Synthese, Struktur und Einlagerungsverhalten von Polyoxadiphosphaplatinaferrocenophanen

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Synthesis, Structure, and Inclusion Behavior of Polyoxadiphosphaplatinaferrocenophanes

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Contents

Abbreviations

Å	Ångström (10^{-10} m)
β_{mn}	Association constant
d	Day
DEPT	Distortionless Enhancement by Polarization Transfer
δ	Chemical shift
δ_{calc}	Calculated chemical shift
$\Delta\delta$	Difference between chemical shifts
FD	Field desorption
g	Gram
G	Guest
h	Hour
H	Host
Hz	Hertz
IR	Infrared spectroscopy
mesylate	Methane sulfonate
µA	Microampere
ml	Milliliter
mmol	Millimol
MHz	Megahertz
NMR	Nuclear magnetic resonance
MS	Mass spectroscopy
mV	Millivolt

ppm	Parts per million
R	Quality factor for the results of fitting procedures
s	Second
v	Scan rate
W_i	Statistical weight attributed to observation i

1. Introduction

Cyclophanes[1] and crown ethers[2] represent prototypic motifs in the development of supramolecular chemistry. The introduction of transition metal complex fragments into macrocyclic systems created the new and fast growing field of supramolecular organometallic chemistry[3]. Compared to their organic analogues, metallacyclophanes, metallocenophanes and metallacrown ethers exhibit a variety of additional features, like catalytic and/or redox activity[4-6]. Transition metals exert also a remarkable influence on the structure of macrocycles with regard to their rigidity and cavity. It was demonstrated that metal-containing macrocycles reveal suitable hosts for the inclusion of guests, like metal ions or small molecules[7,8].

The objective of the present work was the incorporation of a potentially catalytic active metal center and a redox active ferrocene unit into a crown ether-like macrocycle. Such a combination is rarely described in the literature[6,9]. The expected heterobimetallic host molecules can be regarded as a crosslink between polyoxaferrocenophanes[10-12] and metallacrown ethers[13-20], which should be capable to include different metal cations of the first or second main group as guests. The ferrocene function offers the possibility to electrochemically manipulate the inclusion characteristics. Electrochemical oxidation of the ferrocene subunit reduces the cation binding capability of the host molecule which is switched from a high to a low binding state and ideally the incorporated cation will be released. Upon reduction the ability of the cation complexation is restored. This characteristic is the fundamental principle of a redox switch[21] and has been employed successfully for cation transport through a liquid membrane[22].

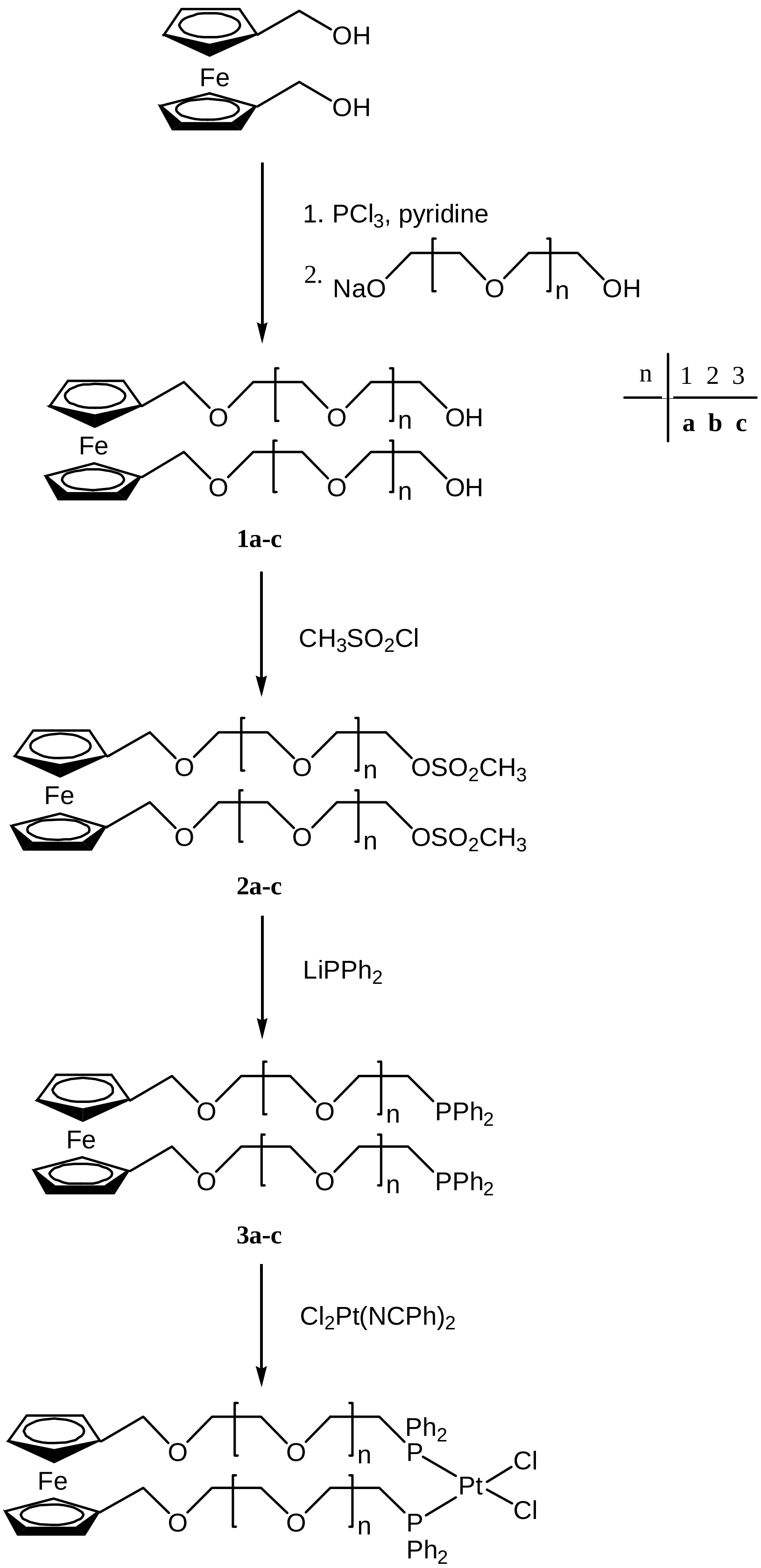
The hitherto succesfully applied bis(triflate) method for the formation of metal-carbon σ bonds which is a necessary precondition for the access to metallacyclophanes[4,23] and metallametallocenophanes[5] failed when heteroatoms are incorporated into the backbone of the bis(triflate)[13]. However, the well-developed phosphine chemistry offers a valuable alternative for the introduction of a second transition metal to generate polyoxametallaferrocenophanes. Suitable bis(phosphine) ligands were built up of oligoethylene glycol chains with different length which are connected to a ferrocene unit in 1,1‘-positions and to two phosphorus donors. If these ligands are reacted with a transition metal precursor in a 1:1 ratio under high dilution conditions the desired bimetallic crown ethers are available.

Herein the synthesis of a series of polyoxadiphosphaplatinaferrocenophanes with four to eight oxygen donors is described and their inclusion behavior toward alkaline metal cations, and NH_4^+, or Mg^{2+} cations was investigated in solution applying the NMR titration technique which offers the possibility to determine association constants of supramolecular complexes by non-linear least-squares curve fitting to the experimental data. Cyclic voltammetry was used to examine the electrochemical properties of the polyoxadiphosphaplatinacyclophanes with regard to the formation of host/guest complexes.

2. General Section

2.1. Synthesis of the Bidentate Phosphine Ligands 3a-c

The bidentate phosphines **3a-c** (Scheme 1) were made accessible by coupling of 1,1‘-bis(hydroxymethyl)ferrocene[24] to functionalized oligoethylene glycols. In the first step of the reaction sequence 1,1‘-bis(hydroxymethyl)ferrocene was converted to 1,1’-bis(chloromethyl)-ferrocene with PCl_3 in THF[25] and *in situ* reacted with a large excess of the mono sodium salt of the appropriate oligoethylene glycol to avoid the formation of oligomeric or cyclic species by a possible template effect of sodium[11,26]. After purification by column chromatography the diols **1a-c** were obtained in moderate yields as dark orange, hygroscopic, viscous oils. Subsequently **1a-c** were treated with excess methanesulfonyl chloride in dichloromethane to give the orange brown oily dimesylates **2a-c** which were due to their sensitivity immediately reacted with $LiPPh_2$ in THF to afford the bisphosphines **3a-c**. After column-chromatographic purification under an atmosphere of argon these ligands were obtained in good yields as dark orange, slightly air-sensitive, viscous oils, which are soluble in all common organic solvents. Their molecular composition was corroborated by elemental analyses and FD mass spectra displaying the expected molecular peak in each case. In agreement with related ligands [13], the $^{31}P\{^1H\}$ NMR spectra of **3a-c** display singlets at δ = - 21 for both chemically equivalent phosphorus nuclei. The ^1H- and $^{13}C\{^1H\}$ NMR spectra of the intermediates **1a-c** and **2a-c**, and of **3a-c** are similar for the ferrocene moiety and oligoethylene glycol chains. Only the resonances of both methylene groups at the open ends of the molecules show differences in the chemical shifts depending on the kind of the attached terminal functional group. The $^{13}C\{^1H\}$ resonance of the methylene groups in α-position to the hydroxy functions of **1a-c** is shifted to lower field by substitution of the hydroxy groups for mesylate functions in **2a-c** and is shifted to higher field for the bisphospines **3a-c**. Furthermore the signal is splitted into a doublet by coupling to the phosphorus nuclei with a coupling constant of $^1J_{PC} \approx 13$ Hz. The same trend is observed for the protons of the α-methylene groups in the ^{1}H NMR spectra of **1a-c**, **2a-c**, and **3a-c**, respectively. Additional signals at high field for the methane sulfonate groups of the dimesylates **2a-c** and in the low field region for the phenyl rings attached to the phosphorus atoms of the diphosphanes **3a-c** are observed in the ^{1}H as well as in the ^{13}C{^{1}H} NMR spectra.


OH
Fe
OH
1. PCl3, pyridine
2. NaO O n OH
n 1 2 3
a b c
O O n OH
Fe
O O n OH
1a-c
CH3SO2Cl
O O n OSO2CH3
Fe
O O n OSO2CH3
2a-c
LiPPh2
O O n PPh2
Fe
O O n PPh2
3a-c
Cl2Pt(NCPh)2
O O n Ph2 P
Fe
Pt Cl Cl
O O n P Ph2
4a-c

Scheme 1.

2.2. Synthesis of the Polyoxadiphosphaplatinaferrocenophanes 4a-c

To enhance the formation of the heterobimetallic macrocycles **4a-c** (Scheme 1) and to suppress the occurrence of oligo- and/or polymeric species, the reaction between the bisphosphines **3a-c** and one equivalent of bis(benzonitrile)dichloroplatinum(II) was carried out under high dilution conditions in dichloromethane[27]. After purification by column chromatography the polyoxadiphosphaplatinaferrocenophanes **4a-c** were obtained as bright yellow, rather air stable solids, which readily dissolve in chlorinated organic solvents and mixtures of them with any other organic solvent. However, solutions of **4a-c** slowly decompose in the presence of air oxygen and traces of an acid. In the FD mass spectra of **4a-c** the molecular peaks are detected with the appropriate isotopic patterns. Compared to **3a-c** the ^{31}P signals in the $^{31}P\{^{1}H\}$ NMR spectra expectedly are shifted to lower field. Resonances with superimposed doublets due to the ^{195}Pt-^{31}P coupling are observed at δ = 4.3 (**4a)** and ≈ 5.3 (**4b,c**). The magnitude of the $^{1}J_{PtP}$ coupling constant of approximately 3630 Hz gives evidence for the *cis*-arrangement of the phosphinyl functions in each case[28]. This finding is confirmed by the $^{195}Pt\{^{1}H\}$ NMR spectra of **4a-c**, displaying each a triplet at δ = - 4400 with the same $^{1}J_{PtP}$ coupling. In the high field part of the $^{13}C\{^{1}H\}$ NMR spectra of **4a-c** the signals of the methylene groups adjacent to the P atoms appear as the A part of an AXX‘ spin system. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **4a** are depicted in Figure 1.

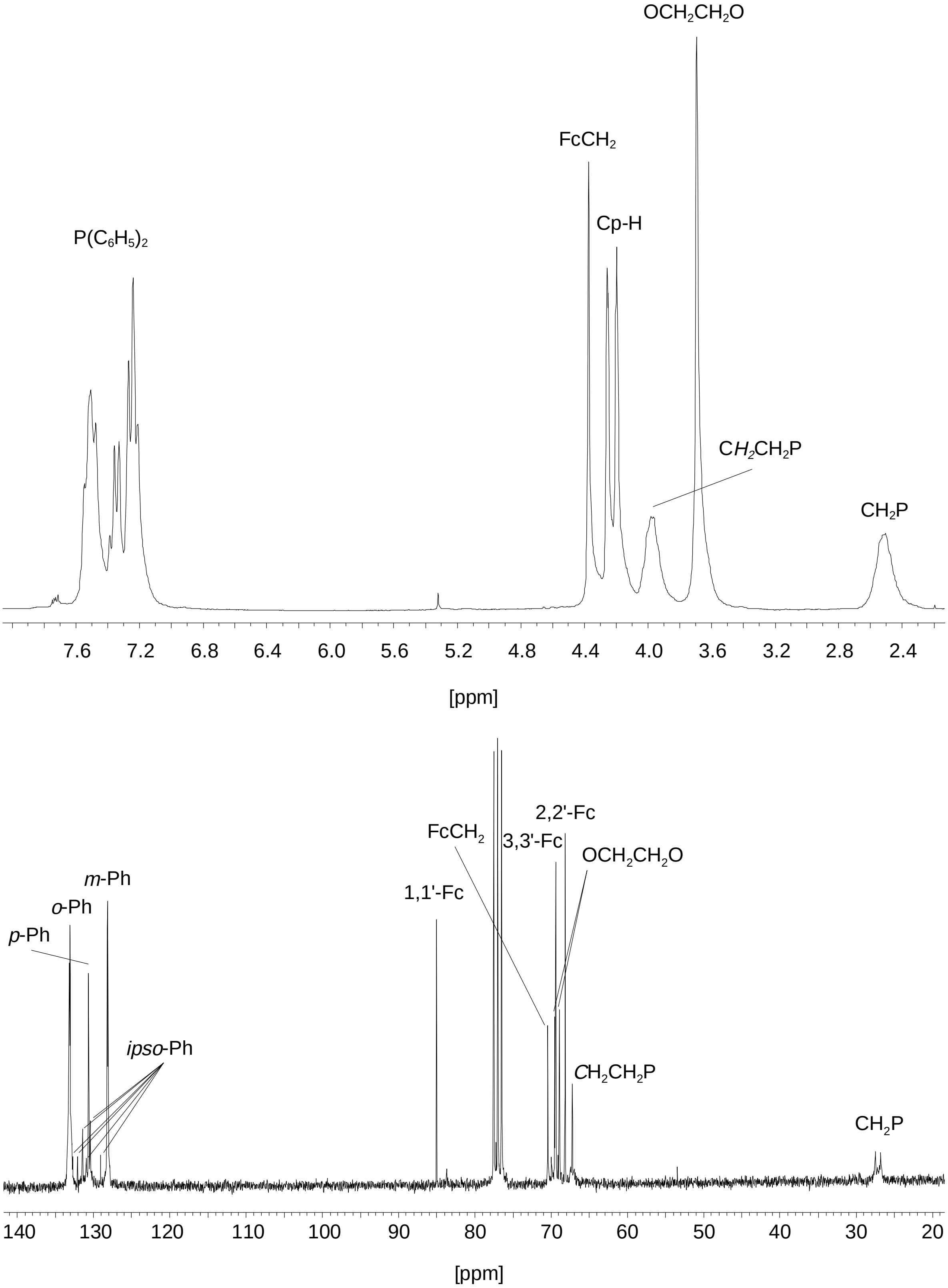


Figure 1. ^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of **4a**.

