Makrocyclische zwei- und vierkernige Osmacycloferrocenophane

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Macrocyclic Di- and Tetranuclear Osmacycloferrocenophanes

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Abbreviations and Definitions

Å	Ångström (10^{-10} m)
c	Concentration
Cp	Cyclopentadienyl
d	Day
δ	Chemical shift
DCM	Dichloromethane
DHP	3,4-Dihydro-2*H*-pyran
EI	Electron Ionisation
EtOH	Ethanol
Fc	Ferrocene
Fc^+	Ferrocenium-cation
FD	Field desorption
g	Gram
h	Hour
Hz	Hertz
IR	Infrared spectroscopy
L	Liter
mL	Milliliter
mmol	Millimol
MHz	Megahertz
MS	Mass spectrometry
mV	Millivolt
μA	Microampere

n-BuLi	*n*-Butyllithium
NMR	Nuclear magnetic resonance
ppm	Parts per million
PPTS	Pyridinium *p*-toluenesulfonate
s	Second
v	Scan rate
THP	Tetrahydropyran

Introduction

Cyclophanes[1–3] with subgroups like calixarenes[4–6] or cryptophanes,[7] and other macromolecules of this type play an important role in the development of supramolecular chemistry,[8] now expanding to supramolecular science,[9] a multidisciplinary field. Soon after the discovery of ferrocene[10] in the early fifties and the discovery of its extraordinary features like aromaticity, thermal stability, and resistance to aerial oxygen, interest has focused on bridged ferrocenes, denoted as ferrocenophanes.[11,12] The collective term of metallocenophanes and cyclophanes is "phanes".[13] Replacing methylene groups of the bridging chains in these macrocycles by transition metals affords metallametallocenophanes[14] and metallacyclophanes.[15–17] Due to the steric requirement of transition metal fragments their introduction into the framework of these systems affect the geometric parameters of the cavities.[15–18] Simultaneously a new reactive center is obtained that is capable of inserting small molecules, like carbon monoxide,[15,16] into metal–carbon σ bonds and of reacting with a new ligand if a vacant coordination site is available.[19] With the incorporation of coordination chemistry into supramolecular chemistry self assembly[20–22] resulted in a breakthrough in the field of molecular manufacturing of molecular polygons and polyhedra. Only a few ligands and metal complexes with predetermined angles are necessary to generate a great variety of highly symmetric macrocycles with remarkable characteristics. The specific integration of heteroatoms (N, O, S) into the framework of cyclophanes or metallocenophanes leads to systems with particular complexation abilities suitable for molecular recognition.[23] Moreover redox active subunits like ferrocenes are able to electrochemically communicate with well-defined binding sites to get a redox switch.[24–26] This offers the possibility to electronically manipulate the inclusion characteristics of hosts and to determine the concentration of the guest molecules.[27–31] Considerable chemical and physical properties are expected if additional metals are in the proximity of the redox active ferrocene unit.[32] Another field of research is the employment of phanes in molecular machines[33] with electrons or photons as matter of motions.

With the intention to merge osmacyclophanes[15–17] and osmaferrocenophanes,[14] the objective of this investigation was the synthesis of the two-dimensional osmacycloferrocenophanes **8a–h** and diosmacycloferrocenophanes **9a–h** containing two and four transition metal centers, respectively. These macrocycles differ in the lengths of the alkyl chains and the different substitution patterns at the aromatic rings. The well known bis(triflate) method[14–17,34] served for the formation of two and four osmium–carbon σ bonds, respectively. The redox potentials of **8a–h** were determined by cyclic voltammetry in dependence on the chain lengths and substitution design. Selected osmacycloferrocenophanes and diosmacycloferrocenophanes were subjected to an X-ray structural investigation.

General Section

1 Synthesis and Properties

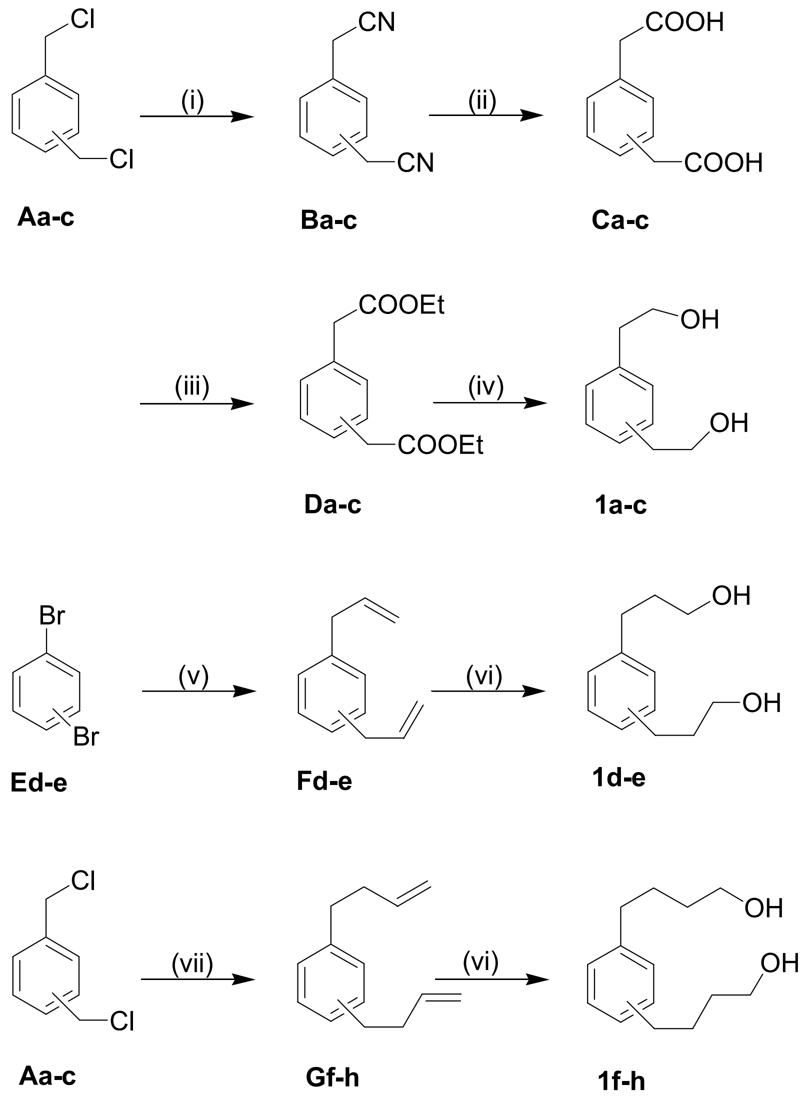
1.1 General Considerations

For the synthesis of the osmacycloferrocenophanes **8** and **9**, advantage of the bis(triflate) method was taken, which is considered as a variant of the cationic alkylation. This route was found to be the most straightforward and efficient way for the concomitant formation of several metal–carbon σ bonds under very mild conditions. The triflate residue is an excellent and inert leaving group stabilizing carbenium-like carbon atoms at the ends of a hydrocarbon chain, thereby enabling an electrophilic attack of the terminal carbon atoms even at a weakly basic metal center. With regard to this method metallacyclophanes[15–17] and four-[35] to fifty-one-membered[36] multimetallacycloalkanes were obtained by reaction of the corresponding bis(triflates) with the metalates $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os). Prior to the application of the bis(triflate) method in this work several primary steps had to be elaborated.

1.2 Starting Materials

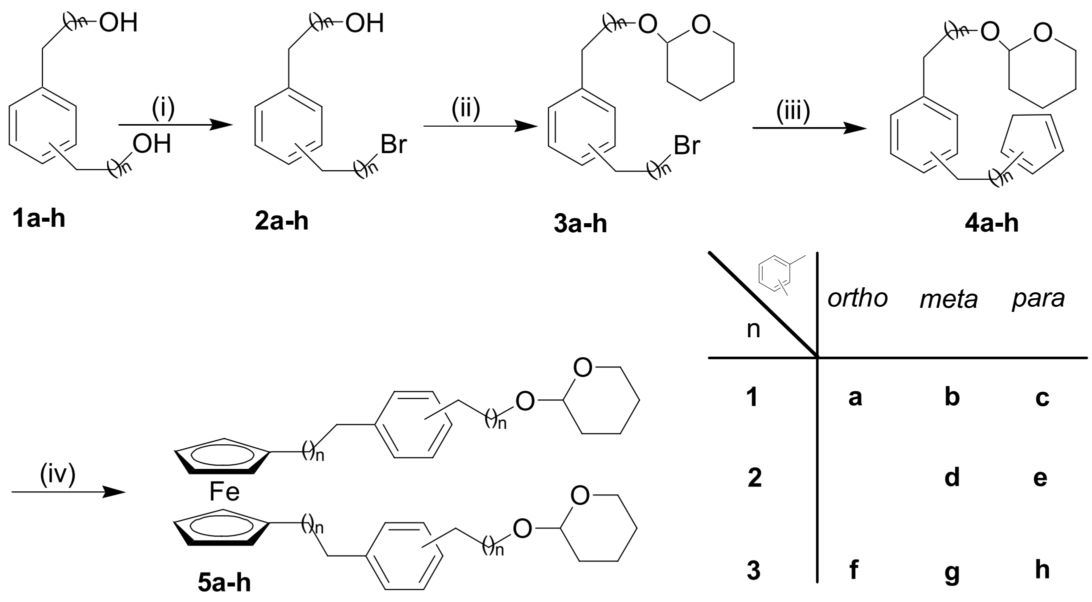
The known bis(alcohols) **1a-h** were used as starting materials. **1a-c** were synthesized by well known procedures, **1d-e** and **1f-h** were obtained by literature or modified literature methods (Scheme 1) whereas for the 1,n-bis(3-butenyl)benzenes (n = 2–4) a large scale (0.5 mol) synthesis was developed (see Experimental Part).

Reacting the bis(alcohols) **1a-h** with $HBr_{(aq)}$ in toluene affords the aromatic α,ω-bromoalkanols **2a-h**, which are reacted with dihydropyran in DCM to attain to **3a-h** (Scheme 2). The tetrahydropyran (THP) protected cyclopentadienyl alcohols are readily available by reacting **3a-h** with NaCp in THF.



Reagents: (i) NaCN, DMSO. (ii) H_2SO_4 (33%). (iii) EtOH, H_2SO_4, $CHCl_3$. (iv) $LiAlH_4$, THF. (v) 1) Mg, THF. 2) Allylbromide. (vi) 1) $NaBH_4$, THF, $BF_3{\cdot}Et_2O$. 2) $NaOH_{(aq)}$, H_2O_2. (vii) Allylmagnesiumbromide, diethyl ether.

