM-CCSD data, which results in a MAD of 0.46 eV. Particularly problematic are excitation energies of substituted phenylborylenes which are underestimated significantly (0.50−0.85 eV). The excitation energies are improved when the CAM-B3LYP functional is used and are underestimated by 0.19−0.37 eV with a MAD of 0.27 eV. Transition energies of substituted phenylborylenes vary from 0.23 to 0.36 eV. *ω*B97X gives further improvement over CAM-B3LYP results. The energies are underestimated by about 0.07−0.30 eV compared to EOM-CCSD results and MAD is only 0.14 eV. TD-DFT excitation energies of second transition are improved in the case of B3LYP and CAM-B3LYP functionals. Overall performance of CAM-B3LYP is somewhat poorer than B3LYP (MAD of 0.22 and 0.21 eV, respectively). *ω*B97X shows the best performance among studied functionals in predicting of second transition excitations but performs slightly worse than for the first excited state (MAD = 0.16 eV).

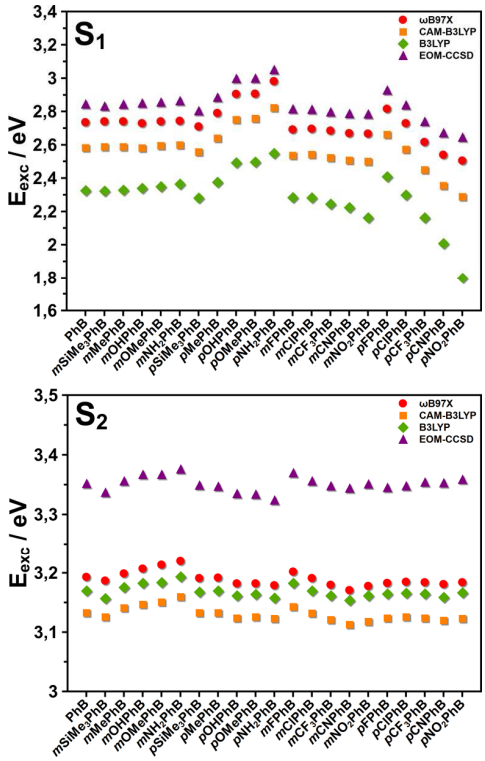

Figure 8. Vertical excitation energies to S_1 and S_2 states of arylborylenes computed at the TD-DFT and EOM-CCSD levels of theory in combination with the aug-cc-pVTZ basis set.

■ CONCLUSIONS

The influence of the substitution in borylenes on their electronic structure and their excited state energies was

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investigated by computational means. The following conclusions can be drawn:

1. All studied borylenes have a singlet ground state. Most of the triplet borylenes have the same symmetry as singlet borylenes. Exceptions are the triplet states of CH_3B, *t*BuB, $SiMe_3B$, and CF_3B that only have C_s symmetry. The R−B bond of triplet borylenes is shorter in almost all cases, except for FB, CH_3B, and *t*BuB. The largest singlet−triplet energy separation was found for the FB molecule (78.7 kcal/mol), whereas the smallest one was obtained for Me_3SiB (8.2 kcal/mol). Introduction of electron-donating groups in the para position of the phenyl ring increases and of electron-withdrawing substituents decreases S−T gaps compared to the case for unsubstituted phenylborylene.
2. Energies of frontier molecular orbitals depend on substitution. Electron-withdrawing substituents like F, Cl, and CF_3 tend to decrease the energy of HOMO with respect to BH molecule. The energy of LUMO is increased upon halogen substitution. Introduction of electron-donating substituents elevates the energies of both the HOMO and LUMO. HOMO energies of substituted arylborylenes are higher than that of BH. Introduction of electron-donating groups in PhB increases, whereas electron-withdrawing groups decrease, the LUMO energies compared to those of BH.
3. HOMO−LUMO gaps are increased by most of the substituents compared to parent borylene. The largest gaps were found in halo- and aminoborylenes. The smallest H−L gaps were obtained for *m*NO_2PhB (2.67 eV) and Me_3SiB (2.80 eV). In the arylborylene series electron-donating substituents increase and electron-withdrawing groups decrease the gap. The effect is stronger in the para position.
4. Two lowest singlet−singlet electronic transitions are of n → π^* type. These transitions involve excitations from the nonbonding HOMO (sp orbital of boron) mainly to the empty p orbitals of boron. Excitation energies of diatomic borylenes increase with increasing electronegativity of the substituent. The highest excitation energy was computed for FB, whereas the lowest excitation energy was obtained for Me_3SiB. The influence of substitution in phenylborylene is stronger in the para position. Electron-donating groups increase and electron-withdrawing groups decrease excitation energies compared to the case for unsubstituted phenylborylene. Excitation energies of the second transition in the arylborylene series remain approximately constant and are independent of substitution.
5. The TD-DFT method underestimates excitation energies of borylenes compared to EOM-CCSD results, especially when the B3LYP functional is used. Functionals with long-range correction (CAM-B3LYP and ωB97X) perform significantly better. ωB97X shows the best performance among tested functionals and gives a MAD of 0.14 eV for the prediction of the first transition, and 0.16 eV for the second transition with respect to results obtained with the EOM-CCSD method. Regardless of deviations from EOM-CCSD results, all functionals used in TD computations give similar trends in predicting excitation energies upon substitution.

■ ASSOCIATED CONTENT

Supporting Information

Tables containing computed structural parameters, energies of frontier orbitals, HOMO−LUMO energy gaps, singlet−triplet energy splittings, vertical excitation energies, σ constants, and figures of molecular structures, natural transition orbitals, mean absolute deviations, correlation plots, full reference 138, and Cartesian coordinates. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.6b04502.

(PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Electronically Excited States of Borylenes

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Table S1. B-R bond lengths (in Å) of borylenes in their lowest singlet and triplet states, energies of molecular orbitals (in eV), HOMO-LUMO energy gap (in eV), and singlet-triplet energy splitting (in kcal/mol) computed at the B3LYP/def2-TZVP+ZPVE level of theory.

	$d(R\text{-}B)^S$	$d(R\text{-}B)^T$	State	E_{HOMO}	E_{LUMO}	E_{LUMO+1}	$\Delta E_{H\text{-}L}$	$\Delta E_{S\text{-}T}$
HB	1.233[a]	1.192	$^3\Pi$	-6.52	-2.60	-2.60	3.92	26.4
FB	1.265[b]	1.315	$^3\Pi$	-7.84	-1.33	-1.33	6.51	78.7
ClB	1.722[c]	1.705	$^3\Pi$	-7.28	-2.13	-2.13	5.14	53.8
MeB	1.530	1.546	^{3}A″	-6.00	-1.64	-1.64	4.36	37.7
***t*BuB**	1.545	1.576	^{3}A″	-5.78	-1.53	-1.53	4.25	36.6
CF_3B	1.650	1.589	^{3}A″	-7.44	-3.38	-3.38	4.06	28.1
$SiMe_3$B	2.115	2.012	^{3}A″	-5.27	-2.47	-2.47	2.80	8.2
NH_2B	1.372	1.369	$^3B_2$	-6.20	-1.45	0.01	4.76	45.8
NHMeB	1.370	1.365	^{3}A′	-6.01	-1.36	0.12	4.65	44.6
NMe_2B	1.371	1.367	$^3B_2$	-5.91	-1.16	0.10	4.75	45.9
PhB	1.529	1.478	$^3B_1$	-5.81	-2.45	-1.60	3.36	30.8
***m*$SiMe_3$PhB**	1.527	1.478	^{3}A″	-5.71	-2.36	-1.52	3.35	30.9
***m*MePhB**	1.528	1.478	^{3}A″	-5.73	-2.38	-1.52	3.36	31.0
***m*OHPhB**	1.529	1.479	^{3}A″	-5.85	-2.47	-1.64	3.38	30.9
***m*OMePhB**	1.528	1.479	^{3}A″	-5.76	-2.38	-1.55	3.38	31.2
***m*NH_2PhB**	1.528	1.480	^{3}A	-5.66	-2.25	-1.43	3.40	31.4
***p*$SiMe_3$PhB**	1.528	1.475	^{3}A″	-5.72	-2.43	-1.52	3.29	30.3
***p*MePhB**	1.525	1.478	^{3}A′	-5.69	-2.30	-1.49	3.39	31.8
***p*OHPhB**	1.521	1.481	^{3}A″	-5.64	-2.14	-1.46	3.50	34.4
***p*OMePhB**	1.520	1.481	^{3}A″	-5.56	-2.07	-1.38	3.50	34.5
***p*NH_2PhB**	1.515	1.480	^{3}A′	-5.36	-1.82	-1.18	3.54	36.1
***m*FPhB**	1.534	1.478	^{3}A″	-6.02	-2.70	-1.81	3.32	29.8
***m*ClPhB**	1.534	1.477	^{3}A″	-6.03	-2.72	-1.84	3.32	29.8
***m*CF_3PhB**	1.535	1.477	^{3}A	-6.15	-2.88	-1.96	3.27	29.1
***m*CNPhB**	1.538	1.477	^{3}A″	-6.31	-3.07	-2.23	3.24	28.6
***m*NO_2PhB**	1.539	1.477	^{3}A″	-6.34	-3.30	-2.94	3.03	28.4
***p*FPhB**	1.527	1.484	^{3}B	-5.92	-2.49	-1.73	3.43	31.8
***p*ClPhB**	1.530	1.476	$^3B_1$	-5.96	-2.64	-1.76	3.31	30.6
***p*CF_3PhB**	1.536	1.473	^{3}A	-6.17	-2.98	-1.97	3.19	27.9
***p*CNPhB**	1.538	1.468	$^3B_1$	-6.30	-3.31	-2.11	2.99	26.4
***p*NO_2PhB**	1.541	1.465	$^3B_1$	-6.38	-3.70	-2.18	2.67	24.7

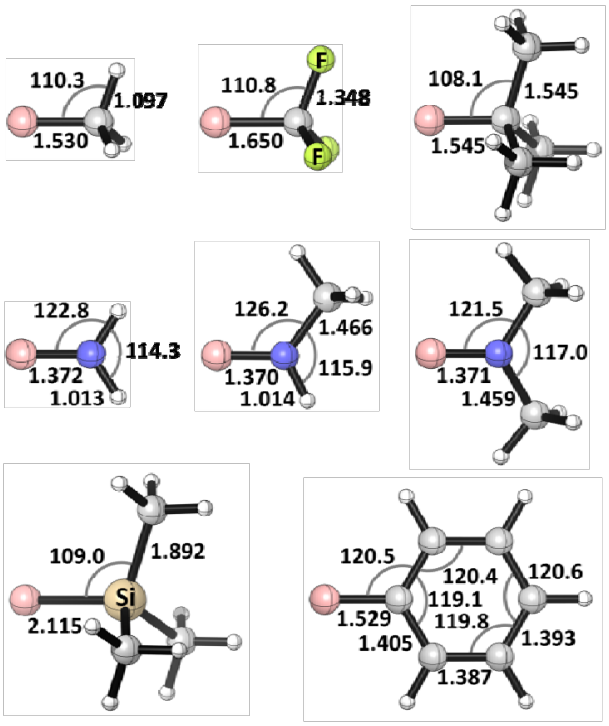

Figure S1. Structures of singlet borylenes as computed at the B3LYP/def2-TZVP level of theory. Important bond lengths and angles are given in Å and degrees, respectively.

