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Preparation, properties, and reactions of metal-containing heterocycles[☆]
Part CV. Synthesis and structure of polyoxadiphosphaplatinaferrocenophanes

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Abstract

A series of novel heterobimetallic crown ether-like polyoxadiphosphaplatinaferrocenophanes *cis*-[1,1′-Fc($CH_2O(CH_2CH_2O)_n$-$CH_2CH_2PPh_2)_2$]$PtCl_2$ ($n = 1$–3) (**4a**–**c**) was synthesized in good yield by cyclization of the bis(phosphine) ligands 1,1′-Fc($CH_2O(CH_2CH_2O)_nCH_2CH_2PPh_2)_2$ ($n = 1$–3) (**3a**–**c**) and $(PhCN)_2PtCl_2$ under high dilution conditions in CH_2Cl_2. The bisphosphines **3a**–**c** are obtained by reaction of the corresponding diols 1,1′-Fc($CH_2O(CH_2CH_2O)_nCH_2CH_2OH)_2$ ($n = 1$–3) (**1a**–**c**) with: (i) CH_3SO_2Cl in CH_2Cl_2 and (ii) $LiPPh_2$ in THF. Although the X-ray crystal structure of **4a** shows that the cavity is large enough for the encapsulation of small metal cations, inclusion experiments of **4a**–**c** with Group 1 cations, and Mg^{2+}, or NH_4^+ in solution applying NMR titration and cyclovoltammetric methods reveal no evidence for the formation of host–guest complexes for **4a**,**b**. In the case of **4c** only the addition of Na^+ or K^+ leads to an insignificant effect. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polyoxaplatinaferrocenophanes; Platinum complexes; Macrocyclization; High dilution

1. Introduction

Cyclophanes [2] and crown ethers [3] represent prototypic motifs in the development of supramolecular chemistry. The introduction of transition metal fragments into macrocyclic systems created a new and fast growing field in supramolecular organometallic chemistry [4]. Compared to their organic analogues, metallacyclophanes, metallocenophanes and metallacrown ethers exhibit a variety of additional features, like catalytic and/or redox activity [5–7]. Transition metals also exert 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 [8].

The objective of the present work was the incorporation of a potentially catalytically active metal center and a redox active ferrocene unit into a crown ether-like macrocycle. Such a combination is rarely described in the literature [7,9,10]. The expected heterobimetallic host molecules can be regarded as a crosslink between polyoxa[*n*]ferrocenophanes [11] and metallacrown ethers [12,13], which should be capable of including different metal cations of the first or second main group as guests. The ferrocene function offers the possibility to electrochemically manipulate the inclusion characteristics.

The hitherto successfully applied bis(triflate) method for the formation of metal–carbon σ bonds which is a necessary precondition for the access to metallacyclophanes [5,14] and metallametallocenophanes [6] failed when heteroatoms are incorporated into the backbone of the bis(triflate) [12]. However, the well-developed phosphine chemistry offers a valuable alternative for the introduction of a second transition metal to