Scheme 1.



n	*ortho*	*meta*	*para*
1	a	b	c
2		d	e
3	f	g	h

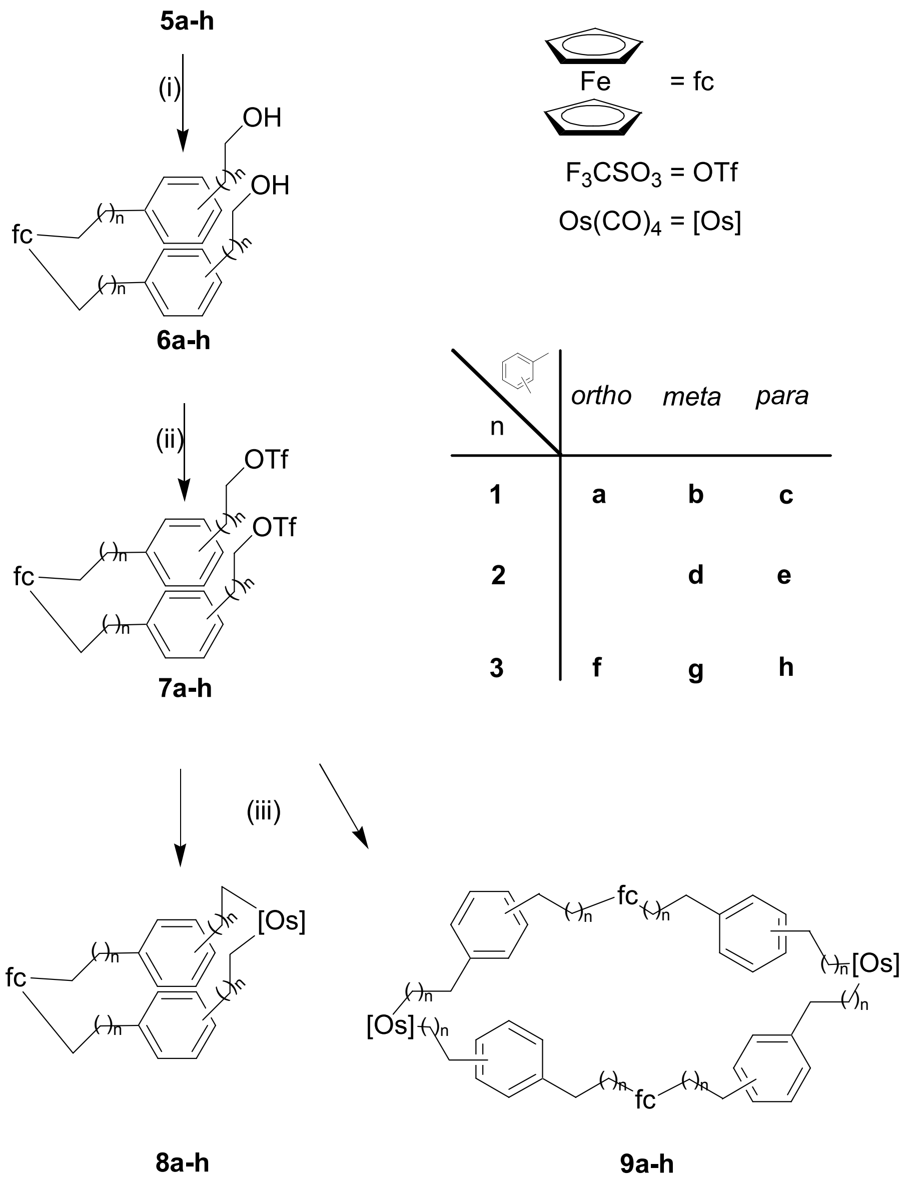
Reagents: (i) HBr, Toluol. (ii) DHP, PPTS, DCM. (iii) NaCp, THF. (iv) 1) *n*-BuLi, Hexane. 2) $FeCl_2$, THF, reflux.

Scheme 2.

Treatment of the THP protected cyclopentadienyl alcohols with $FeCl_2 \cdot THF_{1.44}$ in THF with subsequent deprotection of the resulting intermediates **5a-h** affords the bis(alcohols) **6a–h** (Scheme 3). After purification by column chromatography **6a–h** were obtained in moderate to satisfying yields. While the *para*-compounds **6c,h** represent orange waxy materials, the bis(alcohols) **6a,b,d–g** are highly viscous yellow oils. All alcohols **6a–h** are readily soluble in chlorinated hydrocarbons and their molecular composition was corroborated by elemental analyses and FD mass spectra, displaying in each case the expected molecular peak.

1.3 Bis(triflates) 7a–h

To attain to the bis(triflates) **7a–h** in good to excellent yields the bis(alcohols) **6a–h** were reacted with trifluoromethanesulfonic acid anhydride in the presence of a slight excess



n	*ortho*	*meta*	*para*
1	a	b	c
2		d	e
3	f	g	h

Reagents: (i) PPTS, Ethanol. (ii) Pyridine, Tf_2O, CH_2Cl_2, -30 °C. (iii) $Na_2[Os(CO)_4]$, Me_2O, reflux.

Scheme 3.

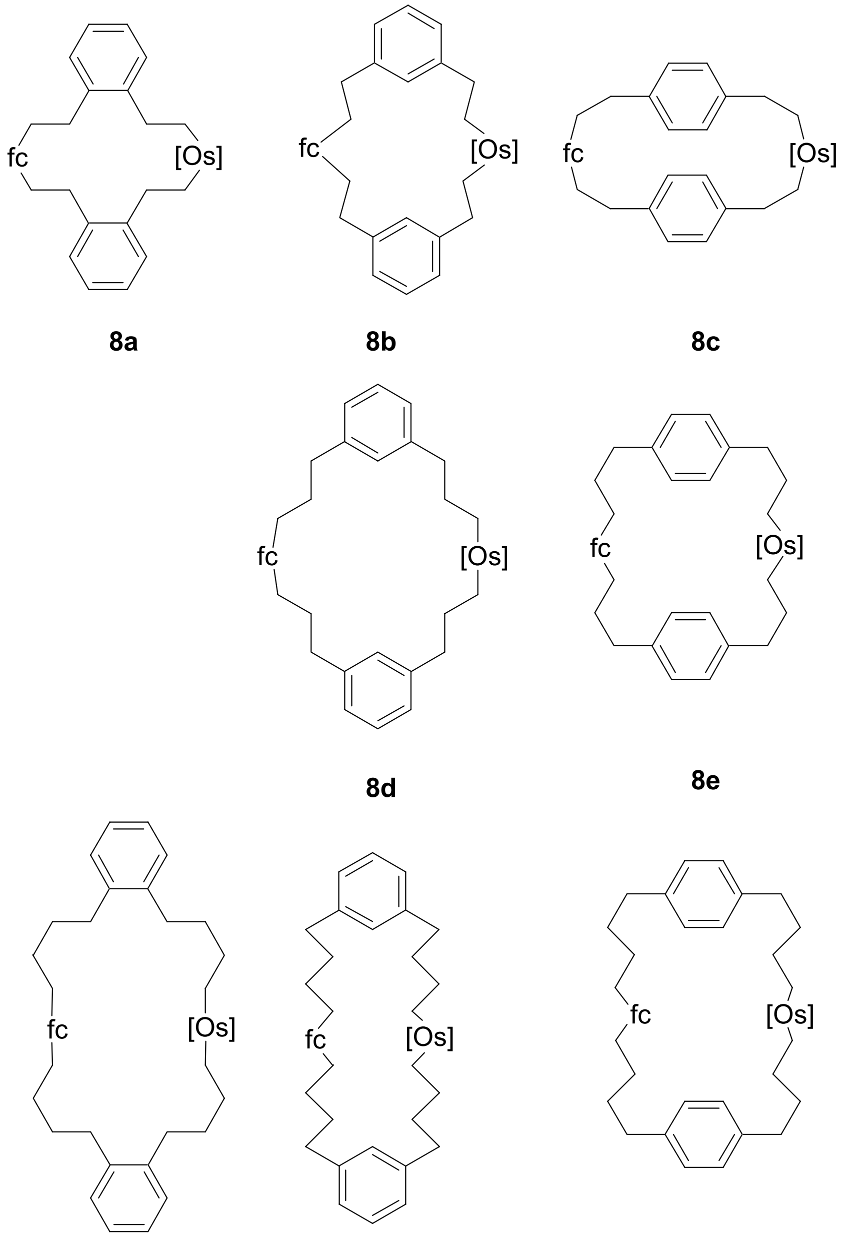
of pyridine at –30 °C in dichloromethane (Scheme 3). The yellow, heat sensitive compounds **7a–h** are easily soluble in common organic solvents and can be stored below –30 °C for some days. However, it is recommendable to use them in situ. **7a–h** were identified by their mass, ^1H, $^{13}C\{^1H\}$ NMR, and IR spectra.

1.4 Osmacycloferrocenophanes 8a-h

The osmacycloferrocenophanes **8a–h** were formed within three days in satisfying yields by adding the corresponding bis(triflates) **7a–h** to a suspension of the sodium salt of the organometallic Lewis base $[Os(CO)_4]^{2-}$ in refluxing dimethyl ether (Scheme 3). Because of the low solubility of $Na_2[Os(CO)_4]$ in this solvent, the necessary dilution was adjusted automatically, hence the formation of oligo- and polymeric products was suppressed as far as possible. A yellow-brown precipitate consists of mainly oligomers, polymers and sodium triflate. For the macrocycles **8a–h** with longer alkyl chains a trend to higher yields was observed. The yellow osmacycloferrocenophanes **8a–h** (Chart 1) are rather stable toward aerial oxygen and can be handled at room temperature without decomposition and dissolve in all common organic solvents. Their molecular composition was confirmed by elemental analyses and by FD mass spectra, displaying in each case the expected isotopic pattern. Between 2130 and 2000 cm^{-1} the IR spectra of **8a–h** exhibit three to four CO absorptions (*n*-pentane) which together with their intensities is consistent with the presence of *cis*-$Os(CO)_4$ arrangements (Figure 1).

1.5 Diosmacycloferrocenophanes 9a-h

In contrast to the occurrence of only dinuclear osmaferrocenophanes,[14] in the case of the osmacycloferrocenophanes not only the dinuclear species **8a–h** are formed. In reproducible yields of 1–2% (exception **9f,g** <0.5%) also the tetranuclear macrocycles **9a–h** (Chart 2) were isolated by column chromatographic separation, eluting **8a–h** at first with *n*-pentane/diethyl ether 50:1. Their molecular composition was corroborated by FD mass spectra. The solubility of the pale yellow heterocycles **9a–h** in non-polar solvents like *n*-



8a **8b** **8c**

8d **8e**

8f **8g** **8h**

Chart 1.

pentane increases with the number of methylene functions. There are no significant differences in the IR data between **8a–h** and **9a–h**.