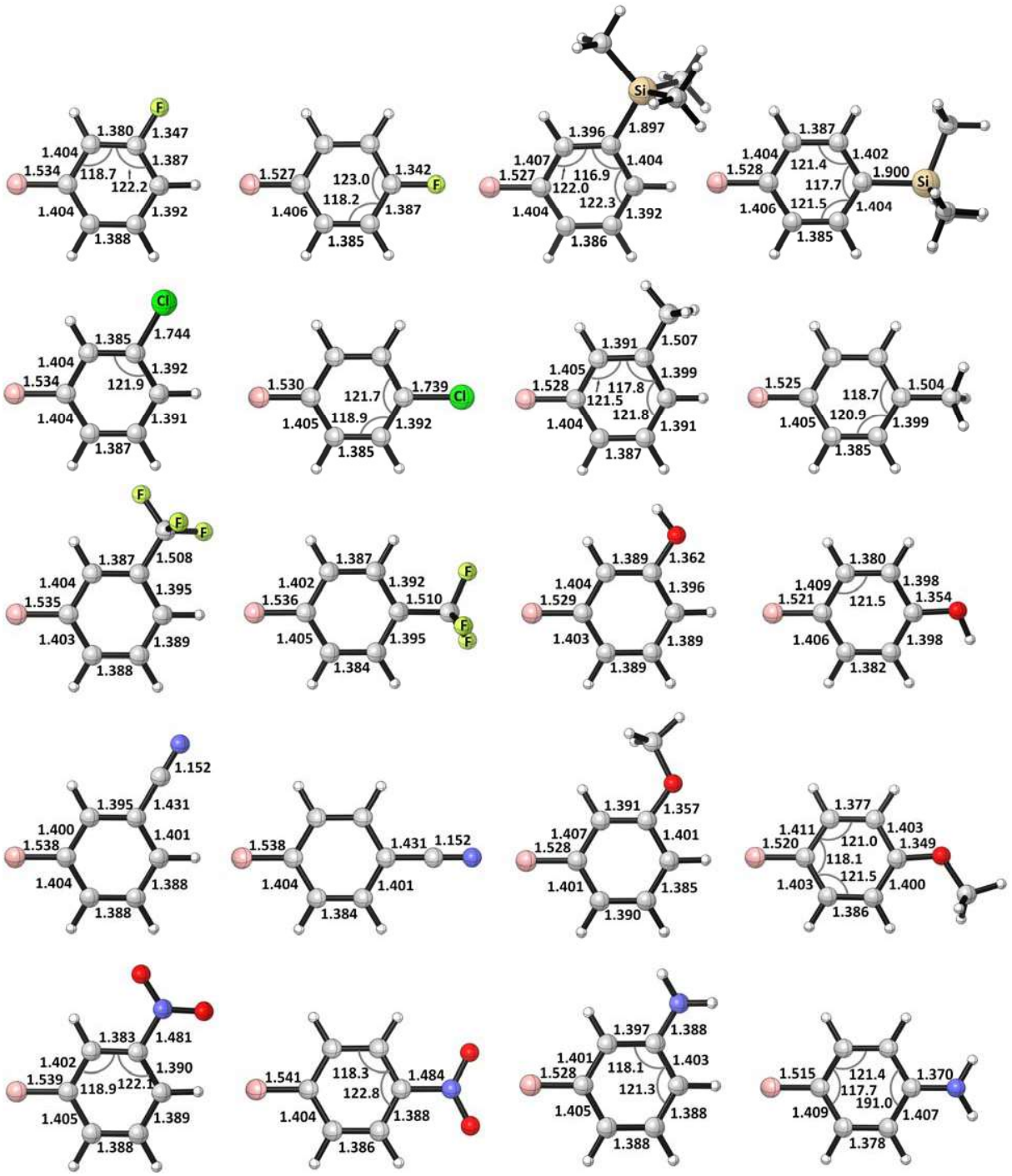

Figure S2. Structures of substituted singlet arylborylenes as computed at the B3LYP/def2-TZVP level of theory. Important bond lengths and angles are given in Å and degrees, respectively.

Table S2. Vertical excitation energies (E_{exc}; in eV) and oscillator strengths (f) of the lowest singlet-singlet electronic transition of substituted borylenes computed at the EOM-CCSD and TD-DFT levels of theory using aug-cc-pVTZ basis set.

Borylene	Transition	ωB97X		CAM-B3LYP		B3LYP		EOM-CCSD	
		E_{exc}	f	E_{exc}	f	E_{exc}	f	E_{exc}	f
HB	$^1\Sigma \rightarrow {}^1\Pi$	2.69	0.026	2.60	0.023	2.69	0.024	2.93	0.025
FB	$^1\Sigma \rightarrow {}^1\Pi$	6.20	0.244	6.15	0.236	6.13	0.237	6.47	0.243
ClB	$^1\Sigma \rightarrow {}^1\Pi$	4.43	0.068	4.39	0.063	4.41	0.062	4.66	0.065
MeB	$^1A_1 \rightarrow {}^1E$	3.33	0.047	3.27	0.042	3.30	0.042	3.51	0.045
***t*BuB**	$^1A_1 \rightarrow {}^1E$	3.19	0.031	3.12	0.026	3.13	0.026	3.30	0.028
CF_3B	$^1A_1 \rightarrow {}^1E$	2.94	0.028	2.88	0.025	2.90	0.024	3.25	0.028
$SiMe_3$B	$^1A_1 \rightarrow {}^1E$	1.42	0.003	1.38	0.003	1.45	0.003	1.63	0.003
NH_2B	$^1A_1 \rightarrow {}^1B_2$	4.11	0.094	4.04	0.082	4.02	0.077	4.31	0.091
NHMeB	$^1A' \rightarrow {}^1A'$	4.03	0.085	3.94	0.073	3.86	0.062	4.19	0.080
NMe_2B	$^1A_1 \rightarrow {}^1B_2$	4.14	0.080	4.04	0.071	3.99	0.067	4.27	0.077
PhB	$^1A_1 \rightarrow {}^1B_1$	2.74	0.023	2.58	0.018	2.33	0.012	2.85	0.021
***m*$SiMe_3$PhB**	$^1A' \rightarrow {}^1A''$	2.74	0.021	2.59	0.017	2.32	0.011	2.83	0.020
***m*MePhB**	$^1A' \rightarrow {}^1A''$	2.74	0.022	2.59	0.017	2.33	0.012	2.84	0.021
***m*OHPhB**	$^1A' \rightarrow {}^1A''$	2.73	0.022	2.58	0.017	2.34	0.012	2.85	0.021
***m*OMePhB**	$^1A' \rightarrow {}^1A''$	2.74	0.022	2.60	0.017	2.35	0.012	2.86	0.021
***m*NH_2PhB**	$^1A \rightarrow {}^1A$	2.74	0.023	2.60	0.018	2.37	0.012	2.86	0.021
***p*$SiMe_3$PhB**	$^1A' \rightarrow {}^1A''$	2.71	0.021	2.56	0.017	2.28	0.011	2.80	0.019
***p*MePhB**	$^1A' \rightarrow {}^{1A'}$	2.79	0.023	2.64	0.019	2.38	0.012	2.89	0.022
***p*OHPhB**	$^1A' \rightarrow {}^1A''$	2.91	0.026	2.75	0.021	2.49	0.014	3.00	0.024
***p*OMePhB**	$^1A' \rightarrow {}^1A''$	2.91	0.026	2.76	0.021	2.50	0.014	3.00	0.024
***p*NH_2PhB**	$^1A' \rightarrow {}^1A'$	2.98	0.027	2.82	0.022	2.55	0.014	3.05	0.025
***m*FPhB**	$^1A' \rightarrow {}^1A''$	2.69	0.022	2.54	0.017	2.28	0.011	2.82	0.020
***m*ClPhB**	$^1A' \rightarrow {}^1A''$	2.70	0.021	2.54	0.017	2.28	0.011	2.81	0.020
***m*CF_3PhB**	$^1A \rightarrow {}^1A$	2.69	0.021	2.52	0.016	2.25	0.011	2.80	0.020
***m*CNPhB**	$^1A' \rightarrow {}^1A''$	2.67	0.021	2.51	0.016	2.22	0.010	2.79	0.019
***m*NO_2PhB**	$^1A' \rightarrow {}^1A''$	2.67	0.021	2.50	0.016	2.16	0.008	2.79	0.019
***p*FPhB**	$^1A_1 \rightarrow {}^1B_1$	2.82	0.024	2.66	0.019	2.41	0.013	2.93	0.023
***p*ClPhB**	$^1A_1 \rightarrow {}^1B_1$	2.73	0.022	2.57	0.017	2.30	0.011	2.84	0.020
***p*CF_3PhB**	$^1A \rightarrow {}^1A$	2.62	0.020	2.45	0.015	2.16	0.010	2.74	0.019
***p*CNPhB**	$^1A_1 \rightarrow {}^1B_1$	2.54	0.018	2.36	0.013	2.01	0.008	2.67	0.017
***p*NO_2PhB**	$^1A_1 \rightarrow {}^1B_1$	2.51	0.017	2.29	0.012	1.80	0.005	2.65	0.017

Table S3. Vertical excitation energies (E_{exc}; in eV) and oscillator strengths (f) of the second electronic transition of substituted borylenes computed at the EOM-CCSD and TD-DFT levels of theory using aug-cc-pVTZ basis set.