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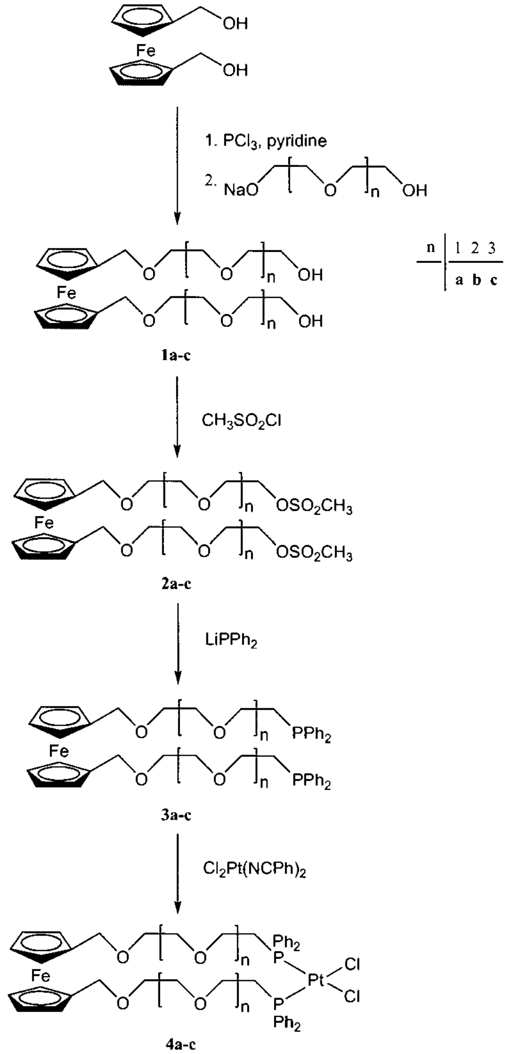
generate polyoxametallaferrocenophanes. Suitable bis(phosphine) ligands were built up of oligoethylene glycol chains with different length which are connected to a ferrocene unit in 1,1′-positions and to two phosphorus donors. If these ligands are reacted with a transition metal precursor in a 1:1 ratio under high dilution conditions, the desired bimetallic crown ethers are available.

2. Results and discussion

2.1. Synthesis of the bidentate phosphine ligands **3a–c**

The bidentate phosphines **3a**–**c** (Scheme 1) were made accessible by coupling of in situ generated 1,1′-bis(chloromethyl)ferrocene [15,16] to functionalized oligoethylene glycols. 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 to give the dimesylates **2a**–**c** which were reacted with $LiPPh_2$ in THF to afford the phosphines **3a**–**c**. 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 [12], the $^{31}P\{^1H\}$-NMR spectra of **3a**–**c** display singlets at $\delta = -21$ 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 attached terminal functional group.



Scheme 1. Synthesis of the bis(phosphine) ligands **3a**–**c** and the polyoxadiphosphaplatinaferrocenophanes **4a**–**c**.

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 [17]. 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 $^{31}P\{^1H\}$-NMR spectra expectedly are shifted to lower field. Resonances with superimposed doublets due to the ^{195}Pt–^{31}P coupling are observed at $\delta = 4.3$ (**4a**) and ≈ 5.3 (**4b,c**). The magnitude of the $^1J(Pt,P)$ coupling constant of approximately 3630 Hz gives evidence for the *cis*-arrangement of the phoshpinyl functions in each case [18]. This finding is confirmed by the $^{195}Pt\{^1H\}$-NMR spectra of **4a**–**c**, displaying each a triplet at $\delta = -4400$ with the same $^1J(Pt,P)$ coupling. In the high field part of the $^{13}C\{^1H\}$-NMR spectra of **4a**–**c** the signals of the methylene groups adjacent to the P atoms appear as the A part of an A′XX′ spin system.

2.3. X-ray crystal structure of **4a**

To prove the mononuclear composition of **4a**–**c** and to obtain more detailed information about the size and