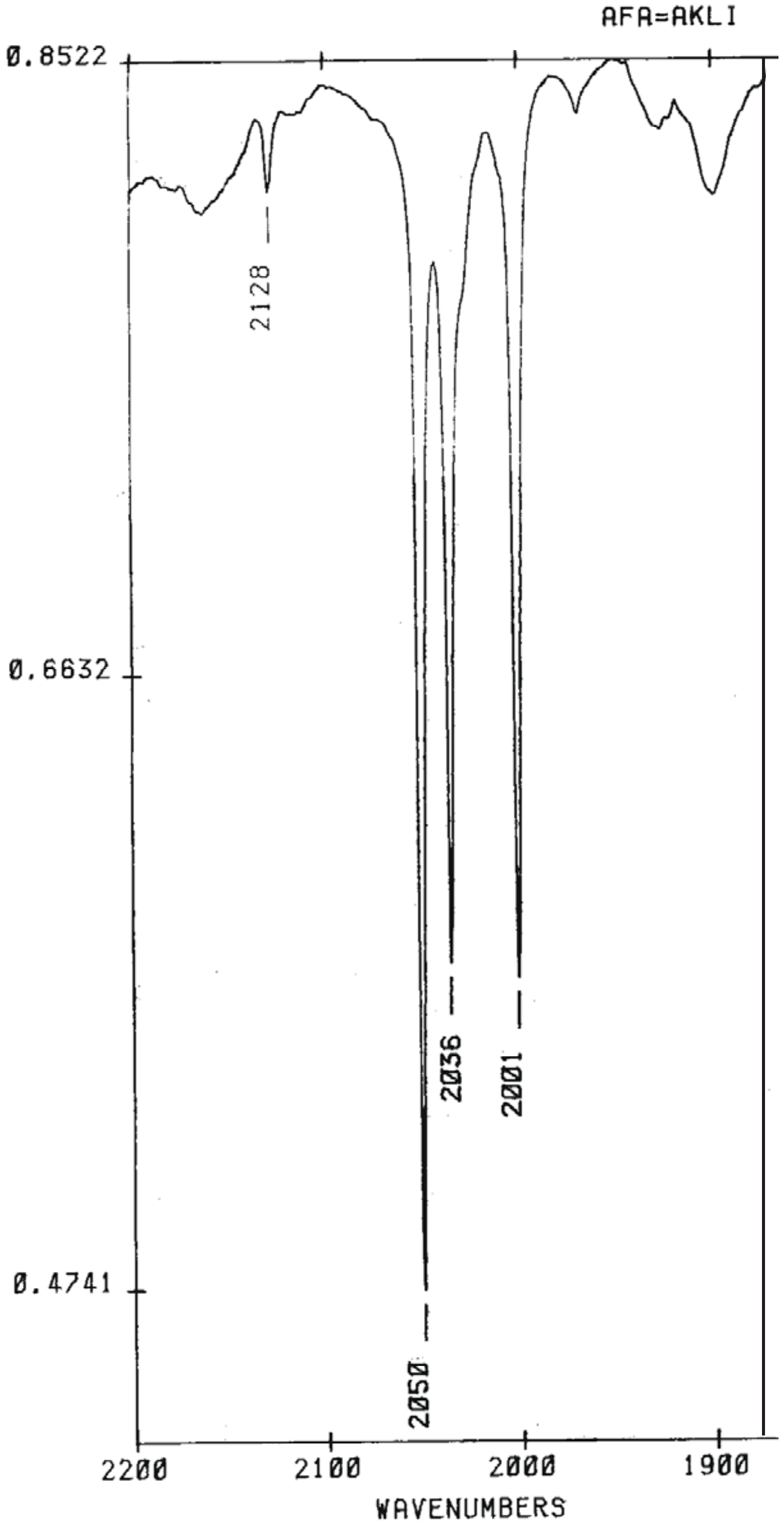
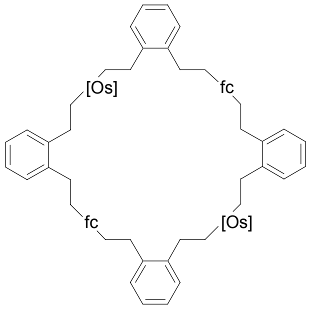
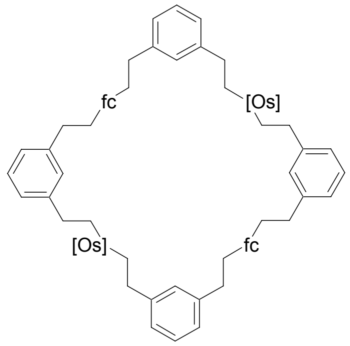


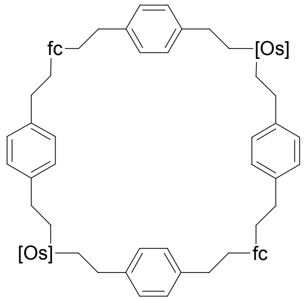
Figure 1. ν(CO) stretching vibrations in the IR spectrum of **8c** in *n*-pentane.



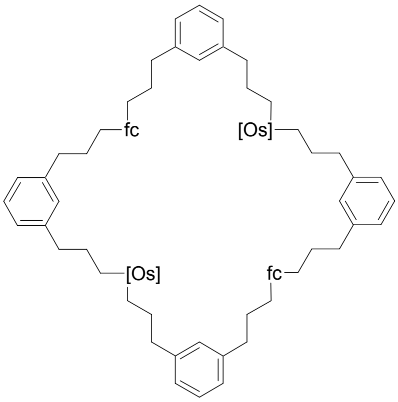
9a



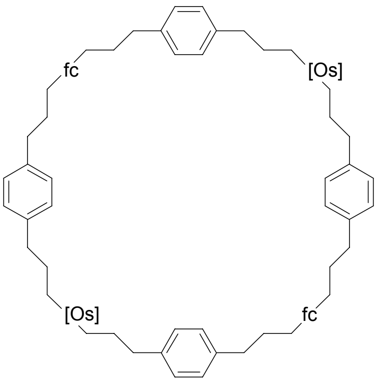
9b



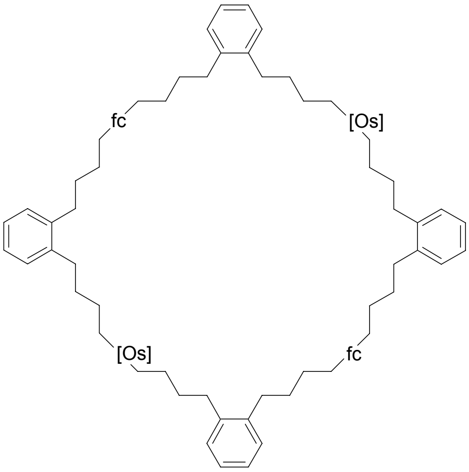
9c



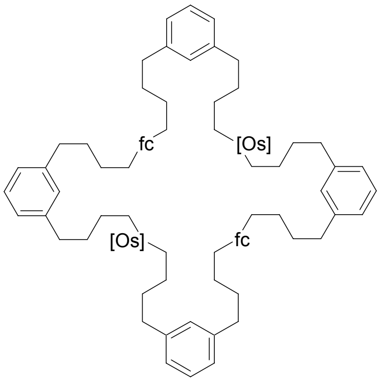
9d



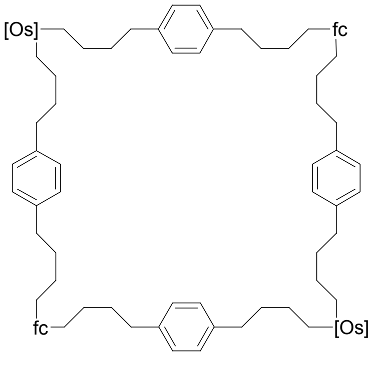
9e



9f



9g



9h

Chart 2.

2 Characterization

2.1 Discussion of the NMR Spectra of the Bis(alcohols) 6a-h, Bis(triflates) 7a-h, Osmacycloferrocenophanes 8a-h, and Diosmacycloferrocenophanes 9a-h

By inspection of the ^{1}H and ^{13}C{^{1}H} NMR spectra it is obvious that most chemical shifts remain largely unchanged on going from the ferrocenediylalcohols **6a–h** to the macrocycles **8a–h** via the bis(triflates) **7a–h**. For the aromatic protons in **6a–h**, **7a–h**, and **8a–h** the centers of the chemical shifts are located between 7.22 and 7.04 ppm. If the ^{1}H NMR spectra of **8c**, **8e**, and **8h** are compared in the aromatic region a particular conspicuous dependence of the splitting pattern on the length of the *para*-positioned alkyl chain appears, revealing an AA´BB´ system for **8c** collapsing into a singlet on going from **8c** to **8e** and **8h**. In **8h** the different functional groups are too far away from the benzene ring. While the spectra of **8a–h** show AA´XX´ patterns for the cyclopentadienyl hydrogen atoms in the case of the bis(alcohols) **6a–h** and bis(triflates) **7a–h** only a broad singlet or a diffuse AA´XX´ spin system occurs. All centers of chemical shifts are found in the range between 4.09 and 3.87 ppm. The multiplets (2.9–2.29 ppm) of the four CH_2 groups adjacent to the aromatic rings in the ^{1}H NMR spectra of **6a–h**, **7f–h**, and **8b**, **8d–h** are not resolved. Only for **7a–e** and **8a,c** separated signals for these functions are observed. On the contrary the resonances of the protons of the methylene groups next to the ferrocene unit in **6d–h**, **7d–h**, and **8d–h** are relatively constant (2.37–2.25 ppm) and give rise to triplets. All other spectra (**6a–c**, **7a-c**, **8a–c)** show only unresolved multiplets (2.74–2.12 ppm). Depending on the electron-donating or electron-withdrawing properties of the respective functions the largest chemical shift differences are detectable for the protons of the methylene groups in direct vicinity to $Os(CO)_4$ (1.41–0.94 ppm), OH (3.83–3.56 ppm), and OTf (4.74–4.55 ppm). Except **8c,h** with a hindered rotation of the C_α–C_β bonds (with respect to osmium), the spectra of the osmacycloferrocenophanes **8a,b,d–f,g** reveal the same splitting pattern[37] for the CH_2Os groups. For example in the case of **8b** the A (CH_2Ar) and X (CH_2Os) parts of the AA′XX′ spin system are characterized by chemical shifts of 3.03 and 1.40 ppm, respectively. The protons of the internal methylene groups between the aromatic rings and the ferrocene and $Os(CO)_4$, OTf, or OH groups, respectively, give only rise to unresolved multiplets between 2.1 and 1.6 ppm.

Like in the ^1H NMR spectra the largest differences of the chemical shifts in the $^{13}C\{^1H\}$ NMR spectra of **6a–h**, **7a–h**, **8a–h** are ascertained for the carbon atoms of the CH_2 functions next to Os, OH, and OTf (Figure 2). The ranges of the ^{13}C resonances vary from 1.8 to –5.5 (CH_2Os), 63.7 to 62.2 (CH_2OH), and 78.1 to 77.3 ppm (CH_2OTf), respectively. Unlike previous results[14,36] the high-field position of the α-methylene carbon atoms in the spectra of the osmacycloferrocenophanes **8a–h** exhibit no significant dependence on the ring size. All other methylene groups (three for **Xa–c**, five for **Xd,e**, seven for **Xf–h**, **X = 6-8**) resonate between 43.6 and 26.7 ppm. Three signals between 91 and 67 ppm are assigned to the cyclopentadienyl carbon atoms in the spectra of **6a–h** to **8a–h**. The one at lowest field is ascribed to the quaternary and the remaining two resonances are attributed to the tertiary C atoms. ^{13}C resonances referring to the phenylene rings occur in the range from 150 to 125 ppm. In the case of the osmacycloferrocenophanes **8a–h** two more peaks are detected which can be traced back to the axial (180.4–176.2 ppm) and equatorial (172.5–171.0 ppm) carbonyl ligands. There are no significant differences in the NMR data between **8a–h** and **9a–h**.