Borylene	Transition	ωB97X		CAM-B3LYP		B3LYP		EOM-CCSD	
		E_{exc}	f	E_{exc}	f	E_{exc}	f	E_{exc}	f
NH_2B	$^1A_1 \rightarrow {}^1B_1$	5.60	0.180	5.55	0.176	5.48	0.178	5.80	0.175
NHMeB	$^1A' \rightarrow {}^1A''$	5.53	0.174	5.43	0.163	5.27	0.142	5.68	0.167
NMe_2B	$^1A_1 \rightarrow {}^1B_1$	5.42	0.156	5.28	0.138	5.06	0.108	5.51[a]	0.144
PhB	$^1A_1 \rightarrow {}^1B_2$	3.19	0.042	3.13	0.038	3.17	0.040	3.35	0.042
***m*$SiMe_3$PhB**	$^1A' \rightarrow {}^1A'$	3.19	0.040	3.13	0.036	3.16	0.037	3.34	0.039
***m*MePhB**	$1A' \rightarrow {}^1A'$	3.20	0.042	3.14	0.038	3.18	0.040	3.36	0.041
***m*OHPhB**	$^1A' \rightarrow {}^1A'$	3.21	0.042	3.15	0.038	3.18	0.041	3.37	0.042
***m*OMePhB**	$^1A' \rightarrow {}^1A'$	3.21	0.042	3.15	0.038	3.18	0.040	3.37	0.041
***m*NH_2PhB**	$^1A \rightarrow {}^1A$	3.22	0.043	3.16	0.039	3.19	0.042	3.38	0.042
***p*$SiMe_3$PhB**	$^1A' \rightarrow {}^1A'$	3.19	0.042	3.13	0.038	3.17	0.040	3.35	0.041
***p*MePhB**	$^1A' \rightarrow {}^1A''$	3.19	0.043	3.13	0.039	3.17	0.041	3.35	0.042
***p*OHPhB**	$^1A' \rightarrow {}^1A'$	3.18	0.043	3.12	0.039	3.16	0.041	3.34	0.042
***p*OMePhB**	$^1A' \rightarrow {}^1A'$	3.18	0.043	3.13	0.040	3.16	0.042	3.33	0.042
***p*NH_2PhB**	$^1A' \rightarrow {}^1A''$	3.18	0.044	3.12	0.040	3.16	0.043	3.32	0.043
***m*FPhB**	$^1A' \rightarrow {}^1A'$	3.20	0.042	3.14	0.038	3.18	0.040	3.37	0.041
***m*ClPhB**	$^1A' \rightarrow {}^1A'$	3.19	0.040	3.13	0.036	3.17	0.037	3.36	0.039
***m*CF_3PhB**	$^1A \rightarrow {}^1A$	3.18	0.040	3.12	0.037	3.16	0.038	3.35	0.040
***m*CNPhB**	$^1A' \rightarrow {}^1A'$	3.17	0.039	3.11	0.036	3.15	0.037	3.34	0.039
***m*NO_2PhB**	$^1A' \rightarrow {}^1A'$	3.18	0.039	3.12	0.035	3.16[b]	0.036	3.35	0.038
***p*FPhB**	$^1A_1 \rightarrow {}^1B_2$	3.18	0.042	3.12	0.038	3.17	0.040	3.35	0.041
***p*ClPhB**	$^1A_1 \rightarrow {}^1B_2$	3.19	0.042	3.13	0.038	3.17	0.040	3.35	0.041
***p*CF_3PhB**	$^1A \rightarrow {}^1A$	3.18	0.042	3.12	0.038	3.17	0.039	3.35	0.041
***p*CNPhB**	$^1A_1 \rightarrow {}^1B_2$	3.18	0.041	3.12	0.037	3.16	0.039	3.35	0.041
***p*NO_2PhB**	$^1A_1 \rightarrow {}^1B_2$	3.18	0.041	3.12	0.037	3.17	0.039	3.36	0.041

[a] in EOM-CCSD calculations this is the third state, second state is of different symmetry than in TD-DFT calculations and its f = 0. [b] third state in TD-B3LYP calculations, second state is of different symmetry than in other TDDFT and EOM-CCSD calculations.

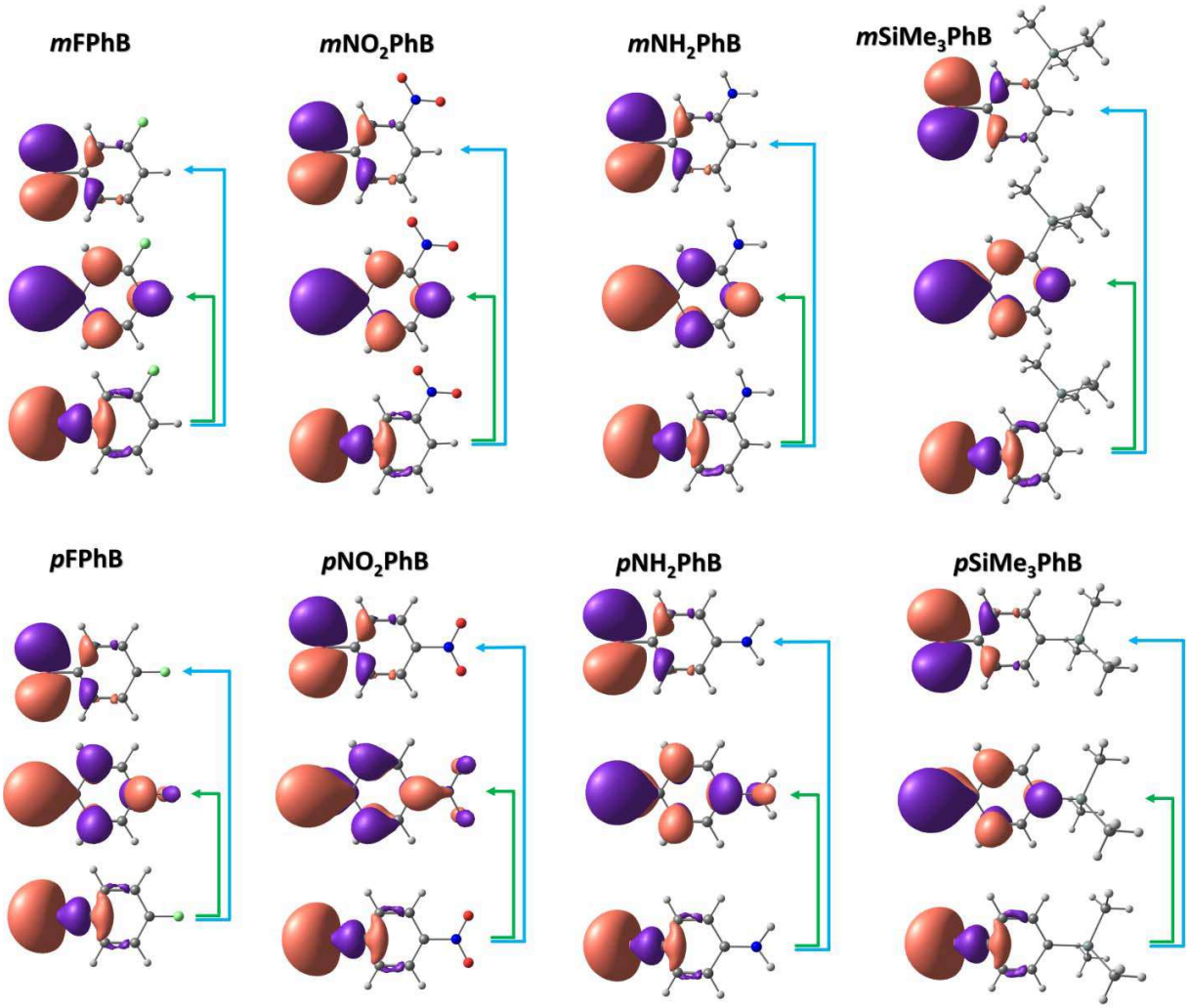

Figure S3. Natural transition orbitals of arylborylenes computed at the ωB97X/aug-cc-pVTZ level of theory. Green arrows indicate first excitation, while the blue ones second excitation.

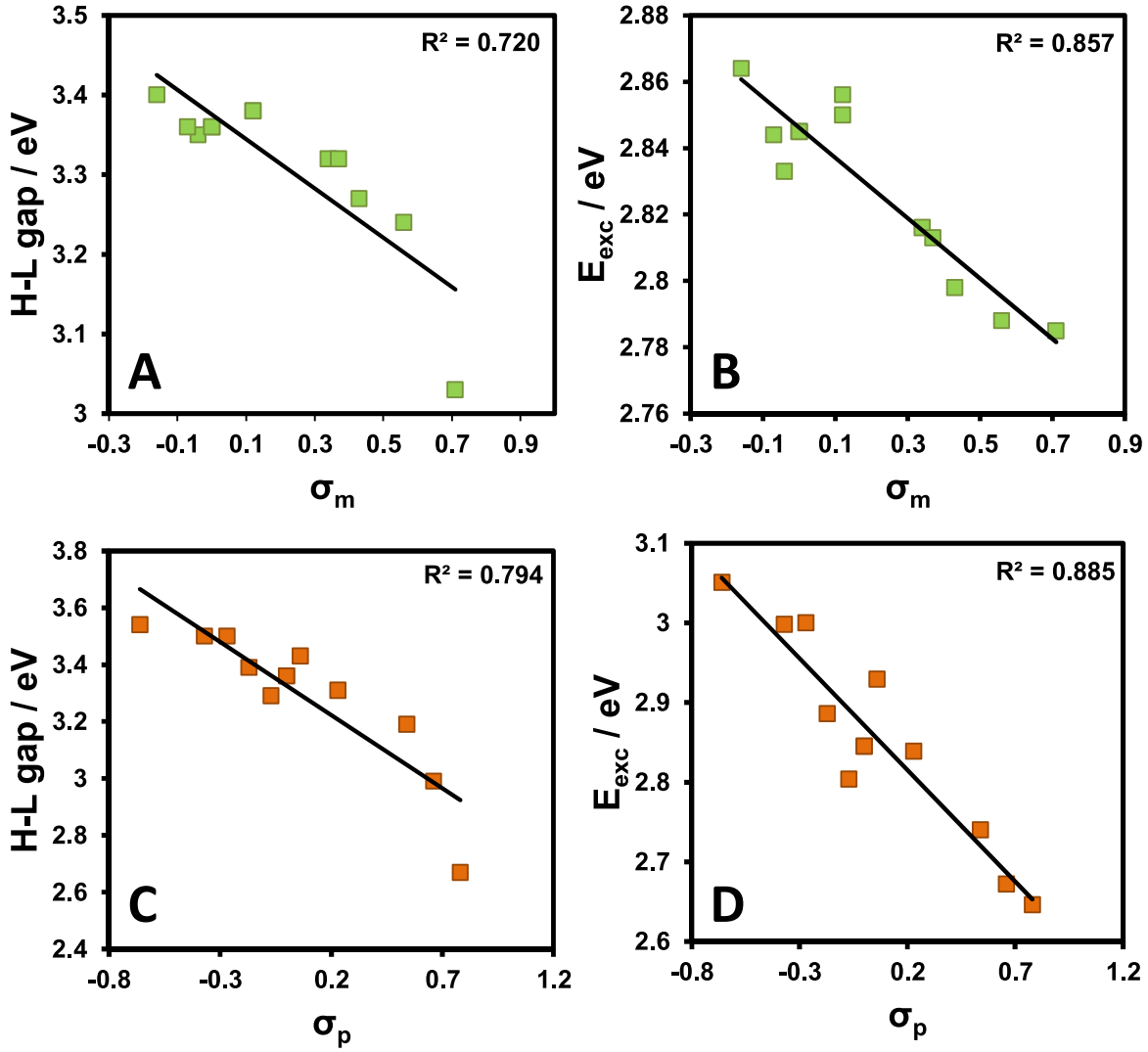

Figure S4. HOMO-LUMO gaps of m-arylborylenes plotted against σ_m substituent constants (A), vertical excitation energies of S_1 state of m-arylborylenes plotted against σ_m substituent constants (B), HOMO-LUMO gaps of p-arylborylenes plotted against σ_p substituent constants (C), vertical excitation energies of S_1 state of p-arylborylenes plotted against σ_p substituent constants (D). H-L gaps gaps were computed at the B3LYP/def2-TZVP level of theory and vertical excitation energies at the EOM-CCSD/aug-cc-pVTZ level of theory.