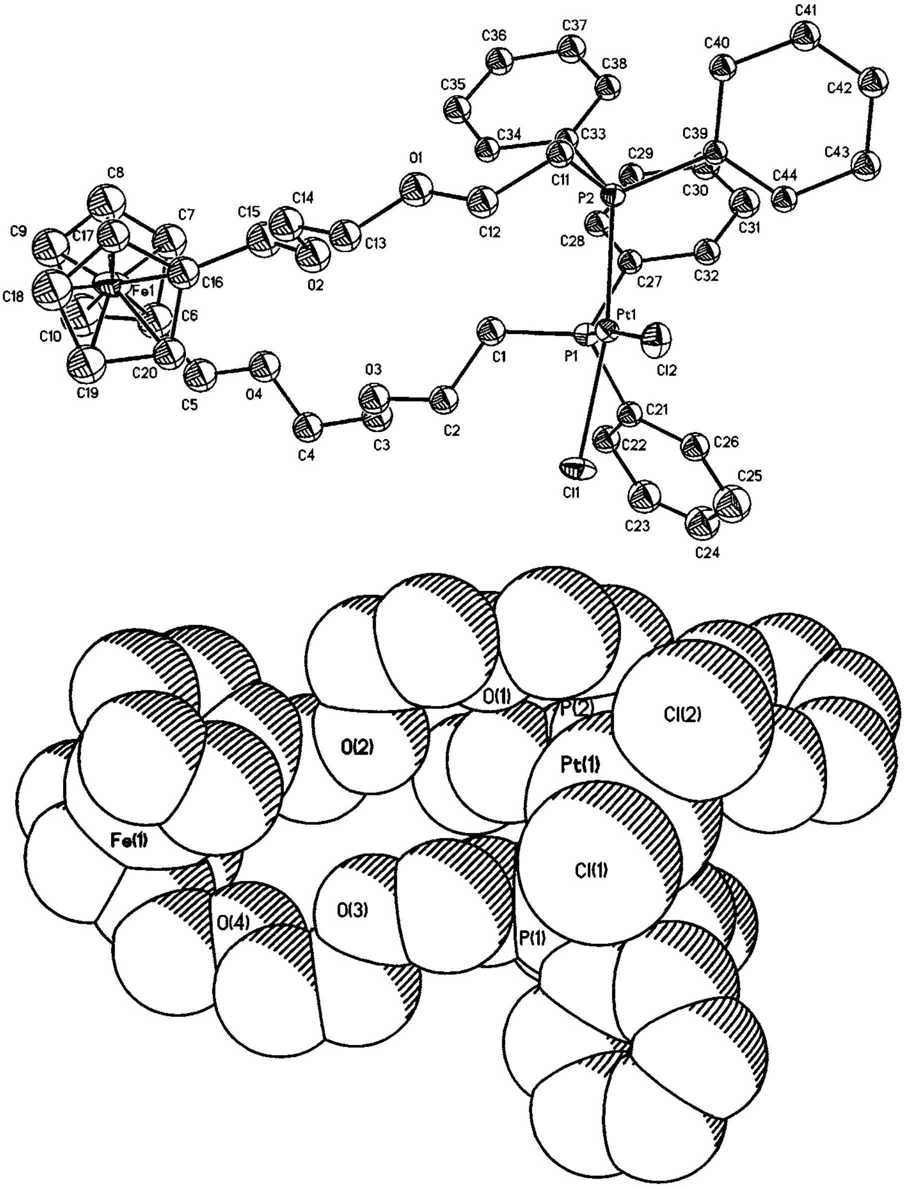


Fig. 1. Top: ORTEP plot of one molecule of the X-ray crystal structure of compound **4a**. Thermal ellipsoids are drawn at 20% probability level, except for H atoms. Bottom: space-filling representation of **4a**.

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 independent molecules of **4a** which differ only in minor conformational changes, mainly in the oligoethylene glycol chains. An ORTEP plot of one selected molecule with atom labeling is depicted in Fig. 1 (top). Selected bond lengths and angles are summarized in Table 1. All four oxygen atoms are approximately located in a plane at the vertices of a distorted trapezoid. The lengths of the parallel edges are 5.62(1) (O(1)–O(3)) and 4.73(1) Å

Table 1
Selected interatomic distances (Å) and interbond angles (°) for **4a**

Interatomic distances			
Pt(1)–Cl(1)	2.35(1)	O(1)–O(2)	2.83(3)
Pt(1)–Cl(2)	2.36(1)	O(1)–O(3)	5.62(3)
Pt(1)–P(1)	2.24(1)	O(2)–O(4)	4.74(3)
Pt(1)–P(2)	2.26(1)	O(3)–O(4)	2.82(3)
Pt(1)–Fe(1)	9.25(1)		
Interbond angles			
P(1)–Pt(1)–P(2)	98.8(2)	C(1)–P(1)–Pt(1)	114.8(10)
P(1)–Pt(1)–Cl(1)	88.6(2)	C(33)–P(2)–Pt(1)	117.5(7)
P(2)–Pt(1)–Cl(2)	86.5(2)	O(2)–C(15)–C(16)	114(3)
Cl(1)–Pt(1)–Cl(2)	88.0(3)	O(4)–C(5)–C(6)	109(4)