The assignment of the $^{13}C\{^1H\}$ resonances of the carbon atoms in 2,2'- and 3,3'-positions of the ferrocene units which are located in the same region as the methylene carbons of the oligoethylene glycol chains was made with the aid of DEPT-135 NMR experiments according to related 1,1'-disubstituted ferrocenes[35].

2.3. X-ray Crystal Structure of 4a

To prove the mononuclear composition of **4a-c** and to get more detailed information about the size and shape of the cavities, efforts to grow single crystals of **4a-c** have been undertaken. Because of the flexibility of the molecular skeleton of the platinaferrocenophanes only **4a** could be crystallized. The triclinic unit cell contains eight symmetrically independant molecules of **4a** which differ only in little conformational changes, mainly in the oligoethylene glycol chains. An ORTEP plot of one selected molecule with atom labeling is depicted in Figure 2. All four oxygen atoms are approximately located in a plane at the vertices of a distorted trapezoid. The lenghts of the parallel edges are 5.62(1) (O1-O3) and 4.73(1) Å (O2-O4) and the O1-O2 and O3-O4 distances are 2.83(3) and 2.82(3) Å, respectively. A distance of 9.25(1) Å was found between Pt(1) and Fe(1). From these proportions it can be deduced that the cavity is big enough to encapsulate smaller alkaline or earth alkaline metal ions. A space-filling model (Figure 3) demonstrates this property. The coordination sphere of platinum is not ideally square-planar, because the Cl-Pt-Cl plane is tilted against the P-Pt-P plane by 14.7°. The coplanar cyclopentadienyl rings of the ferrocene unit are arranged in an almost eclipsed conformation and the two substituents are displaced by one ring carbon position.

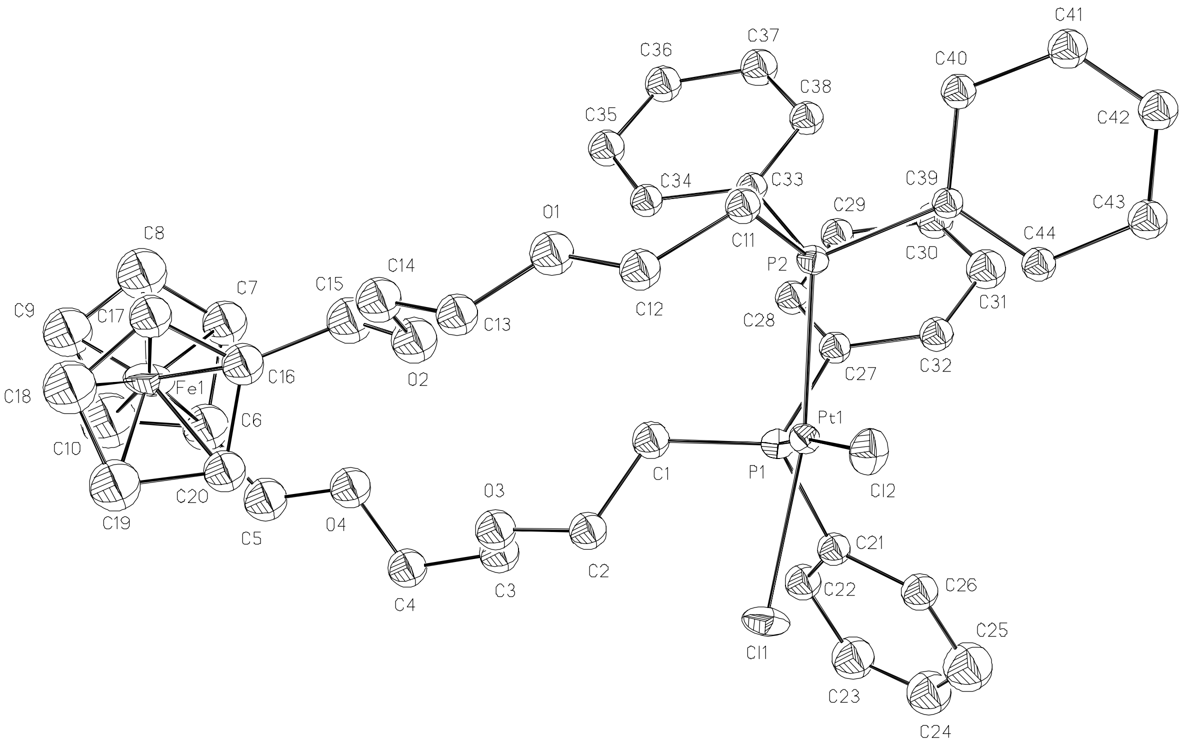


Figure 2. ORTEP plot of one molecule of the X-ray crystal structure of compound **4a**. Thermal ellipsoids are drawn at 20% probability level, except for H atoms. Selected interatomic distances (Å) and interbond angles (°): Pt1-Cl1 2.35(1), Pt1-Cl2 2.36(1), Pt1-P1 2.24(1), Pt1-P2 2.26(1), O1-O2 2.83(3), O1-O3 5.62(3), O3-O4 2.82(3), O2-O4 4.74(3), Pt1-Fe1 9.25(1); P1-Pt1-P2 98.8(2), P1-Pt1-Cl1 88.6(2), P2-Pt1-Cl2 86.5(2), Cl1-Pt1-Cl2 88.0(3), C1-P1-Pt1 114.8(10), C33-P2-Pt1 117.5(7), O2-C15-C16 114(3), O4-C5-C6 109(4).

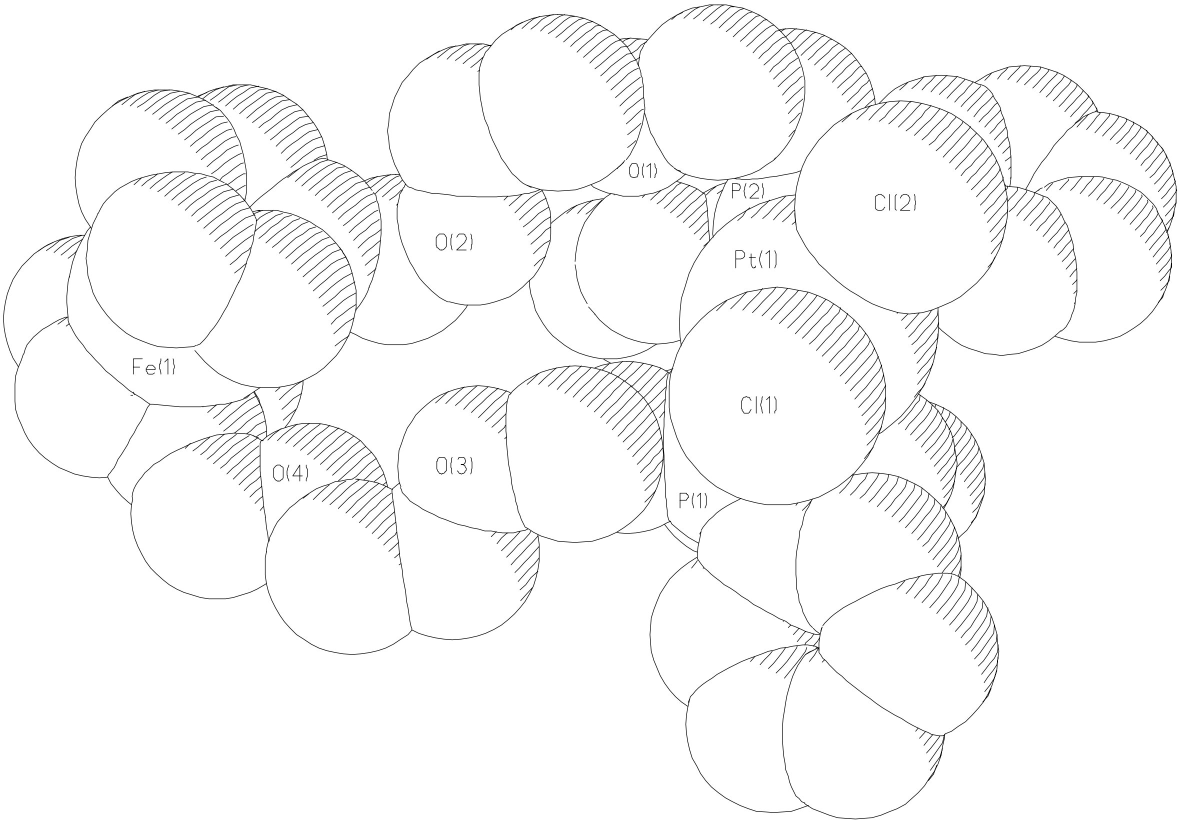


Figure 3. Space-filling representation of compound **4a**. Hydrogen atoms are omitted for clarity.

2.4. Investigations on the Inclusion Behavior and Electrochemical Properties of the Polyoxadiphosphaplatinaferrocenophanes 4a-c

2.4.1. NMR Titrations

NMR titrations are among the most employed methods for the determination of association constants in host/guest chemistry[29]. In addition to ^{1}H NMR spectroscopy, the polyoxadiphosphaplatinaferrocenophanes **4a-c** offer the possibility to use the ^{31}P nucleus as a probe for NMR titrations. Because ^{31}P provides a larger chemical shift dispersion compared to ^{1}H, a larger effect upon the formation of supramolecular complexes may be observed and therefore the determination of association constants is more reliable. Attempts to include alkaline metal cations and Mg^{2+}, or NH_4^+, respectively, as potential guests were performed in a mixture of $CDCl_3/CD_3CN$ (v/v 1:1) for several different starting concentrations of **4a-c**, covering the accessible concentration range, which is limited by the lowest measureable host concentration and the solubility of the guests. This combination of solvents was chosen because **4a-c** as well as the salts of the guest cations [$LiBF_4$, $MBPh_4$ (M = Na, K, Rb,Cs,NH_4), $Mg(ClO_4)_2$] are soluble in such a mixture and the solvent has a low donating capability[30]. After each addition of the guest solutions ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were recorded. In Figures 4-6 the ^{31}P chemical shifts are plotted versus the molar ratio cation : **4a-c**.

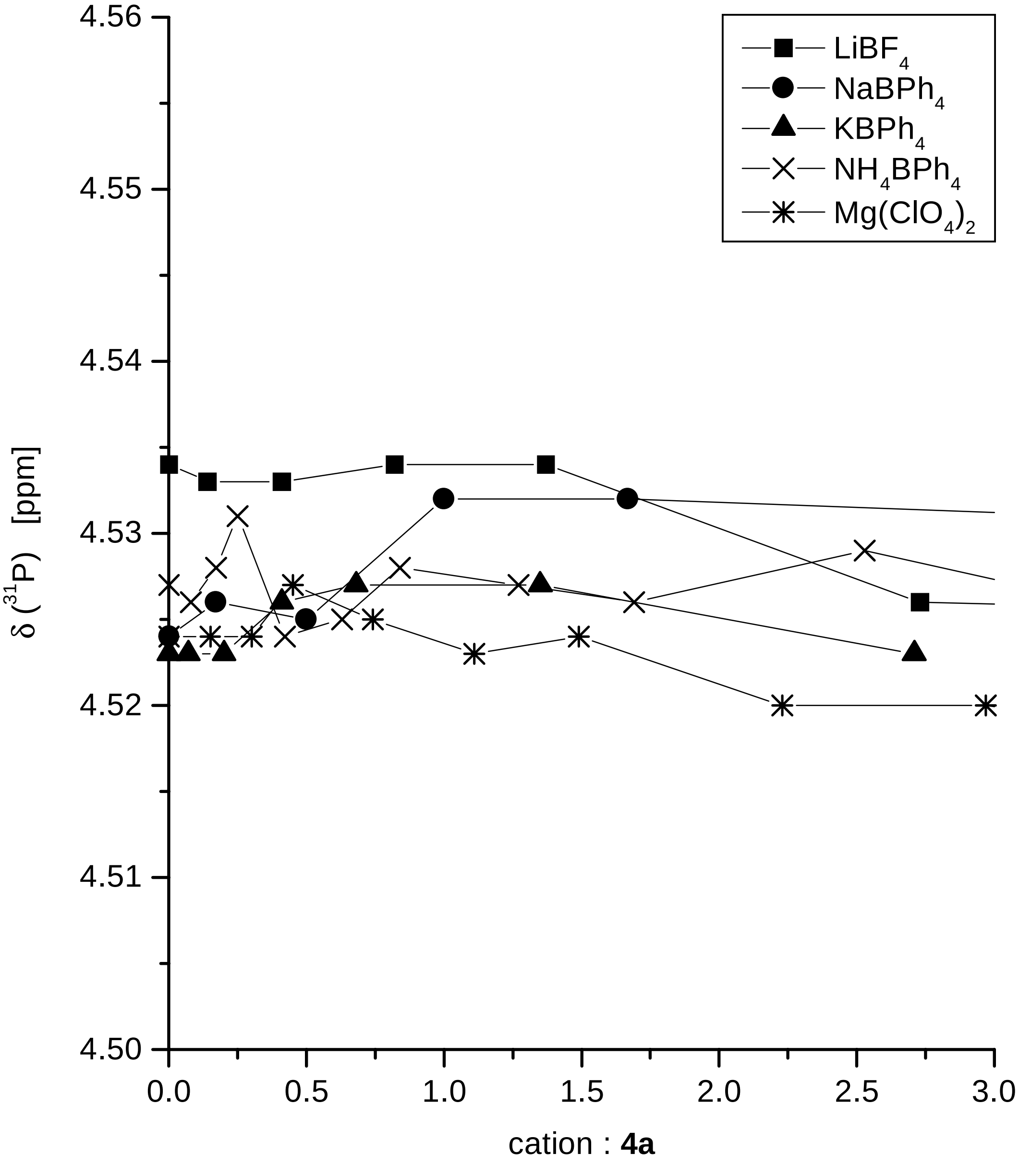


Figure 4. ^{31}P chemical shifts *vs* molar ratio cation : **4a** in $CDCl_3/CD_3CN$ (1:1) solutions. The concentrations of **4a** range between 0.01M and 0.005M.