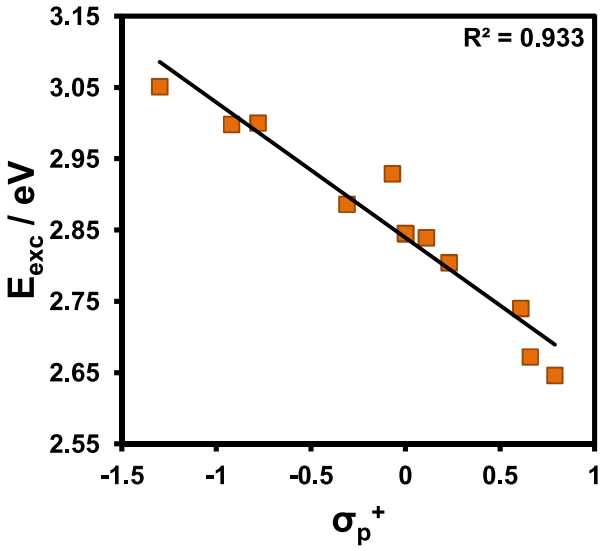

Figure S5. Vertical excitation energies of S_1 state of p-arylborylenes computed at the EOM-CCSD/aug-cc-pVTZ level of theory plotted against σ_p^+ substituent constants.

Table S4. Values of σ substituent constants.

Substituent	σ_m	σ_p	σ_p^+
H	0.00	0.00	0.00
$SiMe_3$	-0.04	-0.07	0.23
Me	-0.07	-0.17	-0.31
OH	0.12	-0.37	-0.92
OMe	0.12	-0.27	-0.78
NH_2	-0.16	-0.66	-1.30
F	0.34	0.06	-0.07
Cl	0.37	0.23	0.11
CF_3	0.43	0.54	0.61
CN	0.56	0.66	0.66
NO_2	0.71	0.78	0.79

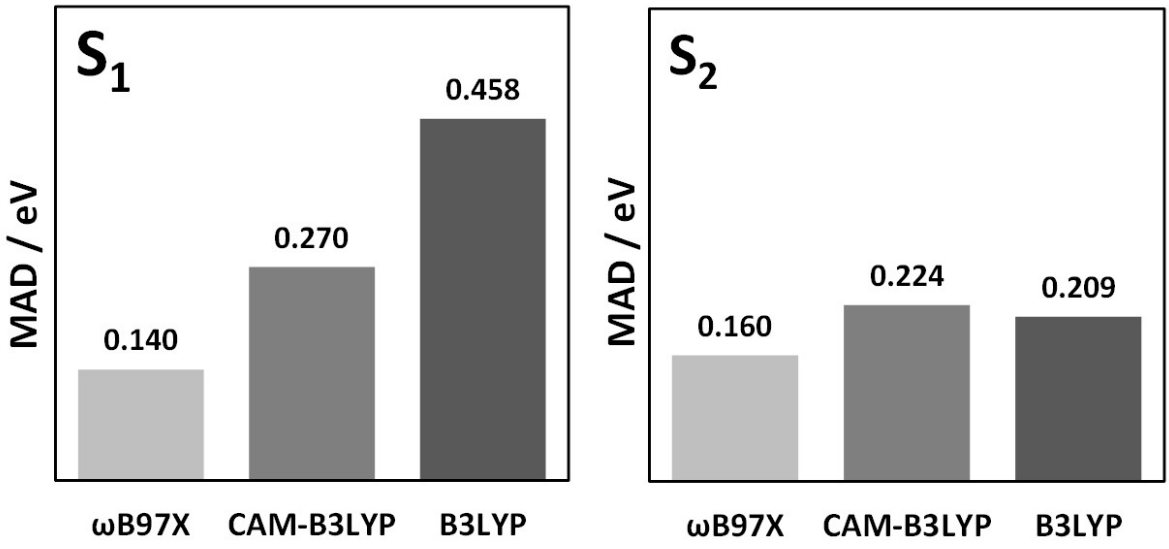

Figure S6. Mean absolute deviation (MAD) of DFT functionals used in time-dependent computations from EOM-CCSD excitation energies estimated for the S_1 and S_2 states.

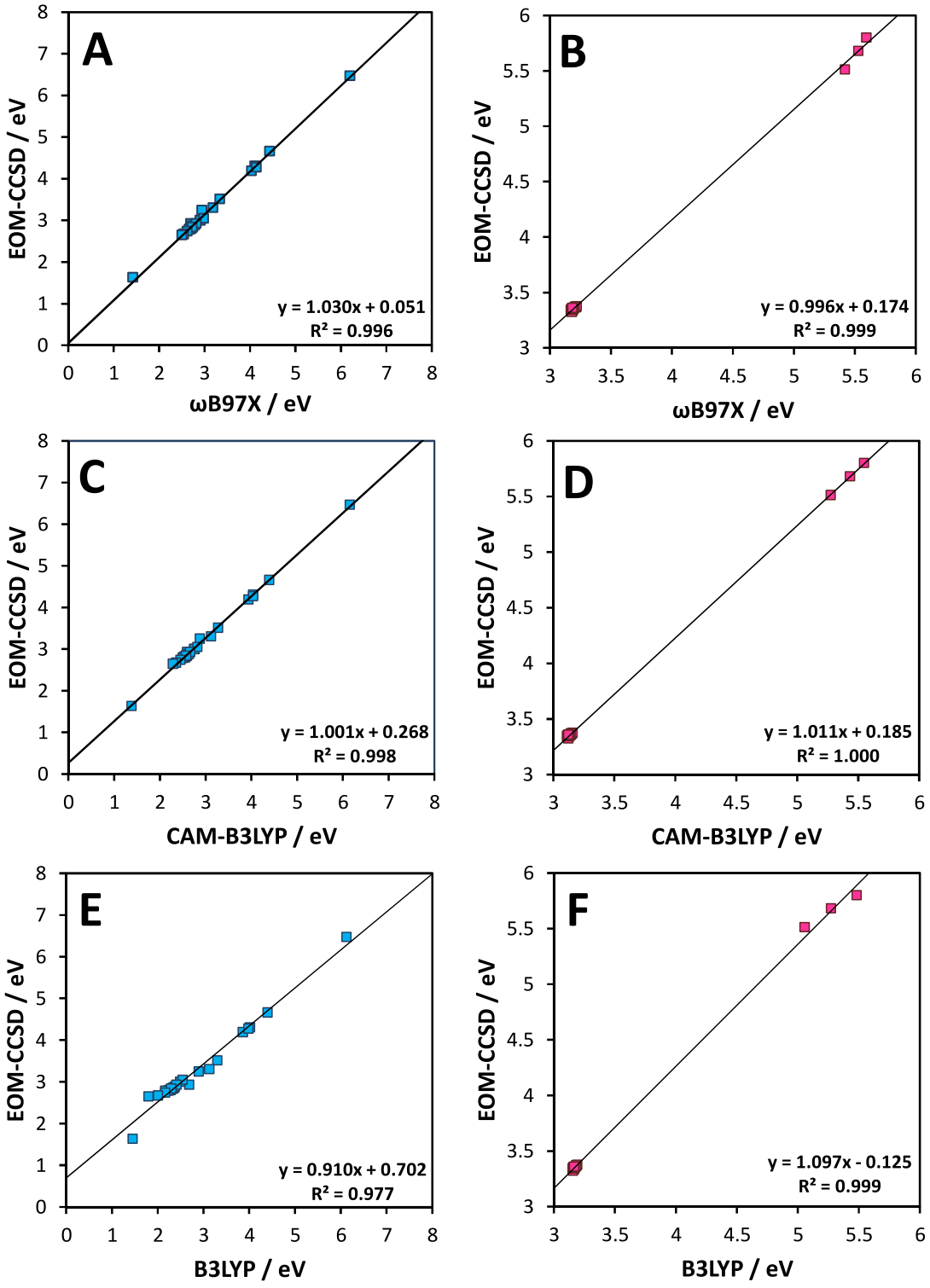

Figure S7. Correlations between vertical excitation energies of borylenes computed at the EOM-CCSD/aug-cc-pVTZ level of theory and vertical excitation energies computed at the TDDFT/aug-cc-pVTZ to the S_1 state (A, C, E) and to the S_2 state (B, D, F).

Table S5. Deviations of TDDFT/aug-cc-pVTZ computed vertical excitation energies (eV) of S_1 and S_2 states from the vertical excitation energies computed at the EOM-CCSD/aug-cc-pVTZ level of theory. Mean absolute deviations (MAD) are calculated (eV).