(O(2)–O(4)) and the O(1)–O(2) and O(3)–O(4) 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 large enough to encapsulate smaller alkaline or earth alkaline metal ions. A space filling model (Fig. 1, bottom) 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.

*2.4. Investigations on the inclusion behavior and electrochemical properties of the polyoxadiphosphaplatinaferrocenophanes **4a–c***

NMR titrations are among the most employed methods for the determination of association constants in host/guest chemistry [19]. In addition to ^{1}H-NMR, the polyoxadiphosphaplatinaferrocenophanes **4a–c** offer the possibility to use the ^{31}P nucleus as a probe for NMR titrations. 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. In the case of the smaller cycles **4a,b** neither in the ^{1}H- nor in the $^{31}P\{^1H\}$-NMR spectra a significant shift of any signal could be observed. Only the addition of Na^+ or K^+ to a solution of **4c** resulted in a remarkable shift, in particular of the ^{31}P resonance up to $\Delta\delta \approx 1$. However, a satisfactory determination of association constants by non-linear curve fitting of the experimental data with EQNMR [20] was not possible. This observation can be traced back to the insufficient fitting results for all applied complexation models. Both 1:1 and 2:1 complexes were taken into consideration, either separate or parallel. Self-association has been ruled out by dilution experiments. A possible explanation for this finding is the fact that the association constants are too small. Due to solubility limitations, the necessary concentrations of the guests could not be achieved.

Cyclovoltammetric measurements of **4a–c** were performed in 5×10^{-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 ($E° = 136$ mV), measured in the same solvent mixture. 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 [21]. 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.

3. 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 ^{1}H- and $^{31}P\{^1H\}$-NMR titrations and cyclic voltammetry. No evidence for the formation of host–guest complexes was found for the smaller cycles **4a**,**b**, whereas in the case of **4c** at least in the $^{31}P\{^1H\}$-NMR spectra a detectable shift was observed upon addition of Na^+ and K^+. 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 large 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 fragments is limiting the flexibility of the macrocycles **4a–c** to an extent that they are not able to adopt an energetically 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 under consideration.

4. Experimental

4.1. General procedures

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. Elemental analyses were carried out with an Elementar Vario EL analyzer. Cl analyses were carried out according to Schöniger [22] and determined as described by Dirscherl and Erne [23] according to Brunisholz and Michot [24]. 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% $Na_2[PtCl_6]6H_2O$, 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 [25] 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 [26]. 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 subtracted from the experimental data. The automatic iR-drop compensation facility was used for all experiments. Bis(hydroxymethyl)ferrocene [25], lithium diphenylphosphide [27] and bis(benzonitrile)dichloroplatinum(II) [28] were synthesized according to literature methods.

4.2. 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 [16]. The resulting solution was transferred to a dropping funnel via a Teflon pipe under an argon stream and was added drop-wise 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 material and 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.

4.3. 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%. ^{1}H-NMR ($CDCl_3$, 22 °C): $\delta = 3.4$–3.6 (m, 16H, OCH_2), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 22 °C): $\delta = 61.3$ (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 ($\mathit{C}H_2CH_2OH$), 83.5 (1,1′-Fc).

4.4. 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%. ^{1}H-NMR ($CDCl_3$, 22 °C): $\delta = 3.4$–3.7 (m, 24H, OCH_2), 3.9–4.0 (m [29], 8H, Cp-H), 4.1 (s, 4H, $FcCH_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 22 °C): $\delta = 61.0$ (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 ($\mathit{C}H_2CH_2OH$), 83.1 (1,1′-Fc).