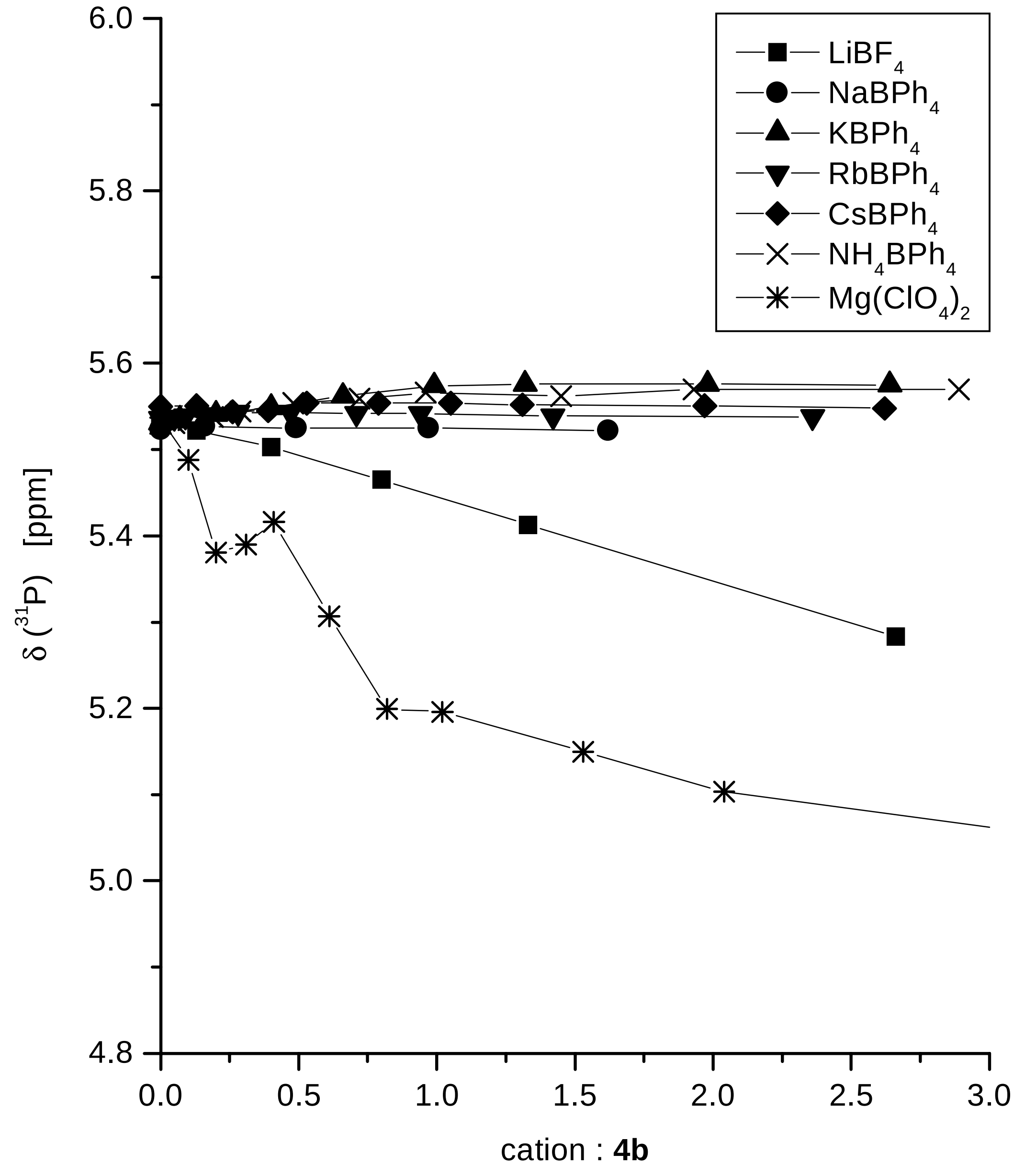


Figure 5. ^{31}P chemical shifts *vs* molar ratio cation : **4b** in $CDCl_3/CD_3CN$ (1:1) solutions. The concentrations of **4b** range between 0.01M and 0.005M.

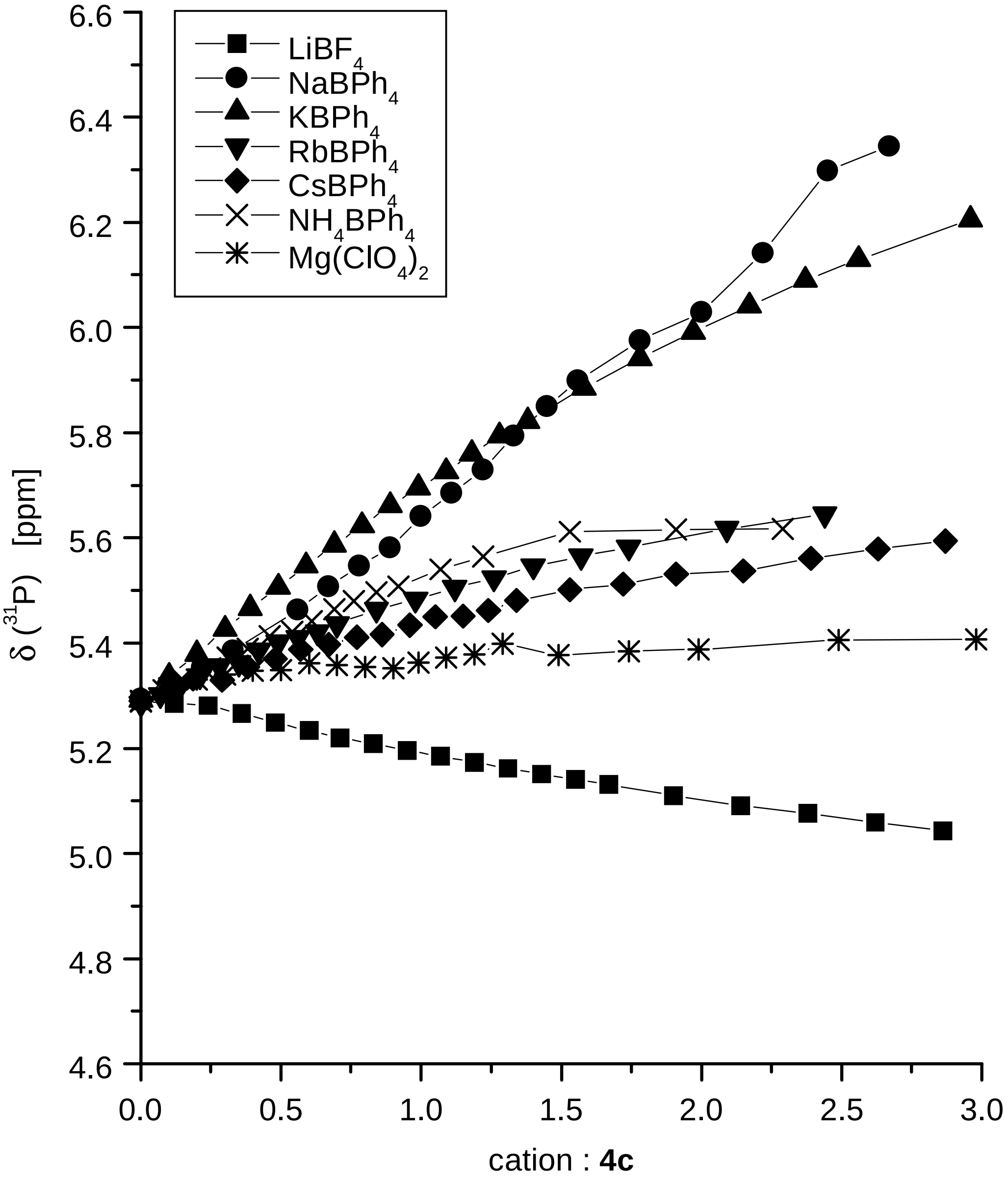


Figure 6. ^{31}P chemical shifts *vs* molar ratio cation : **4c** in $CDCl_3$/CD_3CN (1:1) solutions. The concentrations of **4c** range between 0.01M and 0.001M.

In the case of the smallest macrocycle **4a** neither in the ^1H nor in the $^{31}P\{^1H\}$ NMR spectra a significant shift of any signal could be observed (Figure 4). Only the successive addition of Li^+ and Mg^{2+} to a solution of **4b** (Figure 5) and Li^+, Na^+, or K^+ to a solution of **4c** (Figure 6) resulted in a remarkable shift, in particular of the ^{31}P resonance up to $\Delta\delta \approx 1$. In the ^1H NMR spectra the shifts of all analyzed resonances were generally smaller than $\Delta\delta \approx 0.3$. A conspicuous observation is that upon addition of Li^+ or Mg^{2+} the $^{31}P\{^1H\}$ signal is shifted to higher field but the addition of Na^+ or K^+ in the case of **4c** leads to a downfield shift. However, a satisfactory determination of association constants by non-linear least-squares curve fitting of the experimental data with EQNMR[31] was not possible. This observation can be traced back to insufficient fitting results for all applied complexation models. 1:1 and 2:1 complexes were taken into consideration, either separate or parallel. Self-association has been ruled out by preliminary dilution experiments. Although low R-factors (< 1%) were obtained for the best fits the errors of the estimated association constants were larger than ± 100% in some cases. The almost linear shape of the titration curves indicates that the association constants are very small and therefore most of the measured points are not in the optimum range of 20-80% complexation. Only if at least 7-10 data points are measured in this range and no systematic deviation of the fit curve is observed the resulting association constants are trustworthy[29]. Due to solubility limitations the necessary high concentrations of the guests to fulfill this precondition could not be achieved.

2.4.2. Cyclic Voltammetry

Cyclic voltammetry is one of the most widely used electrochemical methods for the study of complex formation equilibria and characterization of redox properties of supramolecular systems[29]. Complexation-induced shifts of the redox potentials can be used for the evaluation of formation constants[32], although this method is less accurate than others.

Cyclovoltammetric measurements of **4a**-**c** were performed in $5{\cdot}10^{-4}$ M dichloromethane/acetonitrile (v/v 1:1) solutions. The half-wave potentials for the reversible oxidation of the ferrocene units in **4a**-**c** are 152, 142, and 144 mV, respectively. These values correspond to a slight anodic shift compared to the redox potential of unsubstituted ferrocene (E^0 = 136 mV), measured in the same solvent mixture. The cyclic voltammogram of **4a** is depicted in Figure 7. The shape of the cyclic voltammograms of **4a**-**c** is similar to that of ferrocene and in contrast to a series of osmaferrocenophanes[5] no significant ring-size dependant shift of the redox potentials was observed. Other cyclovoltammetric signals could not be detected within the accessible potential range. Electrochemical response to the formation of host-guest complexes of ferrocene-containing crown ethers or cryptands, and metal cations, resulting in shifts of the redox potential up to 300 mV have been reported[33-35]. However, no perturbation of the cyclic voltammograms of **4a**-**c** upon successive addition of group 1 cations, Mg^{2+}, or NH_4^+ ions could be observed. This finding is consistent with the results of the NMR titrations of **4a** but in contrast to that of **4b** for Li^+ and $Mg^{2+}$and of **4c** for Li^+, Na^+, and K^+ which indicate an interaction of the mentioned guest cations with the host molecules.

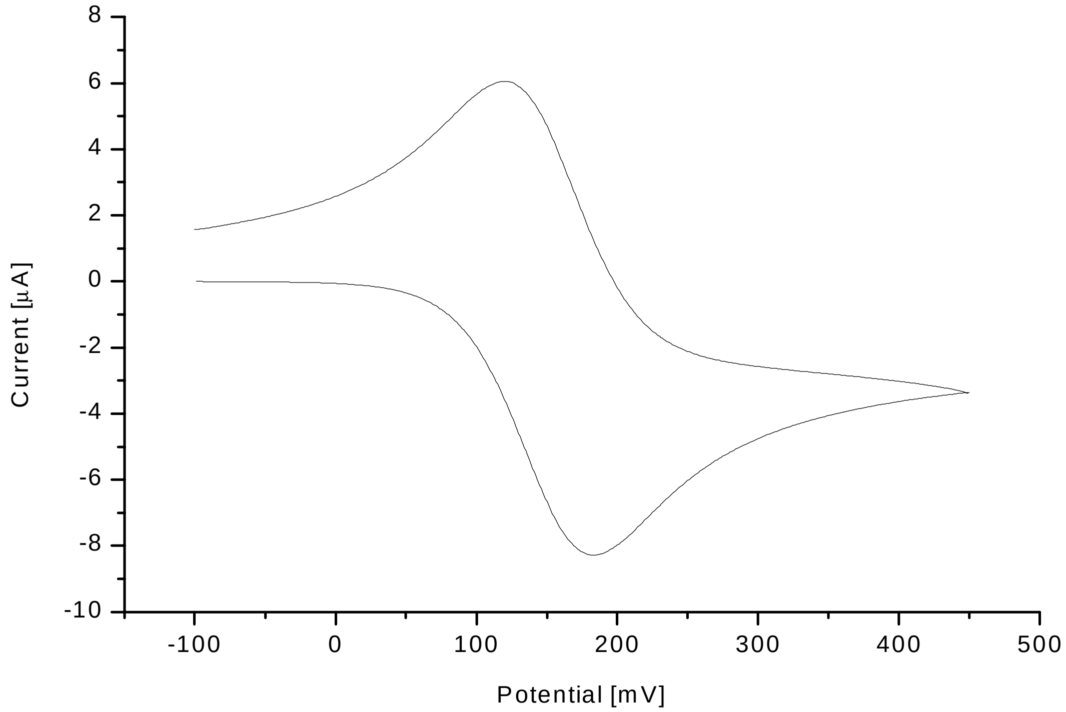


Figure 7. Cyclic voltammogram (v = 100 mV/s) of **4a** in $CHCl_2/CH_3CN$ (1:1) solution ($5{\cdot}10^{-4}$ M).