Molecule	S_1			S_2		
	ωB97X	CAM-B3LYP	B3LYP	ωB97X	CAM-B3LYP	B3LYP
HB	0.242	0.333	0.239			
FB	0.271	0.319	0.346			
ClB	0.227	0.272	0.255			
MeB	0.178	0.238	0.210			
***t*BuB**	0.115	0.185	0.177			
CF_3B	0.303	0.372	0.347			
$SiMe_3$B	0.213	0.252	0.180			
NH_2B	0.200	0.269	0.288	0.205	0.253	0.318
NHMeB	0.157	0.252	0.327	0.152	0.248	0.408
NMe_2B	0.130	0.232	0.285	0.093	0.237	0.456
PhB	0.110	0.262	0.519	0.159	0.219	0.182
***m*$SiMe_3$PhB**	0.093	0.244	0.509	0.150	0.211	0.180
***m*MePhB**	0.104	0.256	0.515	0.157	0.215	0.180
***m*OHPhB**	0.120	0.269	0.510	0.160	0.220	0.184
***m*OMePhB**	0.115	0.261	0.506	0.153	0.216	0.183
***m*NH_2PhB**	0.121	0.265	0.499	0.156	0.216	0.182
***p*$SiMe_3$PhB**	0.094	0.246	0.522	0.158	0.216	0.181
***p*MePhB**	0.095	0.246	0.509	0.155	0.214	0.177
***p*OHPhB**	0.093	0.246	0.504	0.153	0.211	0.173
***p*OMePhB**	0.093	0.242	0.502	0.152	0.208	0.170
***p*NH_2PhB**	0.069	0.228	0.501	0.145	0.201	0.166
***m*FPhB**	0.124	0.279	0.532	0.168	0.227	0.187
***m*ClPhB**	0.117	0.271	0.530	0.165	0.224	0.186
***m*CF_3PhB**	0.113	0.275	0.552	0.168	0.227	0.186
***m*CNPhB**	0.119	0.281	0.564	0.173	0.231	0.190
***m*NO_2PhB**	0.119	0.284	0.622	0.173	0.233	0.189
***p*FPhB**	0.113	0.267	0.519	0.162	0.221	0.180
***p*ClPhB**	0.110	0.266	0.539	0.163	0.222	0.182
***p*CF_3PhB**	0.123	0.290	0.577	0.170	0.230	0.189
***p*CNPhB**	0.132	0.316	0.663	0.172	0.233	0.194
***p*NO_2PhB**	0.141	0.357	0.847	0.175	0.236	0.192
MAD	**0.140**	**0.270**	**0.458**	**0.160**	**0.224**	**0.209**

Full reference 138:

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

B3LYP/def2-TZVP geometries		
Molecule	**Singlet**	**Triplet**
BH	HF=-25.2995151 B 0.000000000 0.000000000 0.205505000 H 0.000000000 0.000000000 -1.027524000	HF=-25.2580535 B 0.000000000 0.000000000 0.198662000 H 0.000000000 0.000000000 -0.993310000
BF	HF=-124.7208733 F 0.000000000 0.000000000 0.451755000 B 0.000000000 0.000000000 -0.813158000	HF=-124.595232 F 0.000000000 0.000000000 0.469554000 B 0.000000000 0.000000000 -0.845197000
BCl	HF=-485.02103 B 0.000000000 0.000000000 -1.330269000 Cl 0.000000000 0.000000000 0.391255000	HF=-484.9354151 B 0.000000000 0.000000000 -1.317667000 Cl 0.000000000 0.000000000 0.387549000
BCH_3	HF=-64.6676083 B 0.000000000 0.000000000 -1.064929000 C 0.000000000 0.000000000 0.464758000 H 1.029362000 0.000000000 0.845366000 H -0.514681000 0.891454000 0.845366000 H -0.514681000 -0.891454000 0.845366000	HF=-64.6083064 B -0.010410000 -1.080683000 0.000000000 C -0.010410000 0.469484000 0.000000000 H 0.554560000 0.818764000 0.873186000 H 0.554560000 0.818764000 -0.873186000 H -0.994606000 0.948987000 0.000000000
***t*BuB**	HF=-182.6453924 B 0.000000000 0.000000000 1.715050000 C 0.000000000 0.000000000 0.170038000 C 0.000000000 1.468523000 -0.311060000 H -0.882583000 2.009197000 0.036266000 H 0.882583000 2.009197000 0.036266000 H 0.000000000 1.494848000 -1.404666000 C -1.271778000 -0.734261000 -0.311060000 H -2.181307000 -0.240259000 0.036266000 H -1.294576000 -0.747424000 -1.404666000 H -1.298724000 -1.768938000 0.036266000 C 1.271778000 -0.734261000 -0.311060000 H 1.294576000 -0.747424000 -1.404666000 H 2.181307000 -0.240259000 0.036266000 H 1.298724000 -1.768938000 0.036266000	HF=-182.5875858 B -0.557976000 1.669882000 0.000000000 C -0.104717000 0.160986000 0.000000000 C -0.557976000 -0.598466000 1.262112000 H -0.208649000 -0.104362000 2.168972000 H -1.646252000 -0.666092000 1.313929000 H -0.162908000 -1.620601000 1.250118000 C 1.442862000 0.290560000 0.000000000 H 1.809886000 0.810416000 0.886613000 H 1.872561000 -0.715820000 0.000000000 H 1.809886000 0.810416000 -0.886613000 C -0.557976000 -0.598466000 -1.262112000 H -0.162908000 -1.620601000 -1.250118000 H -1.646252000 -0.666092000 -1.313929000 H -0.208649000 -0.104362000 -2.168972000
BCF_3	HF=-362.4984526 B 0.000000000 0.000000000 1.772788000 C 0.000000000 0.000000000 0.123089000 F 0.000000000 1.260574000 -0.355647000 F 1.091689000 -0.630287000 -0.355647000 F -1.091689000 -0.630287000 -0.355647000	HF=-362.4538553 B 0.485641000 1.665810000 0.000000000 C 0.070433000 0.131982000 0.000000000 F 0.485641000 -0.569345000 1.077536000 F -1.288037000 0.125252000 0.000000000 F 0.485641000 -0.569345000 -1.077536000
BNH_2	HF=-80.7763647 B 0.000000000 0.000000000 -0.960242000 N 0.000000000 0.000000000 0.411419000 H 0.000000000 0.850814000 0.960638000 H 0.000000000 -0.850814000 0.960638000	HF=-80.7045898 B 0.000000000 0.000000000 -0.960895000 N 0.000000000 0.000000000 0.407913000 H 0.000000000 0.840851000 0.974541000 H 0.000000000 -0.840851000 0.974541000
BNHMe	HF=-120.0952697 N 0.000000000 0.494354000 0.000000000 B -1.345475000 0.753291000 0.000000000 H 0.635089000 1.285329000 0.000000000 C 0.626504000 -0.830827000 0.000000000 H 1.242835000 -0.968011000 0.889222000 H -0.152410000 -1.591282000 0.000000000 H 1.242835000 -0.968011000 -0.889222000	HF=-120.0247004 N 0.000000000 0.489179000 0.000000000 B -1.328764000 0.801164000 0.000000000 H 0.699897000 1.225700000 0.000000000 C 0.609996000 -0.847501000 0.000000000 H 1.232535000 -0.988360000 0.887432000 H -0.181124000 -1.594049000 0.000000000 H 1.232535000 -0.988360000 -0.887432000

$BNMe_2$	HF=-159.4176427 B 0.000000000 0.000000000 1.639237000 N 0.000000000 0.000000000 0.267995000 C 0.000000000 1.243948000 -0.494917000 H 0.000000000 2.093041000 0.188609000 H 0.889232000 1.304931000 -1.127590000 H -0.889232000 1.304931000 -1.127590000 C 0.000000000 -1.243948000 -0.494917000 H -0.889232000 -1.304931000 -1.127590000 H 0.889232000 -1.304931000 -1.127590000 H 0.000000000 -2.093041000 0.188609000	HF=-159.3448192 B 0.000000000 0.000000000 1.674148000 N 0.000000000 0.000000000 0.306727000 C 0.000000000 1.218986000 -0.513453000 H 0.000000000 2.091223000 0.134140000 H 0.885880000 1.247464000 -1.156168000 H -0.885880000 1.247464000 -1.156168000 C 0.000000000 -1.218986000 -0.513453000 H -0.885880000 -1.247464000 -1.156168000 H 0.885880000 -1.247464000 -1.156168000 H 0.000000000 -2.091223000 0.134140000
$BSiMe_3$	HF=-434.0437806 B 0.000000000 0.000000000 2.271860000 Si 0.000000000 0.000000000 0.157143000 C 0.000000000 1.789485000 -0.457523000 H -0.881969000 2.333115000 -0.111976000 H 0.881969000 2.333115000 -0.111976000 H 0.000000000 1.817573000 -1.550680000 C -1.549740000 -0.894743000 -0.457523000 H -2.461521000 -0.402750000 -0.111976000 H -1.574065000 -0.908787000 -1.550680000 H -1.579552000 -1.930365000 -0.111976000 C 1.549740000 -0.894743000 -0.457523000 H 1.574065000 -0.908787000 -1.550680000 H 2.461521000 -0.402750000 -0.111976000 H 1.579552000 -1.930365000 -0.111976000	HF=-434.0311784 B -0.675259000 2.072397000 0.000000000 Si -0.080941000 0.149698000 0.000000000 C 1.804203000 0.289959000 0.000000000 H 2.172160000 0.811835000 -0.884661000 H 2.172160000 0.811835000 0.884661000 H 2.235418000 -0.715445000 0.000000000 C -0.675259000 -0.773966000 -1.533360000 H -0.311419000 -0.300034000 -2.446327000 H -0.318834000 -1.808399000 -1.517682000 H -1.765943000 -0.800635000 -1.582730000 C -0.675259000 -0.773966000 1.533360000 H -0.318834000 -1.808399000 1.517682000 H -0.311419000 -0.300034000 2.446327000 H -1.765943000 -0.800635000 1.582730000
BPh	HF=-256.4703441 B 0.000000000 0.000000000 -2.666459000 C 0.000000000 0.000000000 -1.137866000 C 0.000000000 1.211284000 -0.425398000 C 0.000000000 -1.211284000 -0.425398000 C 0.000000000 1.209709000 0.961316000 C 0.000000000 -1.209709000 0.961316000 C 0.000000000 0.000000000 1.651498000 H 0.000000000 2.151965000 -0.964377000 H 0.000000000 -2.151965000 -0.964377000 H 0.000000000 2.144802000 1.506867000 H 0.000000000 -2.144802000 1.506867000 H 0.000000000 0.000000000 2.734496000	HF=-256.420327 B 0.000000000 0.000000000 -2.639558000 C 0.000000000 0.000000000 -1.161467000 C 0.000000000 1.218438000 -0.425790000 C 0.000000000 -1.218438000 -0.425790000 C 0.000000000 1.203543000 0.955902000 C 0.000000000 -1.203543000 0.955902000 C 0.000000000 0.000000000 1.662107000 H 0.000000000 2.166387000 -0.948719000 H 0.000000000 -2.166387000 -0.948719000 H 0.000000000 2.144367000 1.493054000 H 0.000000000 -2.144367000 1.493054000 H 0.000000000 0.000000000 2.743933000
***m*$SiMe_3$PhB**	HF=-665.2237876 B -1.855815000 3.528893000 0.000000000 C -0.677312000 2.557356000 0.000000000 C -0.908749000 1.169489000 0.000000000 C 0.644424000 3.030281000 0.000000000 C 0.137398000 0.245064000 0.000000000 C 1.699613000 2.131562000 0.000000000 C 1.442229000 0.763670000 0.000000000 H -1.935676000 0.819742000 0.000000000 H 0.837132000 4.097173000 0.000000000 H 2.721910000 2.489116000 0.000000000 H 2.288149000 0.084029000 0.000000000 Si -0.151607000 -1.629818000 0.000000000 C -1.996276000 -1.989955000 0.000000000 H -2.164577000 -3.069858000 0.000000000 H -2.493227000 -1.582817000 0.883459000 H -2.493227000 -1.582817000 -0.883459000 C 0.644424000 -2.365604000 -1.539091000 H 0.522003000 -3.451592000 -1.557519000 H 0.192465000 -1.963232000 -2.448449000 H 1.715561000 -2.154738000 -1.581154000 C 0.644424000 -2.365604000 1.539091000 H 0.192465000 -1.963232000 2.448449000 H 0.522003000 -3.451592000 1.557519000	HF=-665.1735352 B -1.843463000 3.500679000 0.000000000 C -0.699036000 2.565912000 0.000000000 C -0.913168000 1.155979000 0.000000000 C 0.643015000 3.033446000 0.000000000 C 0.141925000 0.251976000 0.000000000 C 1.690137000 2.132086000 0.000000000 C 1.455079000 0.758474000 0.000000000 H -1.931567000 0.786906000 0.000000000 H 0.849354000 4.096197000 0.000000000 H 2.707745000 2.504806000 0.000000000 H 2.301643000 0.081829000 0.000000000 Si -0.148737000 -1.617391000 0.000000000 C -1.993394000 -1.993127000 0.000000000 H -2.153905000 -3.074307000 0.000000000 H -2.492716000 -1.589211000 0.883709000 H -2.492716000 -1.589211000 -0.883709000 C 0.643015000 -2.364404000 -1.537627000 H 0.519175000 -3.450409000 -1.552772000 H 0.191089000 -1.962937000 -2.447487000 H 1.713872000 -2.152941000 -1.580784000 C 0.643015000 -2.364404000 1.537627000 H 0.191089000 -1.962937000 2.447487000 H 0.519175000 -3.450409000 1.552772000