4.5. 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%. ^{1}H-NMR ($CDCl_3$, 22 °C): $\delta = 3.4$–3.6 (m, 32H, OCH_2), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 22 °C): $\delta = 61.1$ (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 ($\mathit{C}H_2CH_2OH$), 83.3 (1,1′-Fc).

4.6. 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 drop-wise 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, 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.

*4.7. 1,1′-Bis(7-methylsulfonyloxy-2,5-dioxaheptyl)-ferrocene (**2a**)*

MS (FD, 30 °C): *m/z* 578.3 [M$^+$]. IR (CH$_2$Cl$_2$): ν(OSO$_2$CH$_3$) = 1177, 1357 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 22 °C): δ = 3.0 (s, 6H, OSO$_2$CH$_3$), 3.4–3.6 (m, 8H, OCH$_2$CH$_2$O), 3.7 (t, ^3J(HH) = 4.3 Hz, 4H, C*H*$_2$CH$_2$-OSO$_2$CH$_3$), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, FcCH$_2$), 4.3 (t, ^3J(HH) = 4.3 Hz, 4H, CH$_2$C*H*$_2$-OSO$_2$CH$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = 37.0 (OSO$_2$CH$_3$), 68.3 (2,2′-Fc), 68.6, 68.7 (OCH$_2$CH$_2$O), 68.8 (*C*H$_2$CH$_2$OSO$_2$CH$_3$), 69.2 (CH$_2$*C*H$_2$OSO$_2$CH$_3$), 69.6 (3,3′-Fc), 70.0 (FcCH$_2$), 83.2 (1,1′-Fc).

*4.8. 1,1′-Bis(9-methylsulfonyloxy-2,5,7-trioxanonyl)-ferrocene (**2b**)*

MS (FD, 30 °C): *m/z* 565.5 [M$^+$]. IR (CH$_2$Cl$_2$): ν(OSO$_2$CH$_3$) = 1177, 1355 cm^{-1}. ^{1}H-NMR (CDCl$_3$, 22 °C): δ = 3.0 (s, 6H, OSO$_2$CH$_3$), 3.4–3.6 (m, 8H, OCH$_2$CH$_2$O), 3.7 (t, ^3J(HH) = 4.4 Hz, 4H, C*H*$_2$CH$_2$OSO$_2$CH$_3$), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, FcCH$_2$), 4.3 (t, ^3J(HH) = 4.4 Hz, 4H, CH$_2$C*H*$_2$OSO$_2$CH$_3$). ^{13}C{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = 37.4 (OSO$_2$CH$_3$), 68.8 (2,2′-Fc), 68.7, 68.8, 68.9, 69.0 (OCH$_2$CH$_2$O), 69.2 (*C*H$_2$CH$_2$OSO$_2$CH$_3$), 69.8 (3,3′-Fc), 70.0 (FcCH$_2$), 70.2 (CH$_2$*C*H$_2$OSO$_2$CH$_3$), 83.3 (1,1′-Fc).

*4.9. 1,1′-Bis(11-methylsulfonyloxy-2,5,7,9-tetraoxaundecyl)ferrocene (**2c**)*

MS (FD, 30 °C): *m/z* 754.3 [M$^+$]. IR (CH$_2$Cl$_2$): ν(OSO$_2$CH$_3$) = 1171, 1344 cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 22 °C): δ = 3.0 (s, 6H, OSO$_2$CH$_3$), 3.5–3.6 (m, 8H, OCH$_2$CH$_2$O), 3.7 (t, ^3J(HH) = 4.2 Hz, 4H, C*H*$_2$CH$_2$OSO$_2$CH$_3$), 4.1–4.2 (m [29], 8H, Cp-H), 4.2 (s, 4H, FcCH$_2$), 4.3 (t, ^3J(HH) = 4.2 Hz, 4H, CH$_2$C*H*$_2$OSO$_2$CH$_3$). ^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$, 22 °C): δ = 37.3 (OSO$_2$CH$_3$), 68.8 (2,2′-Fc), 68.7, 68.9, 69.1, 69.5, 69.6 (OCH$_2$CH$_2$O), 69.8 (3,3′-Fc), 70.2 (FcCH$_2$), 70.3 (*C*H$_2$CH$_2$OSO$_2$CH$_3$), 70.4 (CH$_2$*C*H$_2$OSO$_2$CH$_3$), 83.7 (1,1′-Fc).