2.5. Conclusion

With regard to the possibility of the electrochemically controllable formation of host-guest complexes, a series of novel heterobimetallic crown ether-like polyoxadiphosphaplatinaferrocenophanes **4a-c** with different ring size and number of oxygen donor atoms was synthesized according to the high dilution method and characterized. Inclusion experiments with alkaline metal cations, and Mg^{2+}, or NH_4^+, respectively, were performed in solution applying ^1H and $^{31}P\{^1H\}$ NMR titrations and cyclic voltammetry. No evidence for the formation of host-guest complexes was found for the smallest macrocycle **4a**, whereas in the case of **4b** upon addition of Li^+ and $Mg^{2+}$and in the case of **4c** upon addition of Li^+, Na^+ and K^+ at least in the $^{31}P\{^1H\}$ NMR spectra a detectable shift was observed. However, the determination of the association constants by non-linear curve-fitting of the experimental data did not lead to a satisfactory result. Although the X-ray crystal structure of **4a** shows that the cavity is big enough to include guest ions of the mentioned type, the results of the inclusion experiments revealed that no or only weak complexation takes place. The steric demand of both transition metal complex fragments is limiting the flexibility of the macrocycles **4a-c** to an extent that they are not able to adopt an energetic favorable conformation in which the oxygen donors can provide an approximately tetrahedral or octahedral environment which is a necessary prerequisite for the complexation of the metal cations being under consideration.

3. Experimental Section

3.1. General Considerations

3.1.1. Working Procedures and Materials

All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents, triethylamine, di-, tri-, and tetraethylene glycol (Merck) were dried with appropriate reagents, distilled and stored under argon. PCl_3 was freshly distilled under argon prior to use. Sodium hydride and methanesulfonyl chloride were of commercial grade (Fluka) and used without further purification; the latter was stored under argon. Column chromatography was performed using activated silica gel, 0.063-0.200 mm (Merck). Column dimensions, eluent mixtures and special conditions are reported in the specific sections describing the synthesis of the compounds. Bis(hydroxymethyl)ferrocene[24], lithium diphenylphosphide[36] and bis(benzonitrile)-dichloroplatinum(II)[37] were synthesized according to literature methods. The tetraphenylborates of potassium, rubidium, and cesium were prepared by a metathetical reaction as described in the literature[38] and dried in vacuo at 70°C for 3d. Lithium tetrafluoroborate (Aldrich) and magnesium perchlorate (Merck) were purchased free of water. Sodium tetraphenylborate (Merck) and ammonium tetraphenylborate (Fluka) were dried in vacuo at 70°C for 3 d.

3.2.2. Characterization

Elemental analyses were carried out with an Elementar Vario EL analyzer. Cl analyses were carried out according to Schöniger[39] and determined as described by Dirscherl and Erne[40] according to Brunisholz and Michot[41]. FD mass spectra were taken on a Finnigan MAT 711 A instrument, modified by AMD. IR data were obtained with a Bruker IFS 48 FT-IR spectrometer. ^{1}H, $^{31}P\{^{1}H\}$, $^{13}C\{^{1}H\}$, and $^{195}Pt\{^{1}H\}$ NMR spectra were recorded at 25°C on a Bruker DRX 250 spectrometer operating at 250.13, 101.25, 62.90, and 53.55 MHz, respectively. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks and deuterated solvent peaks, respectively, which are reported relative to TMS. ^{31}P and ^{195}Pt chemical shifts were measured relative to external 85% H_3PO_4 and 37.5% $Na_2[PtCl_6] \times 6\ H_2O$, respectively. Cyclic voltammograms were recorded with a Bioanalytical Systems (BAS, West Lafayette, IN) CV-100 W electrochemical workstation. A Metrohm Pt electrode tip (Filderstadt, Germany) was used as working electrode, the counter electrode was a Pt wire of 1 mm diameter. A single-unit Haber-Luggin double reference-electrode[42] was used. The resulting potential values refer to Ag/Ag^+ (0.01 M in CH_3CN/0.1 M NBu_4PF_6). A gas-tight full-glass three-electrode cell was used, its assembly has been described elsewhere[43]. The cell was purged with argon before it was filled with the electrolyte. NBu_4PF_6 (0.1 M) was used as supporting electrolyte. Background curves were recorded before adding the substrate to the solution and substracted from the experimental data. The automatic iR-drop compensation facility was used for all experiments.

3.2. General Procedure for the Preparation of the Diols 1a-c

In a 2000 ml three necked flask sodium hydride (7.80 g, 325 mmol) was suspended in 400 ml of THF and the appropriate oligoethyleneglycol (325 mmol) in 50 ml of THF was slowly added at room temperature under vigorous stirring. 1,1'-Bis-(chloromethyl)ferrocene was freshly prepared from 1,1'-bis(hydroxymethyl)ferrocene (20.00 g, 81 mmol) with PCl_3 (10.00 g, 73 mmol) and pyridine (4 ml) in 400 ml of THF according to a literature procedure[25]. The resulting solution was transferred to a dropping funnel via a teflon pipe under a stream of argon and was added dropwise to the above-mentioned suspension. The mixture was heated to reflux for 12 h, then 500 ml of water was added and the resulting solution was neutralized with 32% hydrochloric acid until pH = 7 was achieved. The organic layer was separated and the aqueous phase was extracted with dichloromethane (5 × 100 ml). The combined organic phases were dried with Na_2SO_4 and the solvent was evaporated. The diols were separated from starting materials and the monosubstituted by-product by column chromatography (ethyl acetate/ethanol 5:1, diameter/length of column 7/20 cm). The last fractions were identified as the diols which were obtained as dark orange hygroscopic viscous oils.

3.2.1. 1,1'-Bis(7-hydroxy-2,5-dioxaheptyl)ferrocene (1a)

Yield: 12.7 g (37%), MS (FD, 30°C): *m/z* 421.9 [M^+]. Anal. Calc. for $C_{20}H_{30}FeO_6 \cdot H_2O$ (440.31): C, 54.56; H, 7.32. Found: C, 54.70; H, 7.35%. ^1H NMR ($CDCl_3$, 22°C): δ = 3.4-3.6 (m, 16H, OCH_2), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$). $^{13}C\{^1H\}$ NMR

($CDCl_3$, 22°C): δ = 61.3 (CH_2OH), 68.6 (2,2‘-Fc), 68.8, 68.9 (OCH_2CH_2O), 69.6 (3,3‘-Fc), 70.0 ($FcCH_2$), 72.4 (*C*H_2CH_2OH), 83.5 (1,1‘-Fc).

3.2.2. 1,1'-Bis(9-hydroxy-2,5,7-trioxanonyl)ferrocene (1b)

Yield: 22.8 g (55%), MS (FD, 30°C): *m/z* 510.5 [M^+]. Anal. Calc. for $C_{24}H_{38}FeO_8 \cdot H_2O$ (528.42): C, 54.55; H, 7.63. Found: C, 54.17; H, 7.96%. ^1H NMR ($CDCl_3$, 22°C): δ = 3.4-3.7 (m, 24H, OCH_2), 3.9-4.0 (m[44], 8H, Cp-H), 4.1 (s, 4H, $FcCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 61.0 (CH_2OH), 68.5 (2,2‘-Fc), 68.4, 68.5, 68.7, 69.8 (OCH_2CH_2O), 69.5 (3,3‘-Fc), 70.1 ($FcCH_2$), 72.2 (*C*H_2CH_2OH), 83.1 (1,1‘-Fc).

3.2.3. 1,1'-Bis(11-hydroxy-2,5,7,9-tetraoxaundecyl)ferrocene (1c)

Yield: 16.3 g (34%), MS (FD, 30°C): *m/z* 598.4 [M^+]. Anal. Calc. for $C_{28}H_{46}FeO_{10} \cdot H_2O$ (616.52): C, 54.55; H, 7.85. Found: C, 55.24; H, 8.00%. ^1H NMR ($CDCl_3$, 22°C): δ = 3.4-3.6 (m, 32H, OCH_2), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 61.1 (CH_2OH), 68.6 (2,2‘-Fc), 68.6, 68.8, 69.9, 70.0, 70.1 (OCH_2CH_2O), 69.6 (3,3‘-Fc), 70.1 ($FcCH_2$), 72.2 (*C*H_2CH_2OH), 83.3 (1,1‘-Fc).

3.3. General Procedure for the Preparation of the Dimesylates 2a-c

Methanesulfonyl chloride (4.12 g, 36 mmol) dissolved in 20 ml of dichloromethane was added dropwise to a solution of the appropriate diol **1a-c** (12 mmol) and triethylamine (4.61 g, 46 mmol) in 150 ml of dichloromethane at 0°C. The reaction mixture was allowed to warm to room temperature, stirred for 2 h, and hydrolyzed with 100 ml of a medium concentrated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 20 ml). The combined organic layers were dried with Na_2SO_4, filtered (P3), and the solvent was removed in vacuo to obtain the dimesylates **2a-c** as dark orange brown oils. Due to their instability, the dimesylates **2a-c** were immediately converted to the diphosphines **3a-c** as described below.

3.3.1. 1,1'-Bis(7-methylsulfonyloxy-2,5-dioxaheptyl)ferrocene (2a)

MS (FD, 30°C): *m/z* 578.3 [M^+]. IR (CH_2Cl_2): $\nu(OSO_2CH_3)$ = 1177, 1357 cm^{-1}. ^1H NMR ($CDCl_3$, 22°C): δ = 3.0 (s, 6H, OSO_2CH_3), 3.4-3.6 (m, 8H, OCH_2CH_2O), 3.7 (t, $^3J_{HH}$ = 4.3 Hz, 4H, $CH_2CH_2OSO_2CH_3$), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 4.3 (t, $^3J_{HH}$ = 4.3 Hz, 4H, $CH_2CH_2OSO_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 37.0 (OSO_2CH_3), 68.3 (2,2'-Fc), 68.6, 68.7 (OCH_2CH_2O), 68.8 ($CH_2CH_2OSO_2CH_3$), 69.2 ($CH_2CH_2OSO_2CH_3$), 69.6 (3,3'-Fc), 70.0 ($FcCH_2$), 83.2 (1,1'-Fc).

3.3.2. 1,1'-Bis(9-methylsulfonyloxy-2,5,7-trioxanonyl)ferrocene (2b)

MS (FD, 30°C): *m/z* 565.5 [M$^+$]. IR (CH_2Cl_2): ν(OSO_2CH_3) = 1177, 1355 cm^{-1}. ^1H NMR ($CDCl_3$, 22°C): δ = 3.0 (s, 6H, OSO_2CH_3), 3.4-3.6 (m, 8H, OCH_2CH_2O), 3.7 (t, $^3J_{HH}$ = 4.4 Hz, 4H, $CH_2CH_2OSO_2CH_3$), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 4.3 (t, $^3J_{HH}$ = 4.4 Hz, 4H, $CH_2CH_2OSO_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 37.4 (OSO_2CH_3), 68.8 (2,2‘-Fc), 68.7, 68.8, 68.9, 69.0 (OCH_2CH_2O), 69.2 ($CH_2CH_2OSO_2CH_3$), 69.8 (3,3‘-Fc), 70.0 ($FcCH_2$), 70.2 ($CH_2CH_2OSO_2CH_3$), 83.3 (1,1‘-Fc).

3.3.3. 1,1'-Bis(11-methylsulfonyloxy-2,5,7,9-tetraoxaundecyl)ferrocene (2c)

MS (FD, 30°C): *m/z* 754.3 [M$^+$]. IR (CH_2Cl_2): ν(OSO_2CH_3) = 1171, 1344 cm^{-1}. ^1H NMR (CD_2Cl_2, 22°C): δ = 3.0 (s, 6H, OSO_2CH_3), 3.5-3.6 (m, 8H, OCH_2CH_2O), 3.7 (t, $^3J_{HH}$ = 4.2 Hz, 4H, $CH_2CH_2OSO_2CH_3$), 4.1-4.2 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 4.3 (t, $^3J_{HH}$ = 4.2 Hz, 4H, $CH_2CH_2OSO_2CH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22°C): δ = 37.3 (OSO_2CH_3), 68.8 (2,2‘-Fc), 68.7, 68.9, 69.1, 69.5, 69.6 (OCH_2CH_2O), 69.8 (3,3‘-Fc), 70.2 ($FcCH_2$), 70.3 ($CH_2CH_2OSO_2CH_3$), 70.4 ($CH_2CH_2OSO_2CH_3$), 83.7 (1,1‘-Fc).

3.4. General Procedure for the Preparation of the Bisphosphines 3a-c

A freshly prepared solution of lithium diphenylphosphide (6.92 g, 36 mmol) in 50 ml of THF was added dropwise to a solution of the corresponding dimesylate **2a-c**, prepared as described above, in 150 ml of THF at 0°C. The solution was allowed to warm to room temperature, stirred for 1 h, and quenched with 50 ml of degassed water. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 20 ml). The solvent of the combined organic phases was removed under reduced pressure. The crude product was purified by column chromatography (degassed ethyl acetate/n-hexane 2:1, diameter/length of column 2.5/30 cm).