	H 1.715561000 -2.154738000 1.581154000	H 1.713872000 -2.152941000 1.580784000
***m*MePhB**	HF=-295.802408 C -0.777690000 -1.195644000 0.000000000 C -1.068644000 0.173122000 0.000000000 C 0.000000000 1.062927000 0.000000000 C 1.331071000 0.611835000 0.000000000 C 1.588345000 -0.767971000 0.000000000 C 0.531287000 -1.665527000 0.000000000 B 2.485232000 1.613199000 0.000000000 C -2.496160000 0.654974000 0.000000000 H -0.197757000 2.129928000 0.000000000 H 2.610543000 -1.128321000 0.000000000 H 0.719538000 -2.731889000 0.000000000 H -1.595195000 -1.908347000 0.000000000 H -3.033370000 0.293327000 0.879634000 H -2.545800000 1.743691000 0.000000000 H -3.033370000 0.293327000 -0.879634000	HF=-295.7520473 C -0.794300000 -1.199593000 0.000000000 C -1.060347000 0.177415000 0.000000000 C 0.000000000 1.068126000 0.000000000 C 1.350827000 0.618556000 0.000000000 C 1.586889000 -0.782870000 0.000000000 C 0.519726000 -1.661285000 0.000000000 B 2.472878000 1.580098000 0.000000000 C -2.482588000 0.674708000 0.000000000 H -0.209138000 2.131292000 0.000000000 H 2.598998000 -1.166396000 0.000000000 H 0.713439000 -2.727362000 0.000000000 H -1.615677000 -1.905804000 0.000000000 H -3.023878000 0.316719000 0.879303000 H -2.525491000 1.763997000 0.000000000 H -3.023878000 0.316719000 -0.879303000
***m*OHPhB**	HF=-331.7261545 B 2.505089000 1.522931000 0.000000000 C 1.307983000 0.571302000 0.000000000 C 1.513786000 -0.816819000 0.000000000 C 0.000000000 1.081374000 0.000000000 C 0.421184000 -1.673658000 0.000000000 C -1.085360000 0.215034000 0.000000000 C -0.870915000 -1.164650000 0.000000000 H 2.521014000 -1.215102000 0.000000000 H -0.162476000 2.155300000 0.000000000 H 0.569076000 -2.746211000 0.000000000 H -1.729759000 -1.823137000 0.000000000 O -2.379123000 0.641700000 0.000000000 H -2.410381000 1.605399000 0.000000000	HF=-331.675958 B -2.502994000 1.476877000 0.000000000 C -1.327306000 0.580214000 0.000000000 C -1.510851000 -0.830101000 0.000000000 C 0.000000000 1.085852000 0.000000000 C -0.410561000 -1.667118000 0.000000000 C 1.079222000 0.217654000 0.000000000 C 0.888349000 -1.166155000 0.000000000 H -2.507810000 -1.250293000 0.000000000 H 0.177105000 2.155882000 0.000000000 H -0.563804000 -2.739504000 0.000000000 H 1.749386000 -1.819744000 0.000000000 O 2.370667000 0.664821000 0.000000000 H 2.381645000 1.628634000 0.000000000
***m*OMePhB**	HF=-371.041142 B -1.017987000 2.948859000 0.000000000 C -0.163538000 1.681750000 0.000000000 C -0.780767000 0.416875000 0.000000000 C 1.233295000 1.783428000 0.000000000 C 0.000000000 -0.733769000 0.000000000 C 2.005213000 0.626948000 0.000000000 C 1.396532000 -0.617548000 0.000000000 H -1.860976000 0.356607000 0.000000000 H 1.706545000 2.757851000 0.000000000 H 3.086098000 0.690797000 0.000000000 H 1.984826000 -1.526252000 0.000000000 O -0.484166000 -2.001814000 0.000000000 C -1.891369000 -2.193542000 0.000000000 H -2.352434000 -1.761922000 0.892847000 H -2.352434000 -1.761922000 -0.892847000 H -2.044567000 -3.269791000 0.000000000	HF=-370.9904272 B 0.979743000 -2.935814000 0.000000000 C 0.167829000 -1.699997000 0.000000000 C 0.782747000 -0.415367000 0.000000000 C -1.249208000 -1.778072000 0.000000000 C 0.000000000 0.728159000 0.000000000 C -2.000420000 -0.615142000 0.000000000 C -1.399419000 0.636712000 0.000000000 H 1.860109000 -0.341412000 0.000000000 H -1.744143000 -2.740207000 0.000000000 H -3.081554000 -0.684448000 0.000000000 H -1.982646000 1.547037000 0.000000000 O 0.500637000 1.995594000 0.000000000 C 1.905649000 2.176604000 0.000000000 H 2.366191000 1.742004000 0.892449000 H 2.366191000 1.742004000 -0.892449000 H 2.068975000 3.251963000 0.000000000
***m*NH_2PhB**	HF=-311.8525082 C -0.807495000 1.191099000 -0.002748000 C -1.091026000 -0.183251000 -0.005997000 C -0.017221000 -1.076434000 -0.004822000 C 1.304785000 -0.612895000 0.000645000 C 1.565212000 0.767379000 0.004509000 C 0.500290000 1.656927000 0.003090000 B 2.465615000 -1.606497000 0.005926000 N -2.401298000 -0.635637000 -0.067838000 H -0.211552000 -2.144445000 -0.010767000 H 2.585472000 1.130458000 0.009673000 H 0.681423000 2.724650000 0.006927000 H -1.628521000 1.899428000 -0.008579000 H -3.112443000 0.000539000 0.254019000 H -2.560645000 -1.585647000 0.225899000	HF=-311.8014691 C -0.812224000 1.200165000 -0.003666000 C -1.085070000 -0.176882000 -0.008215000 C -0.028553000 -1.082492000 -0.001623000 C 1.317005000 -0.636688000 0.001853000 C 1.569769000 0.763466000 0.005166000 C 0.506238000 1.645364000 0.004899000 B 2.451020000 -1.587437000 0.002407000 N -2.402522000 -0.628393000 -0.075039000 H -0.247211000 -2.144190000 -0.005558000 H 2.584652000 1.138159000 0.007787000 H 0.704100000 2.710692000 0.009199000 H -1.629541000 1.910879000 -0.014050000 H -3.095945000 0.012894000 0.276218000 H -2.556493000 -1.570087000 0.249170000