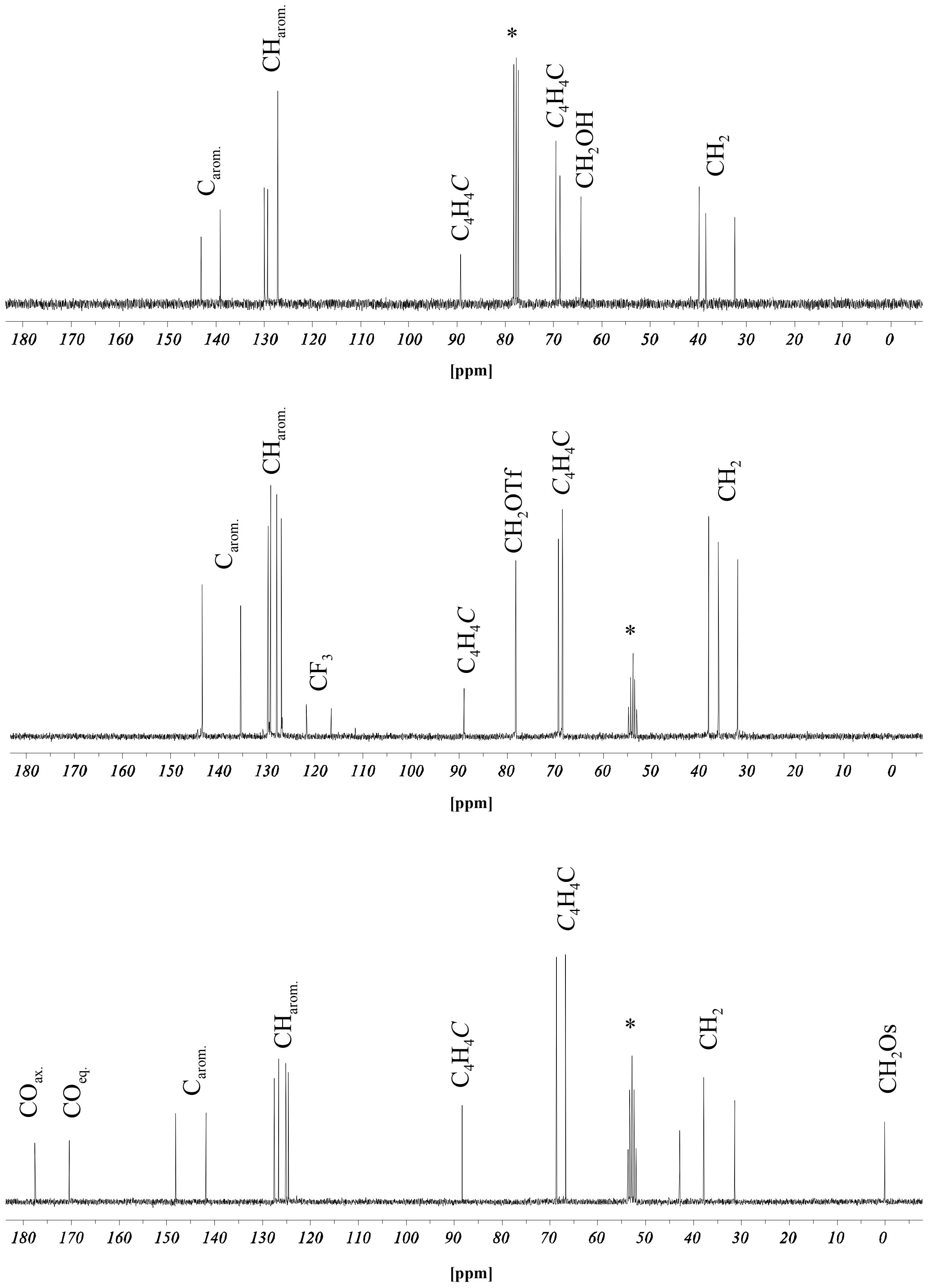


Figure 2. Comparison of the ^{13}C {^{1}H} NMR spectra of **6b** (top) in $CDCl_3$, **7b** (middle), and **8b** (bottom) in DCM (solvent: *).

2.2 Crystallographic Anlaysis

2.2.1 Discussion of the Crystal Structures of 8b, 8c, and 8e

To obtain more detailed information about the structures of the osmacycloferrocenophanes, X-ray structural investigations were performed with the examples of **8b**, **8c**, and **8e.** Selected bond distances and angles are summarized and the corresponding ORTEP plots with atom labeling are depicted in Figures 3–5. Four molecules are found in the monoclinic (**8b,c**) and orthorhombic (**8e**) unit cells. With approximately 1.65 Å the iron atoms are nearly equidistant from the centers of the cyclopentadienyl rings which are almost

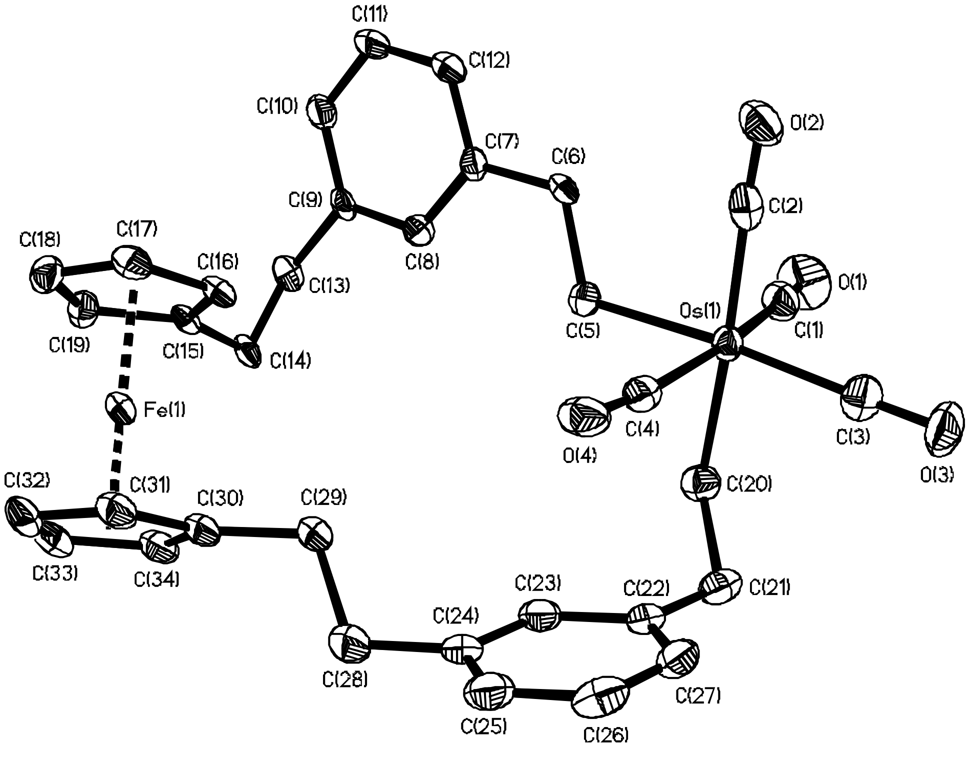


Figure 3. Crystal Structure of 8b. Selected bond lengths and angles in Å, deg: Os(1)–Fe(1) 8.139(2), Os(1)–C(5) 2.221(4), Os(1)–C(20) 2.229(4), center Ph(1)–center Ph(2) 8.41, Fe–Cp(1) 1.65, Fe–Cp(2) 1.65, C(5)–Os(1)–C(20) 83.66(16), δ 178.1, α 2.31(32), C(14)–Cp(1)–Cp(2)–C(29) 66.3, interplanar angle (Ph(1)–Ph(2)) 82.29(14).

parallel to each other with angles of δ = 178.1 (**8b**), 177.9 (**8c**), and 178.2 (**8e**) (ring center–metal–ring center). The resulting dihedral angle (tilt angle α) was found to be 2.31(32), 3.77(41), and 2.17(30) for **8b,c,e**. All three frameworks of the macrocycles roughly reveal a boat shaped structure in which the phenylene building blocks including the $(CH_2)_n$-spacers form the hull and the ferrocene and $Os(CO)_4$ fragments the stern and bow, respectively. Due to the different substitution patterns and the different number of CH_2 units the boat is more or less distorted. In **8b** the two metals and the centers of the phenylene rings have nearly the same distance (8.139(2) and 8.41 Å, respectively). Both phenylene rings in **8b** deviate from a perpendicular arrangement by an angle of 7.71°. For the ferrocene units a deviation of 5.7° from the synclinal (*gauche*) eclipsed (72°) conformation is established. In contrast to **8b,e** the molecule **8c** resembles most closely a boat shaped structure. The cyclopentadienyl rings are

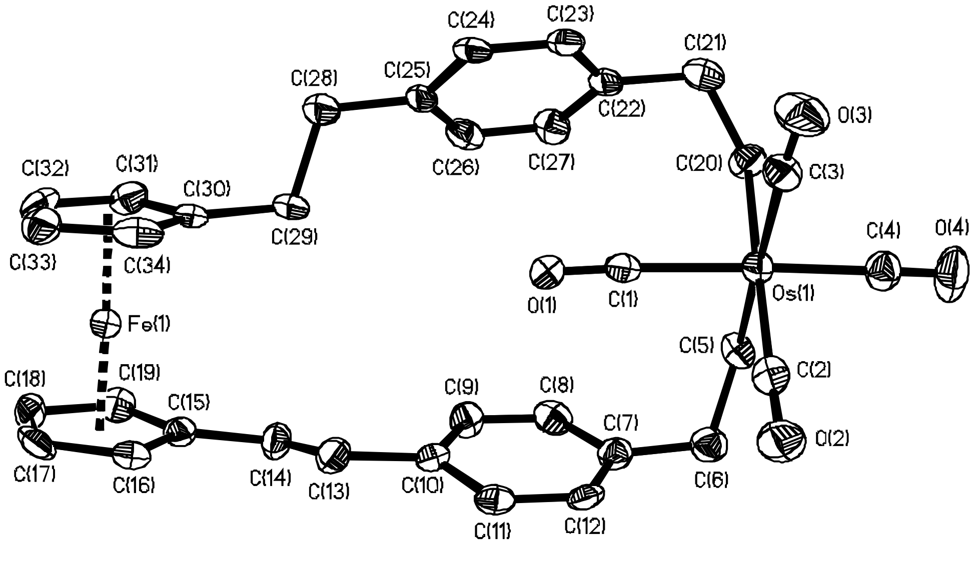


Figure 4. Crystal Structure of 8c. Selected bond lengths and angles in Å, deg: Os(1)–Fe(1) 9.727(2), Os(1)–C(5) 2.220(7), Os(1)–C(20) 2.236(7), center Ph(1)–center Ph(2) 5.58, Fe–Cp(1) 1.66, Fe–Cp(2) 1.66, C(5)–Os(1)–C(20) 82.8(3), δ 177.9, α 3.77(41), C(14)–Cp(1)–Cp(2)–C(29) 0.1, interplanar angle (Ph(1)–Ph(2)) 53.73(17).

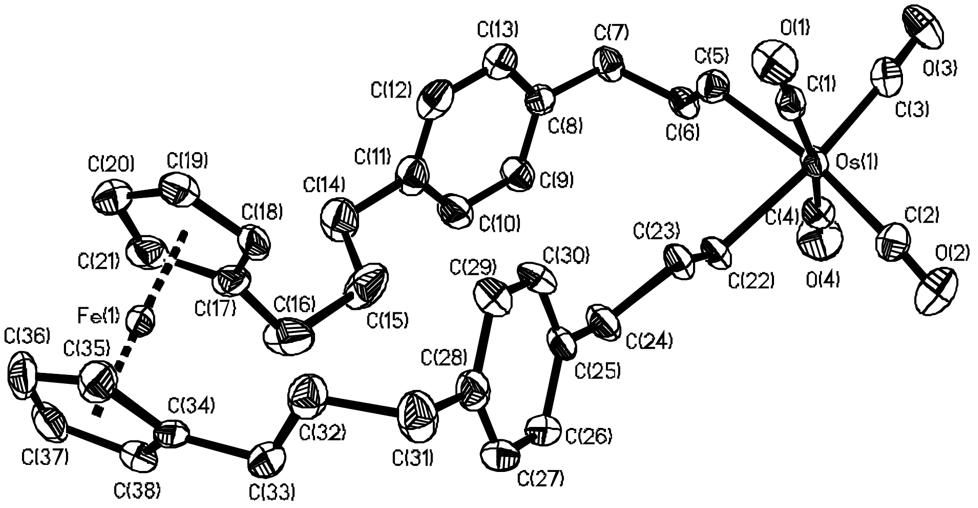


Figure 5. Crystal Structure of 8e. Selected bond lengths and angles in Å, deg: Os(1)–Fe(1) 11.468(3), Os(1)–C(5) 2.203(5), Os(1)–C(22) 2.219(20), center Ph(1)–center Ph(2) 6.52, Fe–Cp(1) 1.65, Fe–Cp(2) 1.64, C(5)–Os(1)–C(22) 83.69(18), δ 178.2, α 2.17(30), C(16)–Cp(1)–Cp(2)–C(33) 62.3, interplanar angle (Ph(1)–Ph(2)) 27.99(24).

almost eclipsed (deviation < 0.1°) and the distances between the centers of the two phenylene groups and metal atoms are 5.58 and 9.727(2) Å, respectively. The interplanar angle of the aromatic rings was found to be 53.73(17)°. At first sight the osmacycloferrocenophane **8e** is reminiscent of the diosma[7.7]paracyclophane[17] by replacing an $Os(CO)_4$ fragment for a ferrocene unit. However, the structures of both macrocycles are rather different. The diosma[7.7]paracyclophane has C_2 symmetry and the two phenylene functions give rise to an interplanar angle of 50.3°. Together with the metal centers they occupy the vertices of a distorted tetrahedron (metal–metal distance 10.07(2) Å). The basic cyclophane framework has a bowl-shaped structure. In the approximate boat-shaped structure of **8e** the hetero-metal–metal distance and the distance between the aromatic rings with interplanar angles of 27.99(24)° is unequal (11.468(3) and 6.52 Å, respectively). Like in **8b** the Cp-rings in **8e** are almost in the synclinal eclipsed conformation with a deviation of 9.7°. In **8b,c,e** one carbonyl ligand is more or less bent toward the "cavity" of the respective macrocycle.