3.4.1. 1,1'-Bis(7-diphenylphosphinyl-2,5-dioxaheptyl)ferrocene (3a)

Yield: 5.9 g (65% based on **1a**). MS (FD, 30°C): *m/z* 758.3 [M^+]. Anal. Calc. for $C_{44}H_{48}FeO_4P_2$ (758.65): C, 69.66; H, 6.38. Found: C, 69.70; H, 6.54%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = -21.2 (s). ^1H NMR ($CDCl_3$, 22°C): δ = 2.3 (m, 4H, CH_2P), 3.4-3.5 (m, 12H, OCH_2), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.2-7.4 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 28.6 (d, $^1J_{PC}$ = 12.8 Hz, CH_2P), 68.4 (d, $^2J_{PC}$ = 25.6 Hz, $\mathit{C}H_2CH_2P$), 68.9 (2,2‘-Fc), 68.8, 69.2 (OCH_2CH_2O), 69.9 (3,3‘-Fc), 70.0 ($FcCH_2$), 83.5 (1,1‘-Fc), 128.3 (p-Ph), 128.4 (d, $^3J_{PC}$ = 7.1 Hz, m-Ph), 132.6 (d, $^2J_{PC}$ = 18.5 Hz, o-Ph) 138.1 (d, $^1J_{PC}$ = 12.1 Hz, ipso-Ph).

3.4.2. 1,1'-Bis(9-diphenylphosphinyl-2,5,7-trioxanonyl)ferrocene (3b)

Yield: 5.7 g (56% based on **1b**). MS (FD, 30°C): *m/z* 846.3 [M^+]. Anal. Calc. for $C_{48}H_{56}FeO_6P_2$ (846.76): C, 68.09; H, 6.67. Found: C, 68.14; H, 6.26%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = -21.1 (s). ^1H NMR ($CDCl_3$, 22°C): δ = 2.3 (m, 4H, CH_2P), 3.5-3.6 (m, 20H, OCH_2), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.2-7.4 (m, 20H, Ph). $^{13}C\{^1H\}$

NMR ($CDCl_3$, 22°C): δ = 28.7 (d, $^1J_{PC}$ = 13.2 Hz, CH_2P), 68.4 (d, $^2J_{PC}$ = 25.3 Hz, $\mathit{C}H_2CH_2P$), 68.9 (2,2‘-Fc), 68.9, 69.1, 70.4, 70.5 (OCH_2CH_2O), 69.9 (3,3‘-Fc), 70.0 ($FcCH_2$), 83.6 (1,1‘-Fc), 128.4 (d, $^3J_{PC}$ = 6.8 Hz, m-Ph), 128.5 (p-Ph), 132.6 (d, $^2J_{PC}$ = 18.9 Hz, o-Ph), 138.7 (d, $^1J_{PC}$ = 12.5 Hz, ipso-Ph).

3.4.3. 1,1'-Bis(11-diphenylphosphinyl-2,5,7,9-tetraoxaundecyl)ferrocene (3c)

Yield: 6.7 g (60% based on **1c**). MS (FD, 30°C): *m/z* 934.2 [M^+]. Anal. Calc. for $C_{52}H_{64}FeO_8P_2$ (934.88): C, 66.81; H, 6.90. Found: C, 66.84; H, 6.79. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = -21.1 (s). ^1H NMR ($CDCl_3$, 22°C): δ = 2.3 (m, 4H, CH_2P), 3.4-3.5 (m, 28H, OCH_2), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.2-7.4 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 28.5 (d, $^1J_{PC}$ = 12.8 Hz, CH_2P), 68.3 (d, $^2J_{PC}$ = 25.6 Hz, $\mathit{C}H_2CH_2P$), 68.7 (2,2‘-Fc), 68.8, 69.0, 70.3, 70.4 (OCH_2CH_2O), 69.7 (3,3‘-Fc), 69.9 ($FcCH_2$), 83.4 (1,1‘-Fc), 128.2 (d, $^3J_{PC}$ = 6.4 Hz, m-Ph), 128.4 (p-Ph), 132.4 (d, $^2J_{PC}$ = 19.2 Hz, o-Ph) 138.0 (d, $^1J_{PC}$ = 12.8 Hz, ipso-Ph).

3.5. General Procedure for the Preparation of the Polyoxadiphospha-platinaferrocenophanes 4a-c

Solutions of $(PhCN)_2PtCl_2$ (1.18 g, 2.5 mmol) and of the appropriate bisphosphine (2.5 mmol) in 200 ml of dichloromethane were simultanously added dropwise during 12 h at room temperture to 500 ml of stirred dichloromethane. After stirring for additional 3 h, the solvent was removed under reduced pressure and the residue was purified by column chromatography (degassed dichloromethane/ethyl acetate 2:1, diameter/length of column 2.5/30 cm). The polyoxadiphosphaplatinaferrocenophanes were obtained from the first fraction as bright yellow powders.

3.5.1. 9,9-Dichloro-2,5,13,16-tetraoxa-8,8,10,10-tetraphenyl-8,10-diphospha-9-platina-[17] ferrocenophane (4a)

Yield: 1.43 g (56%). Mp. 196°C (dec.). MS (FD, 30°C): *m/z* 1024.0 [M^+]. Anal. Calc. for $C_{44}H_{48}Cl_2FeO_4P_2Pt$ (1024.64): C, 51.58; H, 4.72; Cl, 6.92. Found: C, 51.33; H, 4.72; Cl, 7.15%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 4.3 (sd, $^1J_{PtP}$ = 3632 Hz). ^1H NMR ($CDCl_3$, 22°C): δ = 2.4 (m, 4H, CH_2P), 3.6 (m, 8H, OCH_2CH_2O), 3.9 (m, 4H, OCH_2CH_2P), 4.1-4.2 (m[44], 8H, Cp-H), 4.3 (s, 4H, $FcCH_2$), 7.1-7.5 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 27.1 (m[45], N = 40.9 Hz, CH_2P), 67.2 (CH_2CH_2P), 68.1 (2,2‘-Fc), 68.9, 69.5 (OCH_2CH_2O), 69.4 (3,3‘-Fc), 70.4 ($FcCH_2$), 85.0 (1,1‘-Fc), 128.1 (m[45], N = 11.0 Hz, m-Ph), 130.6 (p-Ph), 131.4 (m[45], N = 63.7 Hz, ipso-Ph), 133.1 (m[45], N = 10.0 Hz, o-Ph). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = - 4400 (t, $^1J_{PtP}$ = 3632 Hz).

3.5.2. 12,12-Dichloro-2,5,8,16,19,22-hexaoxa-11,11,13,13-tetraphenyl-11,13-diphospha-12-platina-[23]ferrocenophane (4b)

Yield: 0.53 g (19%). Mp. 95°C. MS (FD, 30°C): *m/z* 1112.2 [M^+]. Anal. Calc. for $C_{48}H_{56}Cl_2FeO_6P_2Pt$ (1112.76): C, 51.81; H, 5.07; Cl, 6.37. Found: C, 51.92; H, 5.24; Cl, 6.40%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 5.4 (sd, $^1J_{PtP}$ = 3632 Hz). ^1H NMR ($CDCl_3$, 22°C): δ = 2.5 (m, 4H, CH_2P), 3.4-3.6 (m, 16H, OCH_2CH_2O), 3.8 (m, 4H, OCH_2CH_2P), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.1-7.5 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 28.9 (m[45], N = 39.1 Hz, CH_2P), 67.0 ($\mathit{C}H_2CH_2P$), 68.5 (2,2'-Fc), 69.0, 69.4, 70.3, 70.6 (OCH_2CH_2O), 69.5 (3,3'-Fc), 70.1 ($FcCH_2$), 84.4 (1,1'-Fc), 128.1 (m[45], N = 11.0 Hz, m-Ph), 129.9 (m[45], N = 63.0 Hz, ipso-Ph), 130.7 (p-Ph), 133.2 (m[45], N = 10.3 Hz, o-Ph). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = - 4399 (t, $^1J_{PtP}$ = 3632 Hz).

3.5.3. 15,15-Dichloro-2,5,8,11,19,22,25,28-octaoxa-14,14,16,16-tetraphenyl-14,16-diphospha-15-platina-[29]ferrocenophane (4c)

Yield: 0.54 g (18%). Mp. 135°C. MS (FD, 30°C): *m/z* 1199.9 [M^+]. Anal. Calc. for $C_{52}H_{64}Cl_2FeO_8P_2Pt \cdot 2\ H_2O$ (1236.88): C, 50.50; H, 5.54; Cl, 5.73. Found: C, 50.58; H, 5.37; Cl, 5.46%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 5.2 (sd, $^1J_{PtP}$ = 3628 Hz). ^1H NMR ($CDCl_3$, 22°C): δ = 2.5 (m, 4H, CH_2P), 3.4-3.6 (m, 24H, OCH_2CH_2O), 3.8 (m, 4H, $OC\mathit{H_2}CH_2P$), 4.0-4.1 (m[44], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.1-7.5 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = 29.3 (m[45], N = 42.0 Hz, CH_2P), 67.1 ($\mathit{C}H_2CH_2P$), 68.8 (2,2'-Fc), 69.2, 69.4, 70.1, 70.7 (OCH_2CH_2O), 69.7 (3,3'-Fc), 70.4 ($FcCH_2$), 84.1 (1,1'-Fc), 128.3 (m[45], N = 11.0 Hz, m-Ph), 129.9 (m[45], N = 63.0 Hz, ipso-Ph), 130.9 (p-Ph), 133.4 (m[45], N = 10.7 Hz, o-Ph). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$, 22°C): δ = - 4400 (t, $^1J_{PtP}$ = 3628 Hz).

3.6. NMR Titration Procedure

In preliminary experiments the absence of influences on the chemical shift resulting from self-association processes was verified by dilution of 0.01 M solutions of **4a-c** in $CDCl_3/CD_3CN$ (v/v 1:1) to 0.0005 M. No change of the chemical shifts of any signal in the ^1H and $^{31}P\{^1H\}$ NMR spectra was observed.

The titration experiments were performed in standard NMR tubes (diameter/length 5/160 mm) containing 500 µl of solutions of **4a-c** in $CDCl_3/CD_3CN$ (v/v 1:1). The starting concentrations of **4a-c** were in the range between 0.01 M and 0.001 M. Stock solutions of the guest salts in CD_3CN (0.05-0.005 M) were added stepwise in 10 µl portions with a microliter syringe until a ratio of cation : host ≥ 1 was achieved. After that the portion size was increased stepwise up to 50 µl. The same amount of $CDCl_3$ was added after each step to maintain the 1:1 proportion of $CDCl_3/CD_3CN$. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded after each addition.

3.7. Calculational Methods

The program EQNMR[31] is used to evaluate equilibrium constants and chemical shifts of complexes in systems where all the species are in rapid exchange on the NMR time-scale and where the NMR chemical shift of at least one suitable nucleus varies on complex formation. Equation (1) shows the general type of reaction beeing under consideration.

$$m\,G + n\,H = G_mH_n \qquad (1)$$

G is the corresponding guest cation and H is the employed host compound which contains the nucleus whose chemical shift is monitored by NMR spectroscopy. The observed chemical shift is the weighted average of the chemical shifts δ_{mn} of all H-containing species present and is defined by equation (2).

$$\delta_{\text{calc}} = \sum_{m=0}^{m=i}\sum_{n=1}^{n=j} \frac{\delta_{mn} \cdot \beta_{mn} \cdot n \cdot [G]^m \cdot [H]^n}{[H]_{total}} \tag{2}$$

The problem consists in a determination of the optimum values of the various δ_{mn} and β_{mn} which best fit the experimental chemical shift data. β_{mn} represents the stability constants of the complexes formed.

The program EQNMR is suitable to calculate the concentration of all species present in solution on the basis of an initial estimate of the stability constants. The program is quite insensitive to relatively “poor” initial guesses of the parameters to be fitted, if the experimental data are of good quality and the selected complexation model is correct[46]. By using equation (2) the program subsequently calculates the chemical shifts δ_{calc}, in consideration of the complexed and uncomplexed species contributing to the overall chemical shift of the nucleus being monitored. This procedure is followed by non-linear least-squares subroutines which are responsible for the refinement of the various parameters. The obtained data were employed for the calculation of the refined stability constants and the whole procedure is repeated until a minimum of the R-factor defined by equation (3) is achieved. The R-factor enables a quantitative comparison of fits.

$$R = 100 \cdot \left(\frac{\sum W_i \cdot (\delta_{obs} - \delta_{calc})^2}{\sum W_i \cdot \delta_{obs}^2} \right)^{\frac{1}{2}} \tag{3}$$

3.8. Crystallographic Analysis

Yellow single crystals of **4a** suitable for X-ray structural determination were obtained by slow diffusion of *n*-heptane into a solution of **4a** in dichloromethane. A thoroughly selected crystal was transferred to a glass capillary and measured on a Stoe IPDS diffractometer, using graphite-monochromated Mo-K_α radiation. No absorption correction was applied. Cell parameters and refinement details are summarized in Table 1. The data fits best with the triclinic space group $P\bar{1}$ with eight independant molecules per unit cell (Z = 16). The structure was solved by direct methods with SHELXS[47] and refined by least-squares methods based on F^2 using SHELXTL 97[48]. The metal, chlorine and phosphorus atoms were refined anisotropically. All hydrogen atoms were located in calculated positions. Atomic coordinates and equivalent isotropic displacement coefficients of **4a** are summarized in Table 2.