***p*SiMe$_3$PhB**	HF=-665.223543 B 0.599941000 4.516941000 0.000000000 C 0.392586000 3.003142000 0.000000000 C 1.490463000 2.125477000 0.000000000 C -0.901765000 2.459269000 0.000000000 C 1.291341000 0.754890000 0.000000000 C -1.087898000 1.084409000 0.000000000 C 0.000705000 0.201101000 0.000000000 H 2.498500000 2.525353000 0.000000000 H -1.761810000 3.119997000 0.000000000 H 2.158320000 0.102974000 0.000000000 H -2.098655000 0.694479000 0.000000000 Si -0.222118000 -1.685318000 0.000000000 C 0.599941000 -2.386962000 1.540675000 H 1.662528000 -2.137272000 1.581543000 H 0.133820000 -1.999300000 2.449192000 H 0.516255000 -3.476598000 1.560931000 C 0.599941000 -2.386962000 -1.540675000 H 1.662528000 -2.137272000 -1.581543000 H 0.516255000 -3.476598000 -1.560931000 H 0.133820000 -1.999300000 -2.449192000 C -2.052461000 -2.113776000 0.000000000 H -2.180982000 -3.199149000 0.000000000 H -2.563873000 -1.725547000 0.883715000 H -2.563873000 -1.725547000 -0.883715000	HF=-665.1743903 B 0.597590000 4.491366000 0.000000000 C 0.393046000 3.030483000 0.000000000 C 1.496463000 2.130497000 0.000000000 C -0.911087000 2.462811000 0.000000000 C 1.287683000 0.767303000 0.000000000 C -1.081376000 1.091733000 0.000000000 C 0.000774000 0.195163000 0.000000000 H 2.508822000 2.515101000 0.000000000 H -1.781455000 3.107200000 0.000000000 H 2.162050000 0.124105000 0.000000000 H -2.095632000 0.708992000 0.000000000 Si -0.219068000 -1.675419000 0.000000000 C 0.597590000 -2.405195000 1.534625000 H 1.659806000 -2.153639000 1.581944000 H 0.129330000 -2.028196000 2.446704000 H 0.516109000 -3.495359000 1.541466000 C 0.597590000 -2.405195000 -1.534625000 H 1.659806000 -2.153639000 -1.581944000 H 0.516109000 -3.495359000 -1.541466000 H 0.129330000 -2.028196000 -2.446704000 C -2.050885000 -2.111136000 0.000000000 H -2.179106000 -3.196593000 0.000000000 H -2.562483000 -1.722083000 0.883418000 H -2.562483000 -1.722083000 -0.883418000
***p*MePhB**	HF=-295.8034578 B -0.009247000 -3.170890000 0.000000000 C -0.006531000 -1.645758000 0.000000000 C -0.006803000 -0.926706000 1.207507000 C -0.006803000 -0.926706000 -1.207507000 C -0.006803000 0.457804000 1.203106000 C -0.006803000 0.457804000 -1.203106000 C -0.004163000 1.171391000 0.000000000 H -0.010516000 -1.461134000 2.150858000 H -0.010516000 -1.461134000 -2.150858000 H -0.011347000 0.999668000 2.141784000 H -0.011347000 0.999668000 -2.141784000 C 0.028899000 2.674545000 0.000000000 H -0.458954000 3.084126000 -0.884957000 H -0.458954000 3.084126000 0.884957000 H 1.061917000 3.034890000 0.000000000	HF=-295.7516576 B -0.008775000 -3.148415000 0.000000000 C -0.005607000 -1.670491000 0.000000000 C -0.007374000 -0.929213000 1.213868000 C -0.007374000 -0.929213000 -1.213868000 C -0.007374000 0.451787000 1.196212000 C -0.007374000 0.451787000 -1.196212000 C -0.004703000 1.179104000 0.000000000 H -0.012579000 -1.446686000 2.164889000 H -0.012579000 -1.446686000 -2.164889000 H -0.011691000 0.984965000 2.140724000 H -0.011691000 0.984965000 -2.140724000 C 0.031944000 2.683101000 0.000000000 H -0.460769000 3.093685000 -0.882994000 H -0.460769000 3.093685000 0.882994000 H 1.061128000 3.056982000 0.000000000
***p*OHPhB**	HF=-331.7298717 B -0.022623000 3.122281000 0.000000000 C -0.016312000 1.601219000 0.000000000 C -1.220250000 0.869955000 0.000000000 C 1.196059000 0.889194000 0.000000000 C -1.218817000 -0.510216000 0.000000000 C 1.209369000 -0.492941000 0.000000000 C 0.000000000 -1.194551000 0.000000000 H -2.166580000 1.398826000 0.000000000 H 2.135869000 1.429648000 0.000000000 H -2.138488000 -1.080114000 0.000000000 H 2.148379000 -1.036141000 0.000000000 O -0.050915000 -2.547952000 0.000000000 H 0.840964000 -2.915961000 0.000000000	HF=-331.6743767 B 0.024395000 -3.107268000 0.000000000 C 0.014108000 -1.626455000 0.000000000 C 1.223560000 -0.876012000 0.000000000 C -1.202540000 -0.893067000 0.000000000 C 1.209861000 0.503212000 0.000000000 C -1.200588000 0.489826000 0.000000000 C 0.000000000 1.199993000 0.000000000 H 2.177354000 -1.388035000 0.000000000 H -2.151415000 -1.413946000 0.000000000 H 2.136460000 1.062806000 0.000000000 H -2.145159000 1.024397000 0.000000000 O 0.054263000 2.567366000 0.000000000 H -0.839717000 2.927204000 0.000000000
***p*OMePhB**	HF=-371.0446594 B 0.865933000 3.467297000 0.000000000 C 0.574017000 1.975526000 0.000000000 C -0.751437000 1.514137000 0.000000000 C 1.610925000 1.019091000 0.000000000 C -1.046785000 0.160256000 0.000000000 C 1.332665000 -0.329262000 0.000000000 C 0.000000000 -0.768692000 0.000000000 H -1.566474000 2.229401000 0.000000000	HF=-370.9890242 B -0.872582000 -3.451296000 0.000000000 C -0.567230000 -2.002477000 0.000000000 C 0.764915000 -1.517070000 0.000000000 C -1.609181000 -1.029886000 0.000000000 C 1.040032000 -0.158052000 0.000000000 C -1.325026000 0.315914000 0.000000000 C 0.000000000 0.772752000 0.000000000 H 1.594390000 -2.212845000 0.000000000

	H 2.643576000 1.348935000 0.000000000 H -2.076858000 -0.164590000 0.000000000 H 2.119761000 -1.071806000 0.000000000 O -0.171378000 -2.107050000 0.000000000 C -1.490378000 -2.641975000 0.000000000 H -2.041180000 -2.337160000 0.893286000 H -2.041180000 -2.337160000 -0.893286000 H -1.370330000 -3.722189000 0.000000000	H -2.644565000 -1.346472000 0.000000000 H 2.072001000 0.162892000 0.000000000 H -2.123478000 1.046986000 0.000000000 O 0.164231000 2.126430000 0.000000000 C 1.480882000 2.648957000 0.000000000 H 2.034915000 2.341112000 0.892249000 H 2.034915000 2.341112000 -0.892249000 H 1.374529000 3.731434000 0.000000000
***p*NH$_2$PhB**	HF=-311.8584604 B -0.000753000 3.140001000 0.000000000 C 0.002052000 1.625237000 0.000000000 C 0.002099000 0.896557000 1.206275000 C 0.002099000 0.896557000 -1.206275000 C 0.002099000 -0.481075000 1.212302000 C 0.002099000 -0.481075000 -1.212302000 C 0.001535000 -1.195956000 0.000000000 H 0.000900000 1.429197000 2.150782000 H 0.000900000 1.429197000 -2.150782000 H 0.004353000 -1.025331000 2.149849000 H 0.004353000 -1.025331000 -2.149849000 N 0.039491000 -2.565421000 0.000000000 H -0.177543000 -3.055631000 -0.850258000 H -0.177543000 -3.055631000 0.850258000	HF=-311.8002877 B 0.000996000 3.128667000 0.000000000 C 0.003164000 1.648716000 0.000000000 C 0.003223000 0.902114000 1.210665000 C 0.003223000 0.902114000 -1.210665000 C 0.003223000 -0.477190000 1.201485000 C 0.003223000 -0.477190000 -1.201485000 C 0.000716000 -1.200092000 0.000000000 H 0.002513000 1.417186000 2.163079000 H 0.002513000 1.417186000 -2.163079000 H 0.008475000 -1.012534000 2.144799000 H 0.008475000 -1.012534000 -2.144799000 N 0.062583000 -2.594440000 0.000000000 H -0.282826000 -3.041190000 -0.835200000 H -0.282826000 -3.041190000 0.835200000
***m*FPhB**	HF=-355.7506859 B -2.000060000 2.144962000 0.000000000 C -0.830292000 1.153197000 0.000000000 C -1.076003000 -0.229515000 0.000000000 C 0.492516000 1.624673000 0.000000000 C 0.000000000 -1.093083000 0.000000000 C 1.553731000 0.730447000 0.000000000 C 1.310693000 -0.639823000 0.000000000 H -2.084113000 -0.625873000 0.000000000 H 0.683021000 2.691164000 0.000000000 H 2.574178000 1.091454000 0.000000000 H 2.120021000 -1.357832000 0.000000000 F -0.221853000 -2.422122000 0.000000000	HF=-355.7024163 B -1.968236000 -2.131528000 0.000000000 C -0.846166000 -1.170222000 0.000000000 C -1.078398000 0.232377000 0.000000000 C 0.501753000 -1.628617000 0.000000000 C 0.000000000 1.086396000 0.000000000 C 1.547032000 -0.725426000 0.000000000 C 1.318210000 0.651393000 0.000000000 H -2.077356000 0.646500000 0.000000000 H 0.713100000 -2.689746000 0.000000000 H 2.565179000 -1.094323000 0.000000000 H 2.125699000 1.369461000 0.000000000 F -0.237781000 2.416705000 0.000000000
***m*ClPhB**	HF=-716.0946071 B -1.776991000 2.692249000 0.000000000 C -0.673246000 1.627125000 0.000000000 C -1.008345000 0.263963000 0.000000000 C 0.677299000 2.010187000 0.000000000 C 0.000000000 -0.685399000 0.000000000 C 1.674000000 1.045795000 0.000000000 C 1.338871000 -0.304518000 0.000000000 H -2.044929000 -0.049211000 0.000000000 H 0.939247000 3.061602000 0.000000000 H 2.717146000 1.335159000 0.000000000 H 2.109794000 -1.062977000 0.000000000 Cl -0.405163000 -2.381691000 0.000000000	HF=-716.0463637 B -1.733734000 -2.680697000 0.000000000 C -0.677845000 -1.647262000 0.000000000 C -1.008129000 -0.264082000 0.000000000 C 0.698466000 -2.009007000 0.000000000 C 0.000000000 0.678387000 0.000000000 C 1.674582000 -1.032522000 0.000000000 C 1.347302000 0.323712000 0.000000000 H -2.038944000 0.061197000 0.000000000 H 0.985739000 -3.052234000 0.000000000 H 2.717342000 -1.325210000 0.000000000 H 2.112479000 1.086005000 0.000000000 Cl -0.430248000 2.372845000 0.000000000
***m*CF$_3$PhB**	HF=-593.6615378 C 2.626860000 0.556617000 0.008784000 C 1.748144000 1.630383000 0.001521000 C 2.139785000 -0.759374000 -0.000668000 H 2.123443000 2.645362000 0.005629000 B 3.115834000 -1.944692000 0.003801000 C 0.377949000 1.401436000 -0.014197000 C 0.753503000 -0.978794000 -0.016077000 H -0.310022000 2.236673000 -0.025851000 H 0.365379000 -1.989666000 -0.027213000 C -0.119988000 0.097966000 -0.023775000 H 3.696319000 0.733388000 0.019654000 C -1.612020000 -0.117112000 -0.002877000 F -2.118077000 0.053684000 1.239104000	HF=-593.6142927 C 2.634629000 0.552859000 0.010333000 C 1.753973000 1.617046000 0.001072000 C 2.150341000 -0.784927000 -0.000616000 H 2.144036000 2.627093000 0.006083000 B 3.074318000 -1.936915000 0.003706000 C 0.376592000 1.411887000 -0.015921000 C 0.741798000 -0.982405000 -0.018300000 H -0.305943000 2.249688000 -0.028312000 H 0.332649000 -1.982739000 -0.030603000 C -0.113147000 0.101955000 -0.025395000 H 3.700130000 0.742487000 0.023847000 C -1.603819000 -0.112891000 -0.002436000 F -2.121047000 0.115366000 1.227334000