*4.10. 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 drop-wise 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).

*4.11. 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$_4$P$_2$ (758.65): C, 69.66; H, 6.38. Found: C, 69.70; H, 6.54%. ^{31}P{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = −21.2 (s). ^{1}H-NMR (CDCl$_3$, 22 °C): δ = 2.3 (m, 4H, CH$_2$P), 3.4–3.5 (m, 12H, OCH$_2$), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, FcCH$_2$), 7.2–7.4 (m, 20H, Ph). ^{13}C{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = 28.6 (d, ^1J(PC) = 12.8 Hz, CH$_2$P), 68.4 (d, ^2J(PC) = 25.6 Hz, *C*H$_2$CH$_2$P), 68.9 (2,2′-Fc), 68.8, 69.2 (OCH$_2$CH$_2$O), 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).

*4.12. 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$_6$P$_2$ (846.76): C, 68.09; H, 6.67. Found: C, 68.14; H, 6.26%. ^{31}P{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = −21.1 (s). ^{1}H-NMR (CDCl$_3$, 22 °C): δ = 2.3 (m, 4H, CH$_2$P), 3.5–3.6 (m, 20H, OCH$_2$), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, FcCH$_2$), 7.2–7.4 (m, 20H, Ph). ^{13}C{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = 28.7 (d, ^1J(PC) = 13.2 Hz, CH$_2$P), 68.4 (d, ^2J(PC) = 25.3 Hz, *C*H$_2$CH$_2$P), 68.9 (2,2′-Fc), 68.9, 69.1, 70.4, 70.5 (OCH$_2$CH$_2$O), 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).

*4.13. 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$_8$P$_2$ (934.88): C, 66.81; H, 6.90. Found: C, 66.84; H, 6.79. ^{31}P{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = −21.1 (s). ^{1}H-NMR (CDCl$_3$, 22 °C): δ = 2.3 (m, 4H, CH$_2$P), 3.4–3.5 (m, 28H, OCH$_2$), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, FcCH$_2$), 7.2–7.4 (m, 20H, Ph). ^{13}C{^{1}H}-NMR (CDCl$_3$, 22 °C): δ = 28.5 (d, ^1J(PC) = 12.8 Hz, CH$_2$P), 68.3 (d, ^2J(PC) = 25.6 Hz, *C*H$_2$CH$_2$P), 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).

4.14. General procedure for the preparation of the polyoxadiphosphaplatinaferrocenophanes ***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 simultaneously added drop-wise during 12 h at room temperature 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.

4.15. 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%); m.p. 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): $\delta = 4.3$ (sd, $^1J(PtP) = 3632$ Hz). ^1H-NMR ($CDCl_3$, 22 °C): $\delta = 2.4$ (m, 4H, CH_2P), 3.6 (m, 8H, OCH_2CH_2O), 3.9 (m, 4H, OCH_2CH_2P), 4.1–4.2 (m [29], 8H, Cp-H), 4.3 (s, 4H, $FcCH_2$), 7.1–7.5 (m, 20H, Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 22 °C): $\delta = 27.1$ (m [30], $N = 40.9$ 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 [30], $N = 11.0$ Hz, m-Ph), 130.6 (p-Ph), 131.4 (m [30], $N = 63.7$ Hz, ipso-Ph), 133.1 (m [30], $N = 10.0$ Hz, o-Ph). $^{195}Pt\{^1H\}$-NMR ($CDCl_3$, 22 °C): $\delta = -4400$ (t, $^1J(PtP) = 3632$ Hz).