Crystallographic data for the structure of **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 158649. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: int. code + 44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for **4a**

Empirical formula	$C_{44}H_{48}Cl_2FeO_4P_2Pt$
Formula weight	1024.64
Temperature (K)	298(2)
Wavelength Mo-K_α (Å)	0.71073

Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 21.990(4) Å	α = 101.72(3)°
	b = 29.865(6) Å	β = 108.69(3)°
	c = 29.877(6) Å	γ = 108.66(3)°
V (Å^3)	16557(6)	
Z	16	
$D_{\mathrm{calc.}}$ (g·cm^{-3})	1.644	
Crystal size (mm^3)	0.3 x 0.3 x 0.2	
Absorption coefficient (mm^{-1})	3.97	
F (000)	65552	
θ Range for data collection (°)	2.17-25.92	
Data reduction/correction	Background, Polarisation, Lorentz	
Reflections collected	218042	
Independent reflections	58730 (R_{int} = 0.1122)	
Completeness to θ = 25.92°	91.1 %	
Index ranges	$-26 \leq h \leq 26$, $-33 \leq k \leq 33$, $-36 \leq l \leq 36$	
Refinement method	Full-matrix-block least-squares on F^2	
Data / restraints / parameters	58730 / 14 / 1963	
Goodness-of-fit	1.579	
Final R-indices [$I>2\sigma(I)$]	R_1 = 0.0800; wR_2 = 0.2064	
R indices (all data)	R_1 = 0.1847, wR_2 = 0.2439	
Max. shift /esd	< 0,0005	
Largest diff. peak and hole (e$^-$·Å^{-3})	2.556 and -3.269	

$$R_1 = \frac{\sum_{hkl} \left\| F_O \right| - \left| F_C \right\|}{\sum_{hkl} \left| F_O \right|}, \quad wR_2 = \sqrt{\frac{\sum_{hkl} w\left(F_O^2 - F_C^2\right)^2}{\sum_{hkl} w\left(F_O^2\right)^2}}, \quad \text{Goodness of fit} = \sqrt{\frac{\sum_{hkl} w\left(F_O^2 - F_C^2\right)^2}{N_{obs} - N_{parameter}}}$$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4a**.

	x	y	z	U(eq)		x	y	z	U(eq)
Pt(1)	3364(1)	8447(1)	2565(1)	36(1)	C(23)	4088(15)	10551(11)	2845(10)	92(7)
Cl(1)	2836(2)	8852(2)	2977(2)	63(1)	C(24)	3492(15)	10409(12)	2493(10)	96(8)
Cl(2)	2306(2)	7714(2)	2218(2)	58(1)	C(25)	3058(18)	9919(13)	2224(12)	111(9)
Fe(1)	6786(2)	9422(2)	5778(1)	101(2)	C(26)	3284(10)	9543(8)	2329(7)	60(5)
P(1)	4249(2)	9197(2)	2792(2)	40(1)	C(27)	4756(9)	9241(7)	2414(6)	46(4)
P(2)	3847(2)	7950(2)	2281(1)	36(1)	C(28)	5476(10)	9454(7)	2589(7)	55(4)
O(1)	4245(8)	7684(6)	3365(5)	72(4)	C(29)	5830(10)	9497(7)	2290(7)	54(4)
O(2)	5156(9)	8536(7)	4240(6)	87(5)	C(30)	5429(11)	9332(8)	1765(8)	67(5)
O(3)	5159(8)	9754(6)	4324(6)	75(4)	C(31)	4697(12)	9128(9)	1569(9)	75(6)
O(4)	6496(9)	10275(7)	5148(6)	84(4)	C(32)	4366(10)	9087(7)	1894(6)	53(4)
C(1)	4903(11)	9422(8)	3426(7)	63(5)	C(33)	4800(8)	8214(6)	2506(5)	38(3)
C(2)	4610(11)	9518(8)	3830(7)	63(5)	C(34)	5230(8)	8386(6)	3030(6)	44(4)
C(3)	5565(13)	10257(10)	4452(9)	79(6)	C(35)	5946(10)	8574(8)	3196(7)	58(5)
C(4)	6029(12)	10504(10)	4990(8)	76(6)	C(36)	6257(11)	8591(8)	2863(7)	60(5)
C(5)	6952(16)	10503(12)	5657(10)	98(8)	C(37)	5869(11)	8424(8)	2363(7)	63(5)
C(6)	7261(18)	10185(13)	5805(12)	110(9)	C(38)	5144(9)	8243(7)	2178(6)	48(4)
C(7)	7495(16)	9824(12)	5524(12)	101(8)	C(39)	3494(8)	7672(6)	1601(5)	37(3)
C(8)	7778(19)	9579(15)	5819(13)	125(11)	C(40)	3666(9)	7285(6)	1404(6)	45(4)
C(9)	7802(19)	9746(14)	6277(13)	119(10)	C(41)	3358(10)	7062(8)	878(7)	57(5)
C(10)	7490(20)	10091(18)	6252(17)	155(15)	C(42)	2931(10)	7205(8)	568(7)	58(5)
C(11)	3643(9)	7375(6)	2458(6)	44(4)	C(43)	2758(10)	7583(7)	750(7)	58(5)
C(12)	3578(10)	7413(8)	2955(7)	59(5)	C(44)	3046(8)	7811(7)	1283(6)	44(4)
C(13)	4206(11)	7753(8)	3830(7)	63(5)	Pt(2)	6511(1)	6280(1)	2265(1)	48(1)
C(14)	4869(13)	8038(9)	4230(9)	78(6)	Cl(3)	7025(4)	5835(3)	1887(3)	95(2)
C(15)	5874(15)	8854(11)	4611(10)	92(7)	Cl(4)	7553(2)	7007(2)	2528(2)	75(2)
C(16)	5968(13)	8920(10)	5152(9)	77(6)	P(3)	5626(2)	5540(2)	2097(2)	46(1)
C(17)	6202(12)	8659(10)	5455(9)	76(6)	P(4)	6028(2)	6789(2)	2510(2)	45(1)
C(18)	6176(18)	8826(14)	5917(13)	119(10)	O(5)	4693(14)	5059(10)	575(9)	133(8)
C(19)	5887(17)	9202(13)	5902(12)	111(9)	O(6)	3419(11)	4762(8)	-188(7)	103(6)
C(20)	5742(12)	9260(9)	5412(8)	76(6)	O(7)	5563(10)	7162(7)	1444(7)	96(5)
C(21)	3945(9)	9679(7)	2704(6)	50(4)	O(8)	5206(14)	6282(10)	626(9)	138(8)
C(22)	4356(11)	10181(8)	2959(8)	63(5)	Fe(2)	3119(2)	5734(1)	-634(2)	84(1)

C(45)	4933(11)	5266(8)	1452(7)	64(5)	C(85)	6507(12)	7736(9)	3908(8)	73(6)
C(46)	5185(14)	5213(11)	1065(9)	87(7)	C(86)	6977(12)	7605(9)	4206(9)	73(6)
C(47)	4350(20)	4601(15)	378(13)	131(12)	C(87)	7174(13)	7232(10)	4021(9)	81(6)
C(48)	3770(13)	4453(10)	-180(9)	84(7)	C(88)	6875(11)	6983(8)	3517(7)	64(5)
C(49)	2801(15)	4636(11)	-632(10)	97(8)	Pt(3)	11647(1)	1199(1)	7788(1)	38(1)
C(50)	2583(14)	5069(11)	-597(10)	89(7)	Cl(5)	12698(2)	1525(2)	8525(2)	63(1)
C(51)	2206(15)	5128(11)	-1094(11)	95(8)	Cl(6)	12169(2)	795(2)	7367(2)	64(1)
C(52)	2080(15)	5539(11)	-898(10)	91(7)	P(5)	11162(2)	1468(2)	8284(1)	36(1)
C(53)	2354(16)	5738(13)	-414(12)	107(9)	P(6)	10764(2)	996(2)	7038(1)	36(1)
C(54)	2671(15)	5448(11)	-189(11)	95(8)	Fe(3)	8141(2)	-1924(1)	6768(1)	79(1)
C(55)	6245(10)	7345(8)	2310(7)	59(5)	O(9)	10787(9)	402(7)	8539(6)	91(5)
C(56)	6261(12)	7277(10)	1788(8)	77(6)	O(10)	9915(10)	-470(8)	7667(7)	100(5)
C(57)	5535(18)	7158(13)	960(12)	112(10)	O(11)	9853(7)	-530(5)	6437(5)	64(3)
C(58)	5600(20)	6805(17)	703(16)	149(14)	O(12)	8487(7)	-1310(6)	5939(5)	67(4)
C(59)	4458(18)	6122(14)	375(12)	116(10)	C(89)	11368(9)	1275(7)	8844(6)	50(4)
C(60)	4152(15)	6080(11)	-155(10)	92(7)	C(90)	11422(11)	797(8)	8820(7)	62(5)
C(61)	3935(16)	6444(12)	-331(11)	103(9)	C(91)	10848(14)	-68(10)	8466(10)	86(7)
C(62)	3641(19)	6286(14)	-825(13)	121(10)	C(92)	10143(14)	-498(11)	8150(9)	86(7)
C(63)	3751(17)	5846(13)	-996(12)	108(9)	C(93)	9214(13)	-795(10)	7333(9)	84(7)
C(64)	4049(14)	5721(11)	-596(9)	87(7)	C(94)	9076(9)	-1332(7)	7266(6)	47(4)
C(65)	5175(9)	5537(7)	2513(6)	52(4)	C(95)	8764(13)	-1669(10)	7504(9)	78(6)
C(66)	4459(10)	5317(8)	2356(7)	58(5)	C(96)	8741(13)	-2119(10)	7329(9)	82(7)
C(67)	4140(11)	5324(8)	2682(7)	64(5)	C(97)	8967(16)	-2107(13)	6945(11)	103(9)
C(68)	4576(12)	5519(9)	3197(8)	75(6)	C(98)	9159(12)	-1635(9)	6917(8)	73(6)
C(69)	5301(12)	5736(9)	3366(9)	74(6)	C(99)	10117(10)	366(7)	6775(7)	58(5)
C(70)	5604(11)	5747(8)	3030(7)	59(5)	C(100)	10401(11)	-44(8)	6677(8)	63(5)
C(71)	5931(9)	5057(7)	2199(7)	53(4)	C(101)	9409(11)	-644(8)	5898(7)	63(5)
C(72)	5487(13)	4547(9)	1944(9)	77(6)	C(102)	8940(9)	-1198(7)	5682(7)	53(4)
C(73)	5716(14)	4194(11)	2058(9)	84(7)	C(103)	7975(15)	-1796(11)	5722(10)	94(8)
C(74)	6378(16)	4330(12)	2440(11)	102(8)	C(104)	7630(14)	-1933(10)	6063(9)	85(7)
C(75)	6785(16)	4807(12)	2684(11)	99(8)	C(105)	7551(15)	-1587(12)	6394(10)	98(8)
C(76)	6581(11)	5206(9)	2596(8)	69(5)	C(106)	7192(19)	-1892(15)	6666(13)	125(11)
C(77)	5084(9)	6543(7)	2285(6)	47(4)	C(107)	7114(18)	-2371(14)	6458(12)	111(10)
C(78)	4672(10)	6376(7)	1769(7)	54(4)	C(108)	7362(17)	-2438(13)	6082(12)	111(9)
C(79)	3953(12)	6190(9)	1570(9)	75(6)	C(109)	10197(8)	1249(6)	8023(5)	37(3)
C(80)	3604(12)	6156(9)	1888(8)	72(6)	C(110)	9791(9)	740(7)	7844(6)	48(4)
C(81)	3974(12)	6300(9)	2372(8)	73(6)	C(111)	9072(11)	557(8)	7642(7)	62(5)
C(82)	4706(11)	6493(8)	2583(8)	62(5)	C(112)	8745(12)	876(9)	7636(8)	68(5)
C(83)	6370(9)	7081(7)	3179(6)	49(4)	C(113)	9137(9)	1389(7)	7802(6)	54(4)
C(84)	6169(11)	7459(8)	3371(7)	62(5)	C(114)	9856(9)	1564(7)	7990(6)	48(4)

C(115)	11509(8)	2148(6)	8578(6)	43(4)
C(116)	11976(8)	2468(6)	8448(6)	44(4)
C(117)	12237(11)	2985(8)	8692(7)	64(5)
C(118)	12089(11)	3176(9)	9070(7)	65(5)
C(119)	11632(12)	2863(9)	9213(8)	71(6)
C(120)	11334(9)	2343(7)	8962(6)	46(4)
C(121)	11103(8)	1119(6)	6563(6)	42(4)
C(122)	11743(10)	1509(7)	6717(7)	56(4)
C(123)	11994(12)	1632(9)	6361(8)	73(6)
C(124)	11558(12)	1369(9)	5838(9)	75(6)
C(125)	10929(13)	1010(9)	5703(9)	77(6)
C(126)	10682(11)	872(8)	6064(7)	60(5)
C(127)	10275(8)	1384(6)	6998(5)	36(3)
C(128)	9543(9)	1194(7)	6785(6)	52(4)
C(129)	9224(12)	1535(9)	6754(8)	68(5)
C(130)	9638(12)	2055(9)	6944(8)	72(6)
C(131)	10343(11)	2228(8)	7141(7)	60(5)
C(132)	10664(10)	1902(7)	7180(6)	51(4)
Pt(4)	-1515(1)	4013(1)	7437(1)	54(1)
Cl(7)	-2577(3)	3707(3)	6709(3)	90(2)
Cl(8)	-2021(4)	4420(3)	7860(3)	106(2)
P(7)	-1050(3)	3739(2)	6923(2)	57(1)
P(8)	-626(2)	4199(2)	8175(2)	58(1)
O(13)	-674(3)	4781(1)	6559(8)	133(8)
O(14)	-125(2)	5634(8)	7309(17)	270(20)
O(15)	299(5)	5715(5)	8623(8)	150(9)
O(16)	1558(2)	6519(7)	8932(6)	99(5)
C(133)	-1297(5)	3901(7)	6354(7)	65(5)
C(134)	-1329(6)	4380(6)	6352(12)	123(11)
C(135)	-735(4)	5226(4)	6547(17)	169(17)
C(136)	-70(20)	5662(18)	6865(15)	250(30)
C(137)	593(5)	5918(2)	7579(17)	190(20)
C(138)	844(16)	6446(6)	7624(11)	99(8)
C(139)	1120(20)	6668(16)	7293(14)	129(12)
C(140)	1340(30)	7160(20)	7434(19)	171(17)
C(141)	1230(30)	7310(20)	7837(18)	163(16)
C(142)	914(15)	6881(12)	7956(11)	98(8)
C(143)	69(3)	4840(6)	8450(7)	62(5)
C(144)	-197(9)	5229(5)	8480(10)	89(7)
C(145)	651(5)	6019(9)	9123(7)	119(10)
C(146)	1232(12)	6500(8)	9259(8)	87(7)
C(147)	2161(12)	6950(8)	9078(9)	119(10)
C(148)	2337(18)	6528(14)	8305(12)	117(10)
C(149)	2680(20)	6784(15)	8010(14)	129(11)
C(150)	2930(20)	7284(15)	8189(13)	126(11)
C(151)	2792(16)	7402(13)	8618(11)	106(9)
C(152)	2425(14)	6968(11)	8690(9)	91(7)
C(153)	-70(10)	3985(8)	7188(7)	59(5)
C(154)	274(10)	3673(8)	7214(7)	57(5)
C(155)	990(12)	3867(9)	7386(8)	74(6)
C(156)	1384(14)	4391(10)	7544(9)	81(6)
C(157)	1024(12)	4697(9)	7512(8)	72(6)
C(158)	308(11)	4487(8)	7330(7)	63(5)
C(159)	-1371(9)	3078(7)	6674(6)	50(4)
C(160)	-1861(9)	2746(7)	6774(7)	53(4)
C(161)	-2151(12)	2242(9)	6539(8)	68(5)
C(162)	-1982(12)	2041(10)	6181(8)	75(6)
C(163)	-1508(14)	2332(10)	6040(9)	85(7)
C(164)	-1197(11)	2854(9)	6272(8)	68(5)
C(165)	-161(9)	3796(7)	8186(6)	48(4)
C(166)	-582(10)	3273(7)	8008(6)	52(4)
C(167)	-270(12)	2927(9)	7996(8)	68(5)
C(168)	442(12)	3116(9)	8227(8)	75(6)
C(169)	875(12)	3631(9)	8423(8)	71(6)
C(170)	557(11)	3961(8)	8394(7)	63(5)
C(171)	-914(9)	4111(7)	8675(6)	47(4)
C(172)	-1561(13)	3745(9)	8551(9)	76(6)
C(173)	-1793(16)	3669(11)	8927(10)	95(8)
C(174)	-1343(14)	3919(10)	9424(10)	86(7)
C(175)	-678(13)	4274(10)	9551(9)	79(6)
C(176)	-468(11)	4380(8)	9184(7)	63(5)
Fe(4)	1904(2)	6970(2)	8002(1)	99(1)
Pt(5)	-1600(1)	6380(1)	4757(1)	59(1)
P(9)	-1125(2)	6085(2)	4258(2)	61(1)
P(10)	-694(2)	6629(2)	5513(2)	58(1)
Cl(9)	-2662(3)	6024(3)	4027(2)	86(2)
Cl(10)	-2123(4)	6799(3)	5163(3)	102(2)
Fe(5)	1759(2)	9590(2)	5572(1)	91(1)
O(17)	-768(8)	7145(6)	3942(5)	76(4)
O(18)	162(11)	8035(8)	4745(8)	112(6)