	F -2.253265000 0.757462000 -0.805271000 F -1.955290000 -1.354372000 -0.401331000	F -2.244510000 0.722236000 -0.847937000 F -1.954961000 -1.367947000 -0.344059000
***m*CNPhB**	HF=-348.743528 B 1.832898000 -2.575673000 0.000000000 C 0.711246000 -1.523168000 0.000000000 C 1.021668000 -0.157694000 0.000000000 C -0.635031000 -1.922638000 0.000000000 C 0.000000000 0.792563000 0.000000000 C -1.650574000 -0.977039000 0.000000000 C -1.337995000 0.375680000 0.000000000 H 2.054298000 0.169456000 0.000000000 H -0.881012000 -2.978336000 0.000000000 H -2.687038000 -1.287997000 0.000000000 H -2.124087000 1.118862000 0.000000000 C 0.313108000 2.189041000 0.000000000 N 0.562689000 3.313701000 0.000000000	HF=-348.6972023 B -1.794010000 -2.555524000 0.000000000 C -0.718977000 -1.542311000 0.000000000 C -1.021942000 -0.156015000 0.000000000 C 0.653713000 -1.923241000 0.000000000 C 0.000000000 0.785894000 0.000000000 C 1.650013000 -0.966893000 0.000000000 C 1.346990000 0.392134000 0.000000000 H -2.048547000 0.183913000 0.000000000 H 0.922691000 -2.971558000 0.000000000 H 2.685729000 -1.282333000 0.000000000 H 2.128052000 1.138559000 0.000000000 C -0.332261000 2.178557000 0.000000000 N -0.597584000 3.300041000 0.000000000
***m*NO$_2$PhB**	HF=-461.055329 B 1.383302000 3.126866000 0.000000000 C 0.409652000 1.934777000 0.000000000 C -0.978378000 2.151084000 0.000000000 C 0.900782000 0.621949000 0.000000000 C -1.862361000 1.080745000 0.000000000 C 0.000000000 -0.427649000 0.000000000 C -1.374190000 -0.220175000 0.000000000 H -1.361066000 3.165279000 0.000000000 H 1.962495000 0.414900000 0.000000000 H -2.930713000 1.251937000 0.000000000 H -2.036932000 -1.073179000 0.000000000 N 0.511906000 -1.817239000 0.000000000 O -0.309514000 -2.719085000 0.000000000 O 1.721181000 -1.970538000 0.000000000	HF=-461.0093623 B -1.314085000 -3.110902000 0.000000000 C -0.388750000 -1.959354000 0.000000000 C 1.025014000 -2.138617000 0.000000000 C -0.888727000 -0.630419000 0.000000000 C 1.875217000 -1.049726000 0.000000000 C 0.000000000 0.422956000 0.000000000 C 1.382050000 0.253749000 0.000000000 H 1.441361000 -3.137595000 0.000000000 H -1.947773000 -0.420750000 0.000000000 H 2.945275000 -1.213517000 0.000000000 H 2.032646000 1.113771000 0.000000000 N -0.547814000 1.799145000 0.000000000 O 0.249755000 2.722624000 0.000000000 O -1.761657000 1.930758000 0.000000000
***p*FPhB**	HF=-355.7528941 B 0.000000000 0.000000000 -3.107430000 C 0.000000000 0.000000000 -1.579966000 C 0.000000000 1.211053000 -0.865715000 C 0.000000000 -1.211053000 -0.865715000 C 0.000000000 1.219156000 0.519241000 C 0.000000000 -1.219156000 0.519241000 C 0.000000000 0.000000000 1.181353000 H 0.000000000 2.152361000 -1.403096000 H 0.000000000 -2.152361000 -1.403096000 H 0.000000000 2.138225000 1.089282000 H 0.000000000 -2.138225000 1.089282000 F 0.000000000 0.000000000 2.523794000	HF=-355.700867 B 0.000000000 0.000000000 -3.089207000 C 0.000000000 0.000000000 -1.604838000 C 0.023523000 1.215981000 -0.868914000 C -0.023523000 -1.215981000 -0.868914000 C 0.000000000 1.212488000 0.513577000 C 0.000000000 -1.212488000 0.513577000 C 0.000000000 0.000000000 1.187249000 H 0.059624000 2.163476000 -1.390798000 H -0.059624000 -2.163476000 -1.390798000 H 0.005417000 2.137063000 1.075589000 H -0.005417000 -2.137063000 1.075589000 F 0.000000000 0.000000000 2.538448000
***p*ClPhB**	HF=-716.0959138 B 0.000000000 0.000000000 -3.550604000 C 0.000000000 0.000000000 -2.021006000 C 0.000000000 1.208857000 -1.305424000 C 0.000000000 -1.208857000 -1.305424000 C 0.000000000 1.215329000 0.079910000 C 0.000000000 -1.215329000 0.079910000 C 0.000000000 0.000000000 0.758318000 H 0.000000000 2.152241000 -1.839292000 H 0.000000000 -2.152241000 -1.839292000 H 0.000000000 2.143634000 0.633978000 H 0.000000000 -2.143634000 0.633978000 Cl 0.000000000 0.000000000 2.496820000	HF=-716.0463335 B 0.000000000 0.000000000 -3.524388000 C 0.000000000 0.000000000 -2.048436000 C 0.000000000 1.216813000 -1.309781000 C 0.000000000 -1.216813000 -1.309781000 C 0.000000000 1.209588000 0.070709000 C 0.000000000 -1.209588000 0.070709000 C 0.000000000 0.000000000 0.762901000 H 0.000000000 2.167233000 -1.827624000 H 0.000000000 -2.167233000 -1.827624000 H 0.000000000 2.142551000 0.618101000 H 0.000000000 -2.142551000 0.618101000 Cl 0.000000000 0.000000000 2.507238000
***p*CF$_3$PhB**	HF=-593.6610256 C -2.609722000 -0.005704000 0.003008000 C -1.888234000 -1.210962000 -0.002906000 C -1.908511000 1.208904000 -0.003057000	HF=-593.6158326 C -2.638258000 -0.002574000 0.006742000 C -1.896393000 -1.219132000 -0.002938000 C -1.906656000 1.218855000 -0.002855000

	H -2.417379000 -2.156687000 0.000089000 H -2.452360000 2.146340000 -0.000154000 C -0.503993000 -1.200610000 -0.014666000 C -0.521392000 1.222578000 -0.014297000 H 0.051811000 -2.128881000 -0.023989000 H 0.018672000 2.158815000 -0.022325000 C 0.175105000 0.017732000 -0.020897000 B -4.145937000 -0.013599000 0.015040000 C 1.684643000 0.006158000 -0.001699000 F 2.154256000 -0.355628000 1.212243000 F 2.185702000 -0.873944000 -0.891503000 F 2.211328000 1.209553000 -0.287600000	H -2.413542000 -2.169639000 0.001014000 H -2.430942000 2.165421000 0.001059000 C -0.519372000 -1.201617000 -0.020473000 C -0.527942000 1.212852000 -0.019894000 H 0.024101000 -2.137405000 -0.032259000 H 0.008163000 2.152143000 -0.030952000 C 0.181280000 0.009285000 -0.031577000 B -4.111429000 -0.010125000 0.022839000 C 1.678784000 0.003390000 -0.002705000 F 2.165767000 -0.183248000 1.250557000 F 2.199269000 -0.988542000 -0.758808000 F 2.206153000 1.162208000 -0.448512000
***p*CNPhB**	HF=-348.7433476 B 0.000000000 0.000000000 -3.456279000 C 0.000000000 0.000000000 -1.918047000 C 0.000000000 1.211292000 -1.207777000 C 0.000000000 -1.211292000 -1.207777000 C 0.000000000 1.216581000 0.176145000 C 0.000000000 -1.216581000 0.176145000 C 0.000000000 0.000000000 0.870420000 H 0.000000000 2.152099000 -1.745710000 H 0.000000000 -2.152099000 -1.745710000 H 0.000000000 2.146811000 0.727728000 H 0.000000000 -2.146811000 0.727728000 C 0.000000000 0.000000000 2.301382000 N 0.000000000 0.000000000 3.453487000	HF=-348.700734 B 0.000000000 0.000000000 -3.412900000 C 0.000000000 0.000000000 -1.945054000 C 0.000000000 1.221979000 -1.208242000 C 0.000000000 -1.221979000 -1.208242000 C 0.000000000 1.212992000 0.166132000 C 0.000000000 -1.212992000 0.166132000 C 0.000000000 0.000000000 0.879387000 H 0.000000000 2.169778000 -1.730154000 H 0.000000000 -2.169778000 -1.730154000 H 0.000000000 2.148080000 0.710426000 H 0.000000000 -2.148080000 0.710426000 C 0.000000000 0.000000000 2.301514000 N 0.000000000 0.000000000 3.456314000
***p*NO_2PhB**	HF=-461.0544154 B 0.000000000 0.000000000 -3.816142000 C 0.000000000 0.000000000 -2.275388000 C 0.000000000 1.212157000 -1.566897000 C 0.000000000 -1.212157000 -1.566897000 C 0.000000000 1.219022000 -0.180923000 C 0.000000000 -1.219022000 -0.180923000 C 0.000000000 0.000000000 0.483460000 H 0.000000000 2.152745000 -2.104892000 H 0.000000000 -2.152745000 -2.104892000 H 0.000000000 2.137208000 0.387228000 H 0.000000000 -2.137208000 0.387228000 N 0.000000000 0.000000000 1.967572000 O 0.000000000 1.081987000 2.529277000 O 0.000000000 -1.081987000 2.529277000	HF=-461.0145301 B 0.000000000 0.000000000 -3.762086000 C 0.000000000 0.000000000 -2.297527000 C 0.000000000 1.225001000 -1.562560000 C 0.000000000 -1.225001000 -1.562560000 C 0.000000000 1.217040000 -0.188541000 C 0.000000000 -1.217040000 -0.188541000 C 0.000000000 0.000000000 0.498020000 H 0.000000000 2.171459000 -2.086598000 H 0.000000000 -2.171459000 -2.086598000 H 0.000000000 2.139127000 0.373760000 H 0.000000000 -2.139127000 0.373760000 N 0.000000000 0.000000000 1.950738000 O 0.000000000 1.084902000 2.524450000 O 0.000000000 -1.084902000 2.524450000
H_2BSiMe_3	HF=-435.3712452 B 1.442797000 -0.000042000 -1.508622000 Si 0.024783000 0.000026000 -0.070738000 C 0.963426000 0.000340000 1.578847000 H 1.599300000 -0.881379000 1.683475000 H 1.595700000 0.884470000 1.684818000 H 0.253617000 -0.001798000 2.410883000 C -1.068117000 -1.539159000 -0.152071000 H -0.471232000 -2.451327000 -0.081259000 H -1.794343000 -1.549604000 0.665090000 H -1.627721000 -1.583927000 -1.089564000 C -1.068547000 1.538821000 -0.152551000 H -1.795021000 1.549278000 0.664397000 H -0.472019000 2.451222000 -0.081724000 H -1.627903000 1.583277000 -1.090215000 H 1.909610000 1.012622000 -1.938621000 H 1.908494000 -1.012998000 -1.939188000	

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