2.2.2 Discussion of the Crystal Structures of 9a and 9h

The macrocycles **9a-h** consist of each two $Os(CO)_4$, $(\eta^5\text{-}C_5H_4)_2Fe$, and four *ortho*-, *meta*-, and *para*-$(CH_2)_nC_6H_4(CH_2)_n$ ($n = 2–4$) units, respectively. In the solid state **9a** is centrosymmetric with four molecules in the unit cell. All four metal atoms are located at the vertices of a distorted square with edges of 7.748(4) [Os(1)–Fe(1)] and 8.202(2) Å [Os(1)–Fe(1A)] (Figure 6). Both diagonals represent the homo-metal–metal distances of 11.611(5) [Os(1)–Os(1A)] and 10.945(3) Å [Fe(1)–Fe(1A)]. Referring to the ferrocene building blocks the cyclopentadienyl rings are between a synclinal staggered (36°) and a synclinal eclipsed (72°) conformation. The basic cyclophane framework has roughly the shape of a part of a

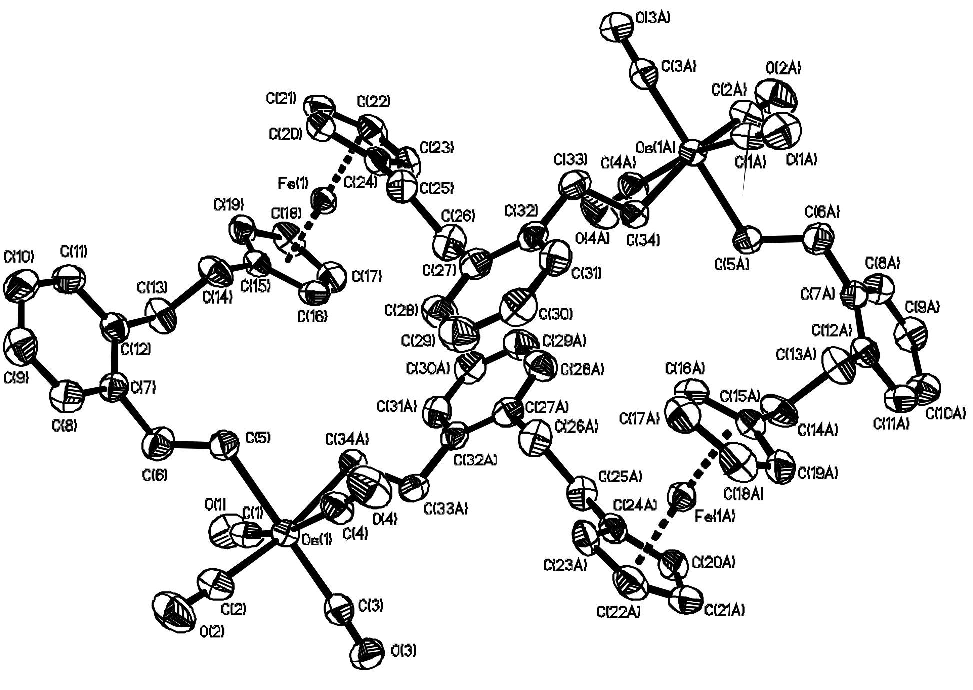


Figure 6. Crystal Structure of 9a. Selected bond lengths and angles in Å, deg: Os(1)–Fe(1) 7.748(4), Os(1)–Fe(1A) 8.202(2), Os(1)–Os(1A) 11.611(5), Fe(1)–Fe(1A) 10.945(3), Os(1)–C(5) 2.214(4), Os(1)–C(34A) 2.212(4), center Ph(1)–center Ph(2) 8.689, center Ph(1)–center Ph(1A) 17.23, center Ph(2)–center Ph(2A) 5.35, Fe–Cp(1) 1.64, Fe–Cp(2) 1.64, C(5)–Os(1)–C(34A) 85.17(15), δ 177.0, α 4.5, C(14)–Cp(1)–Cp(2)–C(25) 54.2, interplanar angle (Ph(1)–Ph(2)) 100.8.

paddle-wheel in which the centers of the phenylene rings are placed above [C(7)–C(12)/C(27)–C(32)] and below [C(7A)–C(12A)/C(27A)–C(32A)] the plane defined by the four metal atoms with distances of 3.54 and 2.54 Å, respectively. The distances of the phenylene rings related by the center of symmetry are 17.23 [C(7)–C(12)/C(7A)–C(12A)] and 5.35 Å [C(27)–C(32)/C(27A)–C(32A)].

Similarly the larger macrocycle **9h** is centrosymmetric and includes each one molecule of **9h** and *n*-hexane in the unit cell. In contrast to **9a** the four metal atoms are positioned at the vertices of a parallelogram and the edges have lengths of 17.292(3) [Os(1)–Fe(1)] and 13.124(2) Å [Os(1)–Fe(1A)]. The Os(1)–Os(1A) and Fe(1)–Fe(1A) distances of 29.850(5) and 7.173(2) Å are the diagonals of this parallelogram (Figure 7). A deviation of 5.4° from the anticlinal (eclipsed) conformation (144°) is observed for the cyclopentadienyl rings in both ferrocene units which has a significant effect on the shape of **9h**. The centers of the phenylene rings of the remarkably stretched macrocycle **9h** are above [C(9)–C(14)/C(33)–C(38)] and below [C(9A)–C(14A)/C(33A)–C(38A)] the plane defined by the four metal atoms with distances of 0.38 and 0.79 Å, respectively.

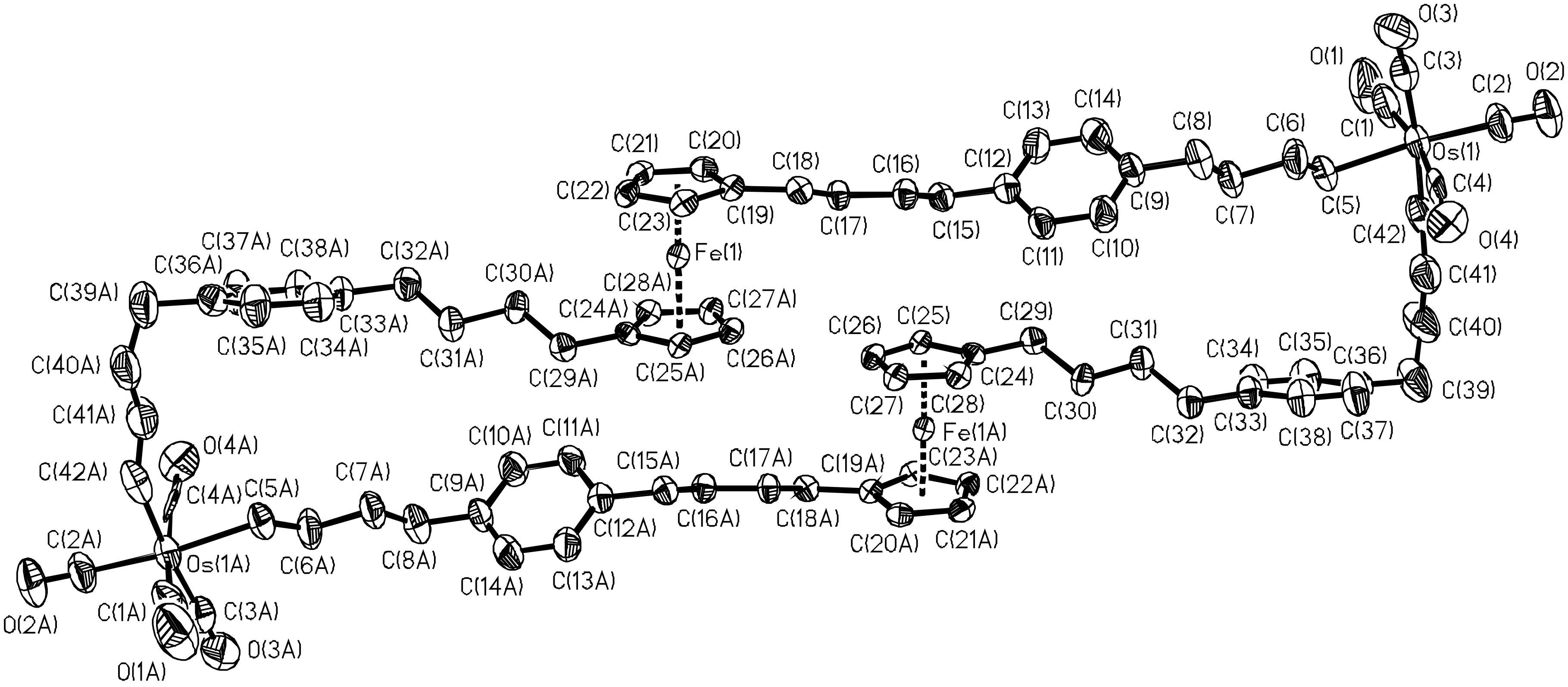


Figure 7. Crystal Structure of 9h. Selected bond lengths and angles in Å, deg: Os(1)–Fe(1) 17.292(3), Os(1)–Fe(1A) 13.124(2), Os(1)–Os(1A) 29.850(5), Fe(1)–Fe(1A) 7.173(2), Os(1)–C(5) 2.228(8), Os(1)–C(42) 2.193(12), center Ph(1)–center Ph(2) 7.650, center Ph(1)–center Ph(1A) 14.093, center Ph(2)–center Ph(2A) 23.566, Fe–Cp(1) 1.66, Fe–Cp(2) 1.66, C(5)–Os(1)–C(42) 84.0(4), δ 178.6, α 1.82(50), C(18)–Cp(1)–Cp(2)–C(29A) 149.4, interplanar angle (Ph(1)–Ph(2)) 149.4.