O(19)	186(8)	8158(6)	5978(6)	81(4)
O(20)	1509(11)	9001(8)	6447(7)	104(6)
C(177)	-1364(11)	6250(8)	3678(7)	62(5)
C(178)	-1431(13)	6742(9)	3696(9)	80(6)
C(179)	-792(13)	7619(10)	3982(9)	83(7)
C(180)	-84(15)	8036(11)	4226(10)	95(8)
C(181)	874(14)	8423(10)	5038(10)	85(7)
C(182)	922(13)	8936(10)	5057(9)	78(6)
C(183)	1167(14)	9238(10)	4815(10)	88(7)
C(184)	1126(15)	9726(11)	4965(10)	94(8)
C(185)	866(17)	9691(14)	5344(12)	115(10)
C(186)	707(15)	9208(11)	5390(10)	95(8)
C(187)	-50(8)	7273(6)	5723(6)	42(4)
C(188)	-344(13)	7660(9)	5764(9)	77(6)
C(189)	605(10)	8282(8)	6466(7)	61(5)
C(190)	1040(13)	8863(10)	6694(9)	81(6)
C(191)	1958(16)	9512(11)	6646(11)	99(8)
C(192)	2256(15)	9671(12)	6310(11)	97(8)
C(193)	2500(16)	9396(13)	6010(11)	102(8)
C(194)	2762(18)	9688(14)	5791(13)	117(10)
C(195)	2760(20)	10128(19)	5877(16)	154(15)
C(196)	2420(20)	10100(17)	6233(15)	146(14)
C(197)	-1465(10)	5399(7)	3991(7)	55(4)
C(198)	-1923(11)	5092(9)	4156(8)	68(5)
C(199)	-2206(11)	4568(8)	3912(7)	65(5)
C(200)	-2079(14)	4355(11)	3516(9)	85(7)
C(201)	-1635(13)	4663(10)	3388(9)	80(6)
C(202)	-1337(13)	5173(9)	3611(8)	77(6)
C(203)	-168(9)	6327(7)	4508(6)	52(4)
C(204)	218(10)	6824(8)	4648(7)	61(5)
C(205)	967(11)	7011(8)	4844(7)	62(5)
C(206)	1278(13)	6679(9)	4876(8)	74(6)
C(207)	900(14)	6184(10)	4711(9)	86(7)
C(208)	157(11)	5987(9)	4530(7)	66(5)
C(209)	-203(11)	6235(8)	5557(7)	61(5)
C(210)	534(11)	6433(9)	5758(7)	64(5)
C(211)	869(12)	6111(8)	5795(8)	67(5)
C(212)	495(12)	5606(9)	5651(8)	74(6)
C(213)	-227(14)	5422(11)	5468(9)	87(7)
C(214)	-571(10)	5728(7)	5407(7)	55(4)
C(215)	-983(10)	6562(7)	6001(7)	54(4)
C(216)	-1631(14)	6182(10)	5905(10)	85(7)
C(217)	-1847(15)	6093(11)	6275(10)	89(7)
C(218)	-1401(16)	6395(12)	6758(11)	100(8)
C(219)	-758(14)	6753(10)	6889(10)	86(7)
C(220)	-524(11)	6832(8)	6507(7)	61(5)
Pt(6)	3383(1)	6049(1)	5106(1)	63(1)
Cl(11)	2861(4)	6480(3)	5494(3)	98(2)
P(12)	4258(3)	6795(2)	5278(2)	58(1)
Cl(12)	2335(3)	5308(3)	4808(3)	96(2)
P(11)	3861(3)	5545(2)	4851(2)	60(1)
Fe(6)	6894(1)	6946(1)	8114(1)	69(1)
O(24)	6549(8)	7815(6)	7529(6)	76(4)
O(23)	5172(9)	7381(6)	6801(6)	81(4)
O(21)	4201(11)	5271(8)	5901(7)	99(5)
O(22)	4966(14)	6143(10)	6750(9)	135(8)
C(234)	6143(14)	8098(11)	7479(9)	87(7)
C(233)	5611(11)	7871(8)	6905(7)	66(5)
C(230)	5909(12)	6868(9)	7927(8)	76(6)
C(232)	4653(11)	7172(9)	6305(8)	68(5)
C(226)	5901(10)	6494(8)	7565(7)	56(5)
C(227)	6206(15)	6236(11)	7857(10)	94(8)
C(228)	6327(14)	6447(11)	8375(10)	90(7)
C(239)	7939(18)	7239(14)	8479(13)	115(10)
C(236)	7426(12)	7629(9)	8090(8)	73(6)
C(237)	7436(13)	7279(10)	7729(10)	84(7)
C(235)	7131(13)	8003(10)	8020(9)	83(7)
C(264)	4344(12)	7774(9)	5384(8)	71(6)
C(259)	3925(11)	7269(8)	5147(7)	62(5)
C(260)	3261(13)	7096(10)	4730(9)	77(6)
C(261)	3049(15)	7461(11)	4619(10)	89(7)
C(262)	3445(15)	7947(11)	4836(10)	94(8)
C(253)	4726(10)	6814(7)	4871(7)	53(4)
C(254)	4338(11)	6618(8)	4361(7)	59(5)
C(231)	4918(9)	7085(7)	5923(6)	49(4)
C(238)	7788(17)	7012(13)	7991(12)	110(9)
C(257)	5740(13)	7047(9)	4688(9)	77(6)
C(256)	5358(13)	6849(10)	4205(9)	80(6)
C(255)	4653(12)	6632(9)	4031(9)	74(6)
C(244)	2905(13)	4704(10)	3148(9)	77(6)

C(245)	3420(12)	4591(9)	3487(9)	77(6)
C(246)	3675(12)	4857(9)	3987(8)	73(6)
C(242)	3053(12)	5366(9)	3857(8)	70(6)
C(241)	3522(11)	5235(8)	4172(8)	64(5)
C(221)	3643(12)	4988(9)	5049(8)	72(6)
C(247)	4833(11)	5819(8)	5080(7)	60(5)
C(225)	5671(14)	6430(11)	7025(9)	88(7)
C(248)	5178(10)	5844(8)	4771(7)	59(5)
C(249)	5909(12)	6053(9)	4952(9)	77(6)
C(250)	6279(16)	6225(11)	5462(10)	93(8)
C(251)	5950(13)	6204(10)	5776(9)	80(6)
C(252)	5235(11)	5990(9)	5579(8)	67(5)
C(258)	5462(12)	7031(9)	5056(8)	70(6)
C(243)	2755(11)	5095(8)	3342(8)	65(5)
C(263)	4114(17)	8103(13)	5234(11)	104(9)
C(240)	7766(15)	7582(12)	8560(11)	97(8)
C(229)	6191(16)	6844(13)	8413(12)	104(9)
C(222)	3609(14)	5010(11)	5533(9)	87(7)
C(223)	4117(17)	5339(13)	6375(11)	108(9)
C(224)	4840(20)	5609(17)	6775(16)	152(15)
Pt(7)	11553(1)	8571(1)	10081(1)	55(1)
Cl(13)	12066(3)	8195(3)	9633(3)	89(2)
Cl(14)	12593(3)	8828(3)	10808(2)	88(2)
P(13)	10674(2)	8412(2)	9342(2)	49(1)
P(14)	11067(3)	8810(2)	10587(2)	55(1)
Fe(7)	8124(2)	5663(1)	9412(1)	77(1)
O(25)	9771(13)	6896(9)	8816(9)	123(7)
O(26)	8412(11)	6170(8)	8482(8)	111(6)
O(27)	10638(12)	7748(9)	10946(8)	113(6)
O(28)	10177(13)	6923(9)	10026(9)	129(7)
C(265)	9997(11)	7785(8)	9067(8)	65(5)
C(266)	10251(14)	7382(10)	8993(10)	87(7)
C(267)	9353(16)	6762(11)	8402(11)	97(8)
C(268)	8799(14)	6159(10)	8182(10)	89(7)
C(269)	7796(15)	5711(11)	8329(10)	93(8)
C(270)	7576(16)	5680(12)	8720(11)	97(8)
C(271)	7194(15)	5236(12)	8795(11)	99(8)
C(272)	7078(15)	5338(11)	9191(10)	94(8)
C(273)	7330(16)	5886(12)	9432(12)	105(9)
C(274)	7620(15)	6072(11)	9110(10)	92(7)
C(275)	11301(11)	8609(8)	11152(8)	66(5)
C(276)	11280(15)	8075(11)	11059(10)	93(8)
C(277)	10570(20)	7228(17)	10900(16)	146(14)
C(278)	10660(30)	6990(20)	10570(20)	210(20)
C(279)	9452(16)	6679(11)	9856(11)	101(8)
C(280)	9123(17)	6120(12)	9797(11)	104(9)
C(281)	9062(17)	5723(12)	9398(12)	107(9)
C(282)	8721(19)	5280(15)	9501(13)	123(11)
C(283)	8610(20)	5416(17)	9951(15)	144(13)
C(284)	8915(15)	5956(11)	10150(11)	95(8)
C(285)	10228(9)	8833(7)	9336(6)	49(4)
C(286)	9495(11)	8649(8)	9107(7)	61(5)
C(287)	9195(13)	9008(9)	9125(8)	74(6)
C(288)	9588(12)	9494(9)	9320(8)	76(6)
C(289)	10292(14)	9665(11)	9514(9)	88(7)
C(290)	10632(11)	9337(8)	9546(7)	62(5)
C(291)	10994(10)	8543(7)	8875(7)	54(4)
C(292)	10568(13)	8296(10)	8373(9)	78(6)
C(293)	10760(16)	8411(12)	7991(11)	98(8)
C(294)	11430(17)	8802(12)	8150(12)	108(9)
C(295)	11859(14)	9052(10)	8647(9)	84(7)
C(296)	11643(12)	8917(9)	9002(8)	72(6)
C(297)	10115(10)	8583(7)	10338(7)	55(4)
C(298)	9713(12)	8072(9)	10166(8)	72(6)
C(299)	8981(13)	7895(10)	9967(9)	78(6)
C(300)	8661(12)	8214(8)	9947(7)	65(5)
C(301)	9017(12)	8691(9)	10101(8)	75(6)
C(302)	9761(12)	8892(9)	10302(8)	69(5)
C(303)	11415(11)	9491(8)	10918(7)	62(5)
C(304)	11223(13)	9669(10)	11279(9)	78(6)
C(305)	11560(14)	10177(10)	11559(10)	87(7)
C(306)	12012(13)	10503(11)	11454(9)	82(7)
C(307)	12200(13)	10341(10)	11084(9)	81(6)
C(308)	11901(11)	9818(9)	10786(8)	69(6)
Pt(8)	3438(1)	1097(1)	212(1)	57(1)
Cl(15)	2368(3)	368(3)	-132(3)	93(2)
Cl(16)	2929(4)	1514(3)	634(3)	93(2)
Fe(8)	6822(2)	1759(2)	3309(2)	127(2)
O(29)	5220(11)	2253(8)	1954(7)	106(6)
O(30)	6518(9)	2641(7)	2791(6)	90(5)