4.16. 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%); m.p. 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): $\delta = 5.4$ (sd, $^1J(PtP) = 3632$ Hz). ^1H-NMR ($CDCl_3$, 22 °C): $\delta = 2.5$ (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 [29], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.1–7.5 (m, 20H, Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 22 °C): $\delta = 28.9$ (m [30], $N = 39.1$ Hz, CH_2P), 67.0 (CH_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 [30], $N = 11.0$ Hz, m-Ph), 129.9 (m [30], $N = 63.0$ Hz, ipso-Ph), 130.7 (p-Ph), 133.2 (m [30], $N = 10.3$ Hz, o-Ph). $^{195}Pt\{^1H\}$-NMR ($CDCl_3$, 22 °C): $\delta = -4399$ (t, $^1J(PtP) = 3632$ Hz).

4.17. 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%); m.p. 135 °C. MS (FD, 30 °C): m/z 1199.9 [M^+]. Anal. Calc. for $C_{52}H_{64}Cl_2FeO_8$-

Table 2
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 (Å)	21.990(4)
b (Å)	29.865(6)
c (Å)	29.877(6)
α (°)	101.72(3)
β (°)	108.69(3)
γ(°)	108.66(3)
V (Å^3)	16 557(6)
Z	16
D_{calc} (g cm^{-3})	1.644
Crystal size (mm^3)	$0.3 \times 0.3 \times 0.2$
Absorption coefficient (mm^{-1})	3.97
F(000)	65 552
θ Range for data collection (°)	2.17–25.92
Data reduction/correction	Background, Polarisation, Lorentz
Reflections collected	218 042
Independent reflections	58 730 ($R_{int} = 0.1122$)
Completeness to $\theta = 25.92°$	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	58 730/14/1963
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

$$R_1 = \frac{\sum_{hkl} ||F_o| - |F_c||}{\sum_{hkl} |F_o|}$$

$$wR_2 = \sqrt{\frac{\sum_{hkl} w(F_o^2 - F_c^2)^2}{\sum_{hkl} w(F_o^2)^2}}$$

$$\text{Goodness of fit} = \sqrt{\frac{\sum_{hkl} w(F_o^2 - F_c^2)^2}{N_{obs} - N_{parameter}}}$$

$P_2Pt\cdot 2H_2O$ (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): $\delta = 5.2$ (sd, $^1J(PtP) = 3628$ Hz). ^1H-NMR ($CDCl_3$, 22 °C): $\delta = 2.5$ (m, 4H, CH_2P), 3.4–3.6 (m, 24H, OCH_2CH_2O), 3.8 (m, 4H, OCH_2CH_2P), 4.0–4.1 (m [29], 8H, Cp-H), 4.2 (s, 4H, $FcCH_2$), 7.1–7.5 (m, 20H, Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 22 °C): $\delta = 29.3$ (m [30], $N = 42.0$ Hz, CH_2P), 67.1 (CH_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 [30], $N = 11.0$ Hz, m-Ph), 129.9 (m [30], $N = 63.0$ Hz, ipso-Ph), 130.9 (p-Ph), 133.4 (m [30], $N = 10.7$ Hz, o-Ph). $^{195}Pt\{^1H\}$-NMR ($CDCl_3$, 22 °C): $\delta = -4400$ (t, $^1J(PtP) = 3628$ Hz).

4.18. 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 2. The data fits best with the triclinic space group $P\bar{1}$ with eight independent molecules per unit cell ($Z = 16$). The structure was solved by direct methods with SHELXS [31] and refined by least-squares methods based on F^2 using SHELXTL-97 [32]. The metal, chlorine and phosphorus atoms were refined anisotropically. All hydrogen atoms were located in calculated positions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 158649. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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