2.3 Electrochemical Investigations

The redox potentials of the bis(alcohols) **6a–h** and the osmacycloferrocenophanes **8a–h** were investigated by cyclic voltammetry in dependence on the chain lengths of the $(CH_2)_n$-spacers and the substitution patterns of the phenylene groups. All cyclic voltammograms of **6a–h** and **8a–h** recorded in acetonitrile as solvent, exhibit only a single oxidation/reduction peak couple within the potential window (–1.6 to 1.6 V) and are similar in shape to the unsubstituted ferrocene (ferrocene/ferrocenium cation) (Figure 8). Due to the peak potential separations (50–70 mV, scan rate v 100–10000 mV/s, theoretical: 59 mV, i_{pc}/i_{pa} ratios (1.0 ± 0.1), i_{pa} vs $v^{1/2}$ plots (linear), and $(E_{pa}+E_{pc})/2$ values (constant over the entire range of the scan rate) the electrochemical and chemical reversibility could be established. If the redox potentials $E°$ of the bis(alcohols) **6a–h** are compared to those of the corresponding osmacycloferrocenophanes

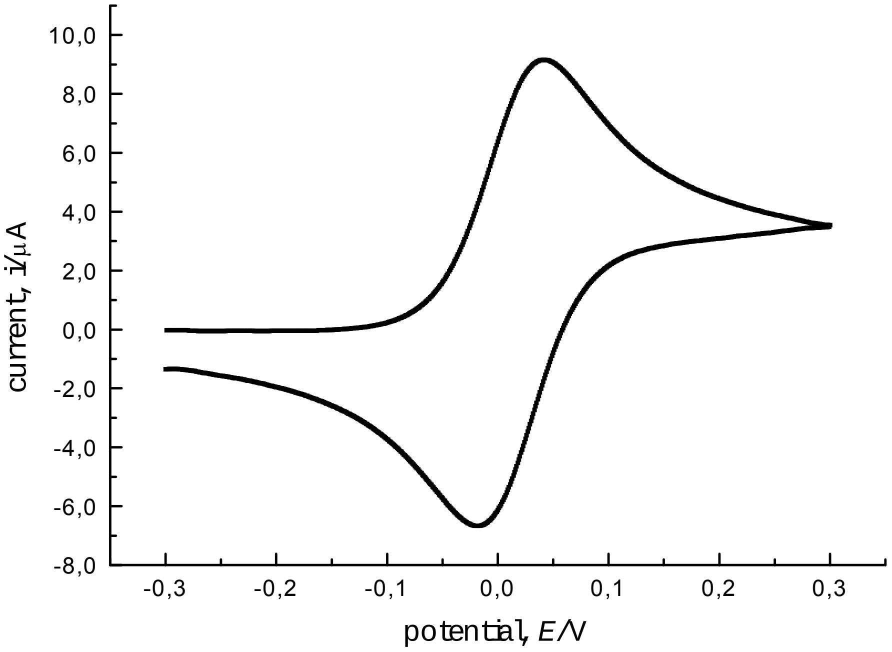


Figure 8. Cyclic voltammogram of **8c** in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate, $c = 5 \cdot 10^{-4}$ mol/L, $v = 100$ mV/s

8a–h (Table 1) only differences of the *E*° values for **6a**/**8a** and **6f**/**8f** (*ortho*-phenylene) are significant beyond the limit of error of the experiment.

Table 1. Formal Potentials of 6a-h and 8a-h versus Fc/Fc$^+$

compound	$E_{1/2}$, mV
6a/8a	-83/-72
6b/8b	-88/-87
6c/8c	-95/-89
6d/8d	-98/-101
6e/8e	-105/-102
6f/8f	-108/-93
6g/8g	-104/-103
6h/8h	-110/-110

Within this series **6a**,**f** are easier oxidized than **8a,f**. In the case of **6b–e**,**g**,**h** and **8b–e**,**g**,**h** nearly no difference was found whether there are either OH or $Os(CO)_4$ groups in the molecule. Nevertheless the *E*° values vary from –83 to –110 and –72 to –110 mV for **6a–h** and **8a–h** (Figure 9 and 10), respectively, indicating that **6a–h** and **8a–h** are easier oxidized than ferrocene itself. Compared to osmaferrocenophanes[14] the osmacycloferrocenophanes **8a–h** reveal slightly higher *E*° values. It seems that the inductive electron-donating effect of the $(CH_2)_2$-spacers in **6a–c** and **8a–c** is partially reduced due to the inductive electron withdrawing effect of the phenylene groups affecting the ferrocenes via the two methylene functions. For example the redox potentials of 1,1′-fc$(C_6H_5)_2$ and 1,1′-fc$(CH_2C_6H_5)_2$, which are provided with either no or one methylene group between the ferrocene and the benzene ring, are 40 and –40 mV,[38] respectively. Compared to these results the influence of the aromatic ring via the $(CH_2)_2$-spacer is small. On going from $(CH_2)_2$- to $(CH_2)_4$- via the $(CH_2)_3$-spacers the redox potentials converge to that one of diethylferrocene ($E°$ = –113 to –117 mV)[39–41] and higher homolgues.[38]

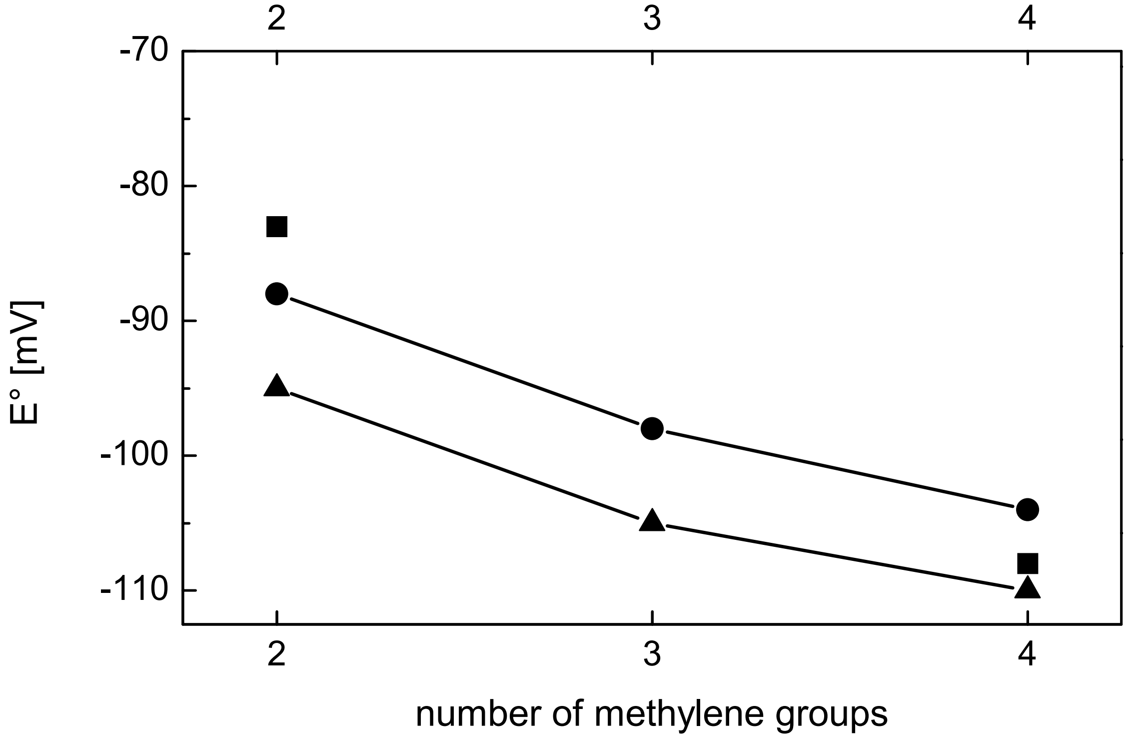


Figure 9. Redox potentials [mV] of **6a-h** as a function of the number of methylene groups; bis(alcohols): *ortho* (■), *meta* (●), *para* (▲)

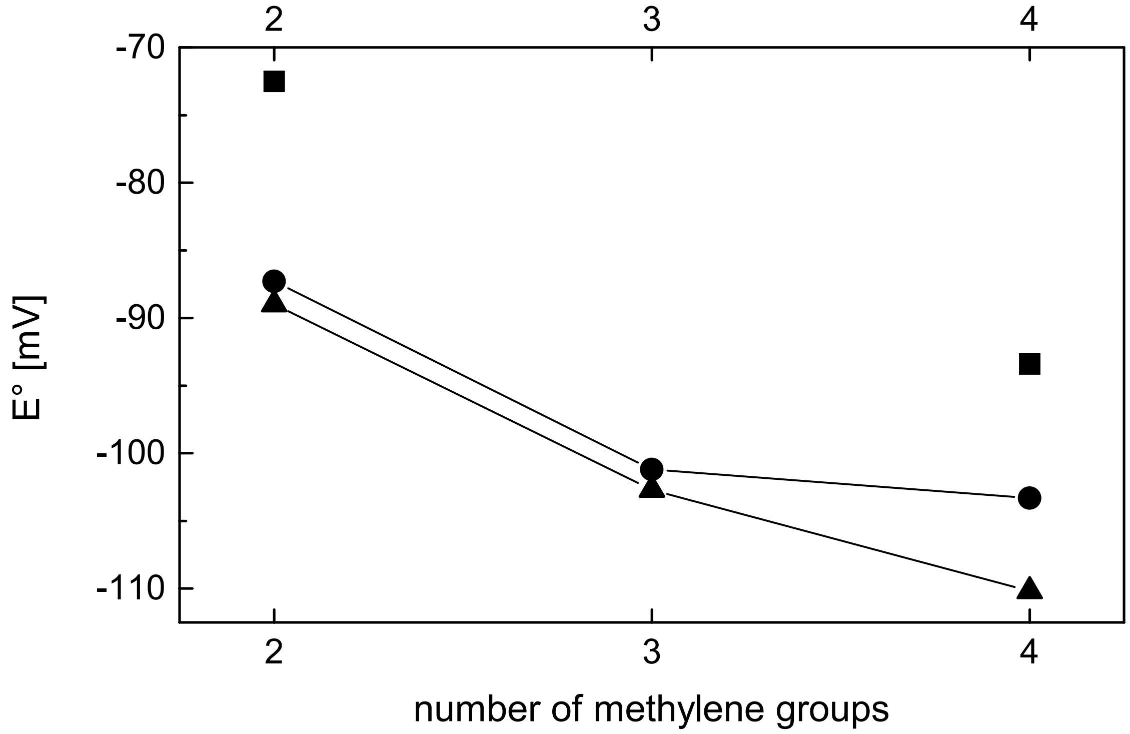


Figure 10. Redox potentials [mV] of **8a-h** as a function of the number of methylene groups; osmacycloferrocenophanes: *ortho* (■), *meta* (●), *para* (▲)

3 Conclusion

As already demonstrated in previous investigations the bis(triflate) method[14,15–17,34–36] is a versatile tool for the concomitant formation of several metal–carbon σ bonds. Dependent on the design of the hydrocarbon framework the formation of macrocycles with one,[16,36] two[14–17,36] or even three[36] transition metal centers was observed. In the present work we applied this route to combine for the first time structural features of typical metallacyclophanes with metallocenophanes. The resulting osmacycloferrocenophanes **8a-h** and **9a–h** attract attention for their thermal stability (> 100 °C) and consist of an extended hydrocarbon skeleton containing additionally two and four transition metal centers, respectively. Macrocycles of this type not only represent aesthetic structures,[15,17] but may also be regarded as valuable building blocks[42] for the synthesis of new materials with interesting properties. If in dinuclear macrocycles one transition metal fragment is replaced for a metallocene, structures may change considerably. A typical example for this observation is the comparison between the diosma[7.7]paracyclophane[17] and the osmacycloferrocenophane **3e**. While in the first case a bowl-shaped structure is preferred in **3e** a boat-like framework was established.

Regarding the yields the formation of monoosmacycloferrocenophanes **8a–h** was favored over that one of the diosmacycloferrocenophanes **9a–h**. A mechanistic reflection of this fact was already described in an earlier paper.[14] Mainly entropic effects[43] are responsible for this observation.

The cyclic voltammograms of the ferrocene derivatives **6a–h** and **8a–h** are characterized by a reversible one-electron oxidation process. However, with the exception of **6a**/**8a** and **6f**/**8f** there is no remarkable difference between the redox potentials of **6a-h** and **8a-h**. Obviously, due to the long distance between the ferrocene and the OH and $Os(CO)_4$ unit, respectively, the redox potentials are scarcely affected. A crucial factor for the *E*° values is the number of methylene functions between the ferrocene and phenylene rings and their substitution patterns. For **6a**/**8a** and **6f**/**8f** with *ortho* substituted aromatic rings, small differences are established between the bis(alcohols) and the corresponding osmacycloferrocenophanes.

Experimental Section

4 General Considerations

4.1 Working Procedures

All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques if not stated otherwise. Solvents were dried with appropriate reagents and stored under argon.

4.2 Characterization

NMR spectra were recorded at 250.13 MHz (^1H NMR), 62.90 MHz ($^{13}C\{^1H\}$ NMR), 235.33 MHz (^{19}F NMR) on a Bruker DRX 250 at 20 °C, if not stated otherwise. ^1H and ^{13}C chemical shifts were measured relative to partially deuterated and to deuterated solvent peaks, respectively, which are reported relative to TMS. ^{19}F chemical shifts were recorded relative to CCl_3F. Elemental analyses were carried out with an Elementar Vario EL analyzer. FD mass spectra were recorded on a Finnigan MAT 711 A instrument, modified by AMD and EI mass spectra were taken on a Finnigan MAT TSQ 80. IR data were obtained with a Bruker IFS 48 FTIR spectrometer.

4.3 Starting Materials

Unless otherwise noted all starting materials were obtained from commercial suppliers and used without further purification. 1,n-diallylbenzene (n = 3, 4),[44] 1,n-bis(3-hydroxypropyl)benzene (n = 3, 4), 1,n-bis(4-hydroxybutyl)benzene (n = 2–4),[45] $FeCl_2(THF)_{1.44}$[46], $Os_3(CO)_{12}$[47], and $Na_2[Os(CO)_4]$[48] were synthesized according to literature or modified literature methods. 1,n-Bis(2-hydroxyethyl)benzene (n = 2–4) was obtained by well known procedures. Subsequent to reacting α,α′-dichloro-1,n-xylene (n = 2, 3, 4) with NaCN in DMSO, the product was saponified in sulfuric acid (H_2O:H_2SO_4 (96%), 2:1), esterified with ethanol and finally reduced with $LiAlH_4$ in THF.

5 Preparation of the Compounds

5.1 General Procedure for the Preparation of the 1,n-Bis(3-butenyl)benzenes (n = 2–4) Gf–h[49]

To a solution of allylmagnesium bromide[50] decanted through a coarse porous frit, and prepared from magnesium (87.5 g, 3.6 mol in 500 mL of diethyl ether) and allyl bromide (101.5 mL, 145.2 g, 1.2 mol in 500 mL of diethyl ether) a solution of the respective α,α′-dichloro-1,n-xylene (**Aa-c**) in 500 mL of diethyl ether (87.5 g, 0.5 mol, n = 2–4) was added dropwise (diethyl ether started to reflux). Then the reaction mixture was refluxed for 12 h. Subsequent to hydrolysis with water and half concentrated sulfuric acid until no precipitate was observed, the organic layer was separated and the water phase was extracted with three portions of diethyl ether (200 mL). The organic fractions were combined and washed with water and a saturated solution of $NaHCO_3$ until no acidic reaction was detected, dried over anhydrous $MgSO_4$, and filtered. Distillation under reduced pressure afforded the pure products as colorless liquids.

5.1.1 1,2-Bis(3-butenyl)benzene (Gf)

Yield 65.3 g (71%), colorless, airstable liquid, bp_{15} = 110 °C . ^1H NMR ($CDCl_3$): δ 7.20 (s, 4H, $CH_{arom.}$), 6.04–5.88 (m, 2H, $CH_2C\mathit{H}CH_2$), 5.18–5.04 (m, 4H, $C_{arom.}CH_2CH_2CHC\mathit{H}_2$), 2.82–2.75 (m, 4H, $C_{arom.}C\mathit{H}_2CH_2CHCH_2$), 2.45–2.36 (m, 4H, $C_{arom.}CH_2C\mathit{H}_2CHCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.4 (s, $C_{arom.}$), 138.1 (s, $CH_2\mathit{C}HCH_2$), 129.0, 126.0 (s, $CH_{arom.}$), 114.8 (s, $C_{arom.}CH_2CH_2CHCH_2$), 35.2, 32.0 (s, CH_2). EI-MS: *m/z* 186.0 [M^+]. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.11; H, 10.09.

5.1.2 1,3-Bis(3-butenyl)benzene (Gg)

Yield 67.7 g (73%), colorless, airstable liquid, bp_{15} = 110 °C . ^1H NMR ($CDCl_3$): δ 7.49–7.27 (m, 4H, $CH_{arom.}$), 6.22–6.06 (m, 2H, $CH_2C\mathit{H}CH_2$), 5.36–5.24 (m, 4H, $C_{arom.}CH_2CH_2CHC\mathit{H}_2$), 2.99–2.93 (m, 4H, $C_{arom.}C\mathit{H}_2CH_2CHCH_2$), 2.69–2.63 (m, 4H, $C_{arom.}CH_2C\mathit{H}_2CHCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.7 (s, $C_{arom.}$), 138.0 (s, $CH_2\mathit{C}HCH_2$), 128.5, 128.2, 125.8 (s, $CH_{arom.}$), 114.8 (s, $C_{arom.}CH_2CH_2CH\mathit{C}H_2$), 35.6, 35.3 (s, CH_2). EI-MS: *m/z* 186.1 [M^+]. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 89.77; H, 9.81.

5.1.3 1,4-Bis(3-butenyl)benzene (Gh)

Yield 68.1 g (73%), colorless, airstable liquid, bp_{15} = 110 °C. ^1H NMR ($CDCl_3$): δ 7.36 (s, 4H, $CH_{arom.}$), 6.20–5.96 (m, 2H, $CH_2C\mathit{H}CH_2$), 5.34–5.22 (m, 4H, $C_{arom.}CH_2CH_2CHC\mathit{H}_2$), 2.97–2.89 (m, 4H, $C_{arom.}C\mathit{H}_2CH_2CHCH_2$), 2.66–2.58 (m, 4H, $C_{arom.}CH_2C\mathit{H}_2CHCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.2 (s, $C_{arom.}$), 138.1 (s, $CH_2\mathit{C}HCH_2$), 128.3 (s, $CH_{arom.}$), 114.8 (s, $C_{arom.}CH_2CH_2CH\mathit{C}H_2$), 35.6, 35.3 (s, CH_2). EI-MS: *m/z* 186.2 [M^+]. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.00; H, 9.78.

5.2 General Procedure for the Preparation of the Aromatic α,ω-Bromoalkanols 2a–h

The starting materials **1a–h** (250 mmol) dissolved in toluene (500 mL) were refluxed for 28 h with hydrobromic acid (31.3 mL, 46%) using a Dean-Stark water separator.[51,52] The reaction mixture was washed with water, and additional with a saturated solution of $NaHCO_3$ (200 mL) and water (200 mL) until no acidic reaction was detected. The organic layer was dried with magnesium sulfate, filtered and evaporated under reduced pressure. Finally the product was purified by column chromatography on silica gel (d = 10 cm, l = 40 cm, CH_2Cl_2/diethyl ether 5:2).

5.2.1 1-(2-Bromoethyl)-2-(2′-hydroxyethyl)benzene (2a)

Yield 31.8 g (56%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.05 (m, 4H, $CH_{arom.}$), 3.62 (t, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2OH), 3.41 (t, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2Br), 3.06 (*t*, $^3J_{HH}$ = 8.0 Hz, 2H, $BrCH_2CH_2C_{arom.}$), 2.90 (s, 1H, OH), 2.69 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $HOCH_2CH_2C_{arom.}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.0, 136.3 (s, $C_{arom.}$), 129.8, 129.4, 126.9, 126.5 (s, $CH_{arom.}$), 62.7 (s, CH_2OH), 35.9, 35.2, 32.1 (s, CH_2). FD-MS: *m/z* 227.7/229.8 [M^+]. Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72. Found: C, 52.70; H, 5.41.

5.2.2 1-(2-Bromoethyl)-3-(2′-hydroxyethyl)benzene (2b)[53]

Yield 38.3 g (67%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.50–7.27 (m, 4H, $CH_{arom.}$), 4.01 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2OH), 3.76 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2Br), 3.34 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $BrCH_2CH_2C_{arom.}$), 3.04 (t, $^3J_{HH}$ = 6.6 Hz, 2H, $HOCH_2CH_2C_{arom.}$) 2.37 (s, 1H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.9, 138.8 (s, $C_{arom.}$), 129.3, 128.6, 127.4, 126.6 (s, $CH_{arom.}$), 63.3 (s, CH_2OH), 39.1, 38.9, 32.9 (s, CH_2). FD-MS: *m/z* 228.0/229.9 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72. Found: C, 52.84; H, 5.59.

5.2.3 1-(2-Bromoethyl)-4-(2′-hydroxyethyl)benzene (2c)

Yield 40.8 g (71%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.16 (s, 4H, $CH_{arom.}$), 3.79 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2OH), 3.54 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2Br), 3.12 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $BrCH_2CH_2C_{arom.}$), 2.82 (t, $^3J_{HH}$ = 6.6 Hz, 2H, $HOCH_2CH_2C_{arom.}$), 2.13 (s, 1H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.1, 136.8 (s, $C_{arom.}$), 129.1, 128.7 (s, $CH_{arom.}$), 63.4 (s, CH_2OH), 38.8, 38.7, 33.0 (s, CH_2). FD-MS: *m/z* 227.8/229.7 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72. Found: C, 52.77; H, 5.28.

5.2.4 1-(3-Bromopropyl)-3-(3′-hydroxypropyl)benzene (2d)

Yield 42.3 g (66%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.19–6.96 (m, 4H, $CH_{arom.}$), 3.60 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2OH), 3.33 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2Br), 2.72–2.60 (m, 4H, $CH_2C_{arom.}$), 2.34 (s, 1H, OH), 2.13–2.04 (m, 2H, $CH_2CH_2CH_2Br$), 1.88–1.77 (m, 2H, $CH_2CH_2CH_2OH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.9, 140.4 (s, $C_{arom.}$), 128.6, 128.3, 126.1, 125.9 (s, $CH_{arom.}$), 61.9 (s, CH_2OH), 34.1, 34.0, 33.8, 33.1, 31.8 (s, CH_2). EI-MS: *m/z* 255.9/258.0 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.04; H, 6.66. Found: C, 56.07; H, 6.14.

5.2.5 1-(3-Bromopropyl)-4-(3′-hydroxypropyl)benzene (2e)

Yield 35.6 g (55%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.08 (s, 4H, $CH_{arom.}$), 3.62 (t, $^3J_{HH}$ = 6.4 Hz, 2H, CH_2OH), 3.34 (t, $^3J_{HH}$ = 6.4 Hz, 2H, CH_2Br), 3.11 (s, 1H, OH), 2.73–2.60 (m, 4H, $CH_2C_{arom.}$), 2.16–2.04 (m, 2H, $CH_2CH_2CH_2Br$), 1.89–1.78 (m, 2H, $CH_2CH_2CH_2OH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.4, 137.9 (s, $C_{arom.}$), 128.4 (s, $CH_{arom.}$), 62.0 (s, CH_2OH), 34.1, 34.0, 33.4, 33.1, 31.5 (s, CH_2). EI-MS: *m/z* 256.1/258.0 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.04; H, 6.66. Found: C, 56.01; H, 6.74.

5.2.6 1-(4-Bromobutyl)-2-(4′-hydroxybutyl)benzene (2f)

Yield 52.1 g (73%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.14 (s, 4H, $CH_{arom.}$), 3.65 (s, broad, 2H, CH_2OH), 3.44 (t, $^3J_{HH}$ = 7.85 Hz, 2H, CH_2Br), 2.65 (t, $^3J_{HH}$ = 7.85 Hz, 4H, $CH_2C_{arom.}$), 2.00–1.89 (m, 3H, $CH_2CH_2CH_2Br$, OH), 1.80–1.63 (m, 6H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.9, 139.3 (s, $C_{arom.}$), 129.1, 129.0, 126.0, 125.9 (s, $CH_{arom.}$), 62.5

(s, CH_2OH), 33.6, 32.5, 32.4, 32.2, 31.6, 29.5, 27.3 (s, CH_2). EI-MS: *m/z* 284.1/286.1 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42 Found: C, 59.03; H, 7.26.

5.2.7 1-(4-Bromobutyl)-3-(4′-hydroxybutyl)benzene (2g)

Yield 48.7 g (68%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.28–7.04 (m, 4H, $CH_{arom.}$), 3.68 (t, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2OH), 3.46 (t, $^3J_{HH}$ = 6.4 Hz, 2H, CH_2Br), 2.66 (t, $^3J_{HH}$ = 7.1 Hz, 4H, $CH_2C_{arom.}$), 1.99–1.58 (m, 9H, $CH_2CH_2CH_2$, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.3, 141.7 (s, $C_{arom.}$), 128.4, 128.2, 125.9, 125.7 (s, $CH_{arom.}$), 62.6 (s, CH_2OH), 35.5, 34.8, 33.7, 32.2, 32.1, 29.8, 27.5 (s, CH_2). EI-MS: *m/z* 284.0/285.9 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42 Found: C, 58.79; H, 7.55.

5.2.8 1-(4-Bromobutyl)-4-(4′-hydroxybutyl)benzene (2h)

Yield 46.1 g (65%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.08 (s, 4H, $CH_{arom.}$), 3.63 (t, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2OH), 3.40 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2Br), 2.60(t, $^3J_{HH}$ = 6.9 Hz, 4H, $CH_2C_{arom.}$), 1.94–1.56 (m, 9H, $CH_2CH_2CH_2$, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.8, 139.1 (s, $C_{arom.}$), 128.3, 128.2 (s, $CH_{arom.}$), 62.7 (s, CH_2OH), 35.1, 34.5, 33.7, 32.3, 32.2, 29.8, 27.5 (s, CH_2). EI-MS: *m/z* 284.1/286.0 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{14}H_{21}BrO$: C, 58.95; H, 7.42 Found: C, 58.55; H, 7.45.

5.3 General Procedure for the Preparation of the Tetrahydropyranylated Aromatic α,ω-Bromoalkanols 3a–h

The starting materials **2a–h** (150.0 mmol) and PPTS[54] (1.0 g, 4.0 mmol) were dissolved in dichloromethane (500 mL). Then 3,4-dihydro-2H-pyran (20.4 mL, 225.0 mmol) was added dropwise. The solution was stirred for 12 h at room temperature, diluted with diethyl ether (1.0 L) and washed with water (200 mL), a saturated solution of $NaHCO_3$ (200 mL) and finally with water (200 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure.

5.3.1 1-(2-Bromoethyl)-2-(2′-tetrahydropyranyloxyethyl)benzene (3a)

Yield 44.9 g (96%), colorless, airstable oil. ^{1}H NMR (CDCl$_3$): δ 7.12–7.04 (m, 4H, CH$_{\text{arom.}}$), 4.48 (t, $^3J_{\text{HH}}$ = 3.5 Hz, 1H, OCHO), 3.88–3.78 (m, 1H, C*H*HOTHP), 3.66–3.30 (m, 5H, CH*H*OTHP, OC*H*$_2$CH$_2$CH$_2$CH$_2$CHO, CH$_2$Br), 3.11 (t, $^3J_{\text{HH}}$ = 8.2 Hz, 2H, BrCH$_2$C*H*$_2$C$_{\text{arom.}}$), 2.83 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 2H, OCH$_2$C*H*$_2$C$_{\text{arom.}}$), 1.73–1.37 (m, 6H, OCH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CHO). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 137.0, 136.9 (s, C$_{\text{arom.}}$), 129.8, 129.4, 126.9, 126.3 (s, CH$_{\text{arom.}}$), 98.4 (s, OCHO), 67.73 (s, OCHO*C*H$_2$), 61.8 (s, CH$_2$OTHP), 36.2, 32.6, 32.0, 30.3, 25.2, 19.2 (s, CH$_2$). FD-MS: *m/z* 311.9/314.0 (^{79}Br/^{81}Br) [M$^+$]. Anal. Calcd for $C_{15}H_{21}BrO_2$: C, 57.52; H, 6.76 Found: C, 57.72; H, 7.13.

5.3.2. 1-(2-Bromoethyl)-3-(2′-tetrahydropyranyloxyethyl)benzene (3b)

Yield 45.5 g (97%), colorless, airstable oil. ^{1}H NMR (CDCl$_3$): δ 7.30–7.06 (m, 4H, CH$_{\text{arom.}}$), 4.63 (t, $^3J_{\text{HH}}$ = 3.3 Hz, 1H, OCHO), 4.03–3.93 (m, 1H, C*H*HOTHP), 3.81–3.44 (m, 5H, CH*H*OTHP, OC*H*$_2$CH$_2$CH$_2$CH$_2$CHO, CH$_2$Br), 3.11 (t, $^3J_{\text{HH}}$ = 8.2 Hz, 2H, BrCH$_2$C*H*$_2$C$_{\text{arom.}}$), 2.83 (t, $^3J_{\text{HH}}$ = 7.2 Hz, 2H, OCH$_2$C*H*$_2$C$_{\text{arom.}}$), 1.73-1.37 (m, 6H, OCH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CHO). ^{13}C{^{1}H}NMR (CDCl$_3$): δ 139.3, 138.6 (s, C$_{\text{arom.}}$), 129.2, 128.3, 127.4, 126.3 (s, CH$_{\text{arom.}}$), 98.4 (s, OCHO), 68.0 (s, OCHO*C*H$_2$, 61.9 (s, CH$_2$OTHP), 39.2, 36.1, 32.8, 30.5, 25.3, 19.3 (s, CH$_2$). FD-MS: *m/z* 312.0/314.1 (^{79}Br/^{81}Br) [M$^+$]. Anal. Calcd for $C_{15}H_{21}BrO_2$: C, 57.52; H, 6.76 Found: C, 57.28; H, 7.22.

5.3.3 1-(2-Bromoethyl)-4-(2′-tetrahydropyranyloxyethyl)benzene (3c)

Yield 46.3 g (99%), colorless, airstable oil. ^{1}H NMR ($CDCl_3$): δ 7.20–7.09 (m, 4H, $CH_{arom.}$), 4.58 (s, broad, 1H, OCHO), 3.97–3.41 (m, 6H, CH_2O, CH_2Br), 3.11 (t, $^3J_{HH}$ = 7.7 Hz, 2H, $BrCH_2CH_2C_{arom.}$), 2.94 (t, $^3J_{HH}$ = 7.2 Hz, 2H, $OCH_2CH_2C_{arom.}$), 1.85–1.49 (m, 6H, $OCH_2CH_2CH_2CH_2CHO$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.7, 136.5 (s, $C_{arom.}$), 129.1, 128.4 (s, $CH_{arom.}$), 98.5 (s, OCHO), 68.0 (s, $OCHOCH_2$, 62.0 (s, CH_2OTHP), 38.9, 35.9, 33.0, 30.6, 25.4, 19.4 (s, CH_2). FD-MS: *m/z* 312.0/313.9 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{15}H_{21}BrO_2$: C, 57.52; H, 6.76 Found: C, 57.16; H, 6.95.

5.3.4 1-(3-Bromopropyl)-3-(3′-tetrahydropyranyloxypropyl)benzene (3d)

Yield 50.8 g (99%), colorless, airstable oil. ^{1}H NMR ($CDCl_3$): δ 7.16–6.91 (s, 4H, $CH_{arom.}$), 4.49 (t, $^3J_{HH}$ = 3.3 Hz, 1H, OCHO), 3.83–3.64 (m, 2H, CH_2O), 3.45–3.27 (m, 4H, CH_2O, CH_2Br), 2.68–2.57 (m, 4H, $CH_2C_{arom.}$), 2.11–2.00 (m, 2H, $CH_2CH_2CH_2$), 1.85–1.49 (m, 8H, $CH_2CH_2CH_2$, $OCH_2CH_2CH_2CH_2CHO$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.1, 140.3 (s, $C_{arom.}$), 128.6, 128.3, 126.1, 125.8 (s, $CH_{arom.}$), 98.7 (s, OCHO), 66.7 (s, $OCHOCH_2$), 62.2 (s, CH_2OTHP), 34.1, 33.8, 33.0, 33.3, 31.2, 30.6, 25.4, 19.5 (s, CH_2). EI-MS: *m/z* 340.0/342.1 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{17}H_{25}BrO_2$: C, 59.83; H, 7.38 Found: C, 60.29; H, 7.90.

5.3.5 1-(3-Bromopropyl)-4-(3′-tetrahydropyranyloxypropyl)benzene (3e)

Yield 48.8 g (95%), colorless, airstable oil. ^{1}H NMR ($CDCl_3$): δ 7.02 (s, 4H, $CH_{arom.}$), 4.49 (s, broad, 1H, OCHO), 3.82–3.64 (m, 2H, CH_2O), 3.44–3.26 (m, 4H, CH_2O, CH_2Br), 2.67–2.56 (m, 4H, $CH_2C_{arom.}$), 2.10–1.99 (m, 2H, $CH_2CH_2CH_2$), 1.85–1.49 (m, 8H, $CH_2CH_2CH_2$, $OCH_2CH_2CH_2CH_2CHO$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.6, 137.6 (s, $C_{arom.}$), 128.3 (s, $CH_{arom.}$), 98.7 (s, OCHO), 66.7 (s, $OCHOCH_2$), 62.2 (s, CH_2OTHP), 34.0, 33.4, 33.0, 31.9, 31.2, 30.6, 25.3, 19.5 (s, CH_2). EI-MS: *m/z* 340.1/342.3 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{17}H_{25}BrO_2$: C, 59.83; H, 7.38 Found: C, 59.51; H, 7.62.

5.3.6 1-(4-Bromobutyl)-2-(4′-tetrahydropyranyloxybutyl)benzene (3f)

Yield 52.7 g (95%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.13 (s, 4H, $CH_{arom.}$), 4.58 (t, $^3J_{HH}$ = 3.5 Hz, 1H, OCHO), 3.91–3.74 (m, 2H, CH_2O), 3.54–3.40 (m, 4H, CH_2O, CH_2Br), 2.64 (t, $^3J_{HH}$ = 7.8 Hz, 4H, $CH_2C_{arom.}$), 1.99–1.51 (m, 14H, $CH_2CH_2CH_2$, $OCH_2CH_2CH_2CH_2CHO$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.0, 139.3 (s, $C_{arom.}$), 129.2, 129.0, 125.9, 125.8 (s, $CH_{arom.}$), 98.7 (s, OCHO), 67.2 (s, $OCHOCH_2$), 62.2 (s, CH_2OTHP), 33.5, 32.5, 32.3, 31.6, 30.7, 29.7, 29.5, 27.8, 25.4, 19.6 (s, CH_2). EI-MS: *m/z* 369.1/371.0 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{19}H_{29}BrO_2$: C, 61.79; H, 7.91 Found: C, 62.17; H, 8.26.

5.3.7 1-(4-Bromobutyl)-3-(4′-tetrahydropyranyloxybutyl)benzene (3g)

Yield 51.5 g (93 %), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.17–6.92 (m, 4H, $CH_{arom.}$), 4.50 (t, $^3J_{HH}$ = 3.3 Hz, 1H, OCHO), 3.83–3.65 (m, 2H, CH_2O), 3.46–3.29 (m, 4H, CH_2O, CH_2Br), 2.57–2.50 (m, 4H, $CH_2C_{arom.}$), 1.87–1.46 (m, 14H, $CH_2CH_2CH_2$, $OCH_2CH_2CH_2CH_2CHO$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.4, 141.6 (s, $C_{arom.}$), 128.4, 128.1, 125.9, 125.6 (s, $CH_{arom.}$), 98.7 (s, OCHO), 67.2 (s, $OCHOCH_2$), 62.1 (s, CH_2OTHP), 35.6, 34.8, 33.5, 32.1, 30.6, 29.7, 29.3, 28.1, 25.4, 19.5 (s, CH_2). EI-MS: *m/z* 368.1/370.2 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{19}H_{29}BrO_2$: C, 61.79; H, 7.91 Found: C, 62.07; H, 8.