O(31)	4205(10)	224(7)	932(7)	95(5)
O(32)	5090(16)	988(11)	1859(10)	149(9)
P(15)	3895(3)	591(2)	-84(2)	56(1)
P(16)	4335(2)	1834(2)	429(2)	54(1)
C(309)	3644(11)	11(8)	71(7)	62(5)
C(310)	3609(13)	10(10)	549(8)	75(6)
C(311)	4154(16)	242(13)	1403(11)	104(9)
C(312)	4896(16)	462(12)	1826(11)	100(8)
C(313)	5810(20)	1244(16)	2198(14)	136(12)
C(314)	5893(17)	1303(13)	2727(12)	105(9)
C(315)	6164(16)	1013(12)	3014(11)	105(9)
C(316)	6206(17)	1217(13)	3502(12)	109(9)
C(317)	5970(20)	1561(15)	3512(14)	128(11)
C(318)	5813(16)	1631(13)	3065(11)	105(9)
C(319)	4984(9)	2045(7)	1056(6)	49(4)
C(320)	4689(13)	2097(10)	1452(8)	77(6)
C(321)	5643(15)	2729(11)	2081(10)	97(8)
C(322)	6115(14)	2927(10)	2698(9)	84(7)
C(323)	7010(20)	2835(16)	3268(15)	139(13)
C(324)	7355(18)	2462(13)	3338(13)	130(12)
C(325)	7440(20)	2487(15)	3835(14)	220(20)
C(326)	7750(20)	2157(17)	3968(12)	270(30)
C(327)	7858(18)	1928(12)	3554(15)	145(14)
C(328)	7620(20)	2116(15)	3165(11)	320(40)
C(329)	4871(10)	842(8)	164(7)	58(5)
C(330)	5248(12)	974(9)	655(8)	70(6)
C(331)	5970(13)	1159(10)	850(10)	82(7)
C(332)	6314(14)	1186(10)	543(9)	84(7)
C(333)	5944(13)	1050(10)	32(9)	81(6)
C(334)	5217(12)	865(9)	-162(8)	70(6)
C(335)	3573(11)	328(8)	-765(7)	60(5)
C(336)	3718(11)	-37(8)	-976(8)	66(5)
C(337)	3460(14)	-255(11)	-1481(10)	91(7)
C(338)	2979(13)	-129(10)	-1791(9)	80(6)
C(339)	2837(11)	237(8)	-1594(8)	67(5)
C(340)	3106(10)	488(8)	-1070(7)	55(5)
C(341)	4814(9)	1872(7)	18(6)	50(4)
C(342)	4433(10)	1717(7)	-479(6)	51(4)
C(343)	4760(10)	1748(8)	-803(7)	56(5)
C(344)	5500(11)	1950(8)	-594(8)	67(5)
C(345)	5872(13)	2117(9)	-99(8)	74(6)
C(346)	5540(9)	2075(7)	222(6)	48(4)
C(347)	4065(8)	2336(6)	375(6)	43(4)
C(348)	3394(14)	2234(11)	16(9)	83(7)
C(349)	3190(16)	2600(12)	-88(11)	100(8)
C(350)	3629(13)	3109(10)	205(9)	80(6)
C(351)	4313(13)	3213(10)	563(9)	80(6)
C(352)	4508(10)	2841(8)	626(7)	57(5)

4. References

[1] [1a] J. L. Atwood, J. E. Davies, D. MacNichol, F. Vögtle, (Eds.), *Comprehensive Supramolecular Chemistry*, Vol. 2, Pergamon, Oxford, **1996**. [1b] J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**. [1c] F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, **1991**. [1d] F. Vögtle, *Cyclophan-Chemie*, Teubner, Stuttgart, **1990**.

[2] J. S. Bradshaw, R. M. Izatt, (Eds.), *Comprehensive Supramolecular Chemistry*, Vol. 1, Pergamon, Oxford, **1996**.

[3] I. Haiduc, F. T. Edelmann, *Supramolecular Organometallic Chemistry*, Wiley-VCH, Weinheim, **1999**.

[4] [4a] E. Lindner, W. Wassing, R. Fawzi, M. Steimann, *Angew. Chem.* **1994**, *106*, 363; *Angew.Chem. Int. Ed. Engl.* **1994**, *33*, 321. [4b] E. Lindner, W. Wassing, M. W. Pitsch, R. Fawzi, M. Steimann, *Inorg. Chim. Acta* **1994**, *220*, 107.

[5] E. Lindner, I. Krebs, R. Fawzi, M. Steimann, B. Speiser, *Organometallics* **1999**, *18*, 480.

[6] A. M. Allgeier, E. T. Singewald, C. A. Mirkin, C. L. Stern, *Organometallics* **1994**, *13*, 2928.

[7] E. Lindner, R. Veigel, K. Ortner, C. Nachtigal, M. Steimann, *Eur. J. Inorg. Chem.* **2000**, 959.

[8] E. Lindner, C. Hermann, G. Baum, D. Fenske, *Eur. J. Inorg. Chem.* **1999**, 679.

[9] A. M. Allgeier, C. S. Slone, C. A. Mirkin, L. M. Liable-Sands, G. P. A. Yap, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 550.

[10] S. J. Rao, C. I. Milberg, R. C. Petter, *Tetrahedron Lett.* **1991**, *32*, 3775.

[11] S. Akabori, Y. Habata, Y. Sakamoto, M. Sato, S. Ebine, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 537.

[12] J. F. Biernat, T. Wilczewski, *Tetrahedron* **1980**, *36*, 2521.

[13] E. Lindner, M. F. Günther, H. A. Mayer, R. Fawzi, M. Steimann, *Chem. Ber./Recl.* **1997**, *130*, 1815.

[14] G. M. Gray, D. C. Smith Jr., C. H. Duffey, *Inorg. Chim. Acta* **2000**, *300-302*, 581.

[15] D. C. Smith Jr., G. M. Gray, *Inorg. Chem.* **1998**, *37*, 1791.

[16] G. M. Gray, F. P. Fish, C. H. Duffey, *Inorg. Chim. Acta* **1996**, *246*, 229.

[17] G. M. Gray, A. Varshney, C. H. Duffey, *Organometallics* **1995**, *14*, 238.

[18] G. M. Gray, C. H. Duffey, *Organometallics* **1995**, *14*, 245.

[19] G. M. Gray, C. H. Duffey, *Organometallics* **1994**, *13*, 1542.

[20] A. Varshney, M. L. Webster, G. M. Gray, *Inorg. Chem.* **1992**, *31*, 2580.

[21] [21a] P. L. Boulas, M. Gomez-Kaifer, L. Echegoyen, *Angew. Chem.* **1998**, *110*, 226; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2116. [21b] A. Kaifer, M. Gomez-Kaifer, *Supramolecular Electrochemistry*, Wiley-VCH, Weinheim, **1999**.

[22] I. Saji, I. J. Kinoshita, *J. Chem. Soc., Chem. Commun.* **1986**, 716.

[23] E. Lindner, M. W. Pitsch, R. Fawzi, M. Steimann, *Chem. Ber.* **1996**, *129*, 639.

[24] [24a] A. S. Carlström, T. Frejd, *J. Org. Chem.* **1990**, *55*, 4175. [24b] I. R. Butler, W. R. Cullen, J. Ni, S. J. Rettig, *Organometallics* **1985**, *4*, 2196.

[25] A. Sonoda, I. Moritani, *J. Organomet. Chem.* **1971**, *26*, 133.

[26] R. N. Greene, *Tetrahedron Lett.*, **1972**, 1973.

[27] [27a] L. Rossa, F. Vögtle in *Sythesis of Medio- and Macrocyclic Compounds by High Dilution Principle Techniques: Topics in Current Chemistry* (Ed.: F. Vögtle), vol. 113, *Cyclophanes I*, Springer, Heidelberg, **1983**. [27b] P. Knops, N. Sendhoff, H.-B. Mekelburger, F. Vögtle in *High Dilution Reactions- New Synthetic Applications:*

Topics in Current Chemistry (Eds.: E. Weber, F. Vögtle), vol. 161, *Macrocycles*, Springer, Heidelberg, **1992**.

[28] W. E. Hill, D. M. A. Minahan, J. G. Taylor, C. A. McAuliffe, *J. Am. Chem. Soc.* **1982**, *104*, 6001.

[29] H.-J. Schneider, A. Yatsimirsky, *Principles and Methods in Supramolecular Chemistry*, Wiley-VCH, Weinheim, **2000**.

[30] W. J. DeWitte, L. Liu, E. Mei, J. L. Dye, A. I. Popov, *J. Sol. Chem.* **1977,** *5*, 337.

[31] M. J. Hynes, *J. Chem. Soc., Dalton Trans.* **1993**, 311.

[32] T. Matsue, D. H. Evans, T. Osa, N. Kobayashi, *J. Am. Chem. Soc.* **1985**, *107*, 3411.

[33] [33a] H. Plenio, C. Aberle, *Organometallics* **1997**, *16*, 5950. [33b] H. Plenio, R. Diodone, *Inorg. Chem.* **1995**, *34*, 3964.

[34] C. D. Hall, S. Y. F. Chu, *J. Organomet. Chem.* **1995**, *498*, 221.

[35] J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer, G. W. Gokel, *J. Am. Chem. Soc.* **1992**, *114*, 10583.

[36] S. Meyer, Ph. D. Thesis, University of Tübingen **1987**.

[37] T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181.

[38] C. M. Goff, M. A. Matchette, N. Shabestary, S. Khazaeli, *Polyhedron* **1996**, *15*, 3897.

[39] [39a] W. Schöniger, *Microchim. Acta* **1955**, 123. [39b] W. Schöniger, *Microchim. Acta* **1956**, 869.

[40] A. Dirscherl, F. Erne, *Microchim. Acta* **1961**, 866.

[41] G. Brunisholz, J. Michot, *Helv. Chim. Acta* **1954**, *37*, 598.

[42] B. Gollas, B. Krauss, B. Speiser, H. Stahl, *Curr. Sep.* **1994**, *13*, 42.

[43] S. Dümmling, E. Eichhorn, S. Schneider, B. Speiser, M. Würde, *Curr. Sep.* **1996**, *15*, 53.

[44] AA’XX‘ spin system.

[45] A part of an AXX‘ spin system, N = $|^{n}J_{PC} + {}^{m}J_{PC}|$.

[46] D. Cunningham, J. McManus, M. J. Hynes, *J. Organomet. Chem.* **1990**, *393*, 69.

[47] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1995**, *51*, 33.

[48] G. M. Sheldrick, *SHELXTL V5.03*, Program for Crystal Structure Refinement, University of Göttingen, Germany, **1997**.

5. Summary

Since the discovery of crown ethers by Pederson in 1967, supramolecular chemistry undergoes a rapid development and is still a focal point of research. In recent years the incorporation of transition metal complex fragments into the synthetical macrocyclic receptors extended the field to supramolecular organometallic chemistry. Transition metal complex fragments introduce a variety of new features like catalytic and/or redox activity into the host molecules and exert a remarkable influence on the structure due to their steric requirements. It was shown that metal-containing macrocycles are able to form supramolecular complexes like their organic analogues.

With regard to the electrochemically controllable formation of host/guest complexes the goal of the present study was to combine a redox active ferrocene unit and a potential catalytically active metal complex fragment in a crown ether-like macrocycle. The expected heterobimetallic polyoxametallaferrocenophanes therefore can be regarded as a crosslink between the well known metallacrown ethers and polyoxaferrocenophanes. Owing to the fact that the hitherto successfully applied bis(triflate) method for the formation of metal-carbon σ-bonds in metallaferrocenophanes failed when heteroatoms are present in the backbone of the bis(triflate), the well-developed phosphine chemistry offered a valuable alternative to introduce a second transition metal into the molecular skeleton of polyoxaferrocenophanes. Suitable bidentate phosphine ligands were built up by coupling of oligoethylene glycols of different chain lengths to 1,1'-bis(hydroxymethyl)ferrocene to give the diols 1,1'-$Fc(CH_2O(CH_2CH_2O)_nCH_2CH_2OH)_2$ ($n = 1-3$) which were subsequently reacted with (i) CH_3SO_2Cl in CH_2Cl_2 and (ii) $LiPPh_2$ in THF. Column-chromatographic work-up afforded the bisphosphines 1,1'-$Fc(CH_2O(CH_2CH_2O)_nCH_2CH_2PPh_2)_2$ ($n = 1-3$) in good yields as dark orange, slightly air-sensitive, viscous oils. To enhance the formation of the heterobimetallic macrocycles the cyclization reaction of the bis(phosphine) ligands 1,1‘-$Fc(CH_2O(CH_2CH_2O)_nCH_2CH_2PPh_2)_2$ (n = 1-3) and the precursor complex $(PhCN)_2PtCl_2$ was carried out under high dilution conditions in CH_2Cl_2. After purification by column chromatography the polyoxadiphosphaplatinaferrocenophanes *cis*-[1,1‘-$Fc(CH_2O(CH_2$-$CH_2O)_nCH_2CH_2PPh_2)_2]PtCl_2$ (n = 1-3) were obtained in medium yields as rather air-stable bright yellow powders. Their molecular composition was corroborated by elemental analyses, FD mass spectra, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra. The *cis*-arrangement of the phosphinyl groups is proved by the magnitude of the $^1J_{PtP}$ coupling constant of approximately 3630 Hz in each case. Single crystals suitable for X-ray crystal structure analysis were obtained only of the smallest macrocycle *cis*-[1,1‘-$Fc(CH_2OCH_2CH_2OCH_2CH_2PPh_2)_2]PtCl_2$. The compound crystallized in the triclinic space group $P\bar{1}$ (Z = 16) with eight symmetrically independant molecules per unit cell, which differ only in little conformational changes. Inspection of a space-filling model of one molecule reveals that the cavity is big enough for the encapsulation of small metal cations.

The inclusion behavior of the polyoxadiphosphaplatinaferrocenophanes *cis*-[1,1‘-$Fc(CH_2O(CH_2CH_2O)_nCH_2CH_2PPh_2)_2]PtCl_2$ (n = 1-3) toward alkaline metal cations, Mg^{2+}, and NH_4^+ was investigated in $CDCl_3/CD_3CN$ (v/v 1:1) solutions applying ^1H and $^{31}P\{^1H\}$ NMR titration methods. Whereas for the smallest macrocycle (n = 1) no significant effect could be detected, the addition of Li^+ or Mg^{2+} to solutions of the medium sized macrocycle (n = 2) and Li^+, Na^+, or K^+ to solutions of the largest host (n = 3) resulted in a detectable shift of the ^{31}P resonance, indicating an interaction of the guest cations with the host molecules. However, a satisfactory determination of association constants by non-linear least-squares curve fitting of the experimental data with EQNMR was not successful due to solubility limitations.

Cyclic voltammetry was used to examine the electrochemical properties of the polyoxadiphosphaplatinaferrocenophanes *cis*-[1,1'-Fc($CH_2O(CH_2CH_2O)_nCH_2CH_2PPh_2)_2$]-$PtCl_2$ (n = 1-3). A single redox couple for the reversible oxidation of the ferrocene subunit was observed in each case. The half-wave potentials are independant from the ring size and show only a slight anodic shift compared to unsubstituted ferrocene. No perturbation of the cyclic voltammograms occured upon addition of the mentioned cations.

In contrast to the metallacrown ethers and the polyoxaferrocenophanes which have affinities for the inclusion of group 1 cations or even transition metal cations, the present study shows that no or only weak complexation takes place in the case of the polyoxadiphosphaplatinaferrocenophanes *cis*-[1,1'-Fc($CH_2O(CH_2CH_2O)_nCH_2CH_2$-$PPh_2)_2$]$PtCl_2$ (n = 1-3) and alkaline metal cations, Mg^{2+}, and NH_4^+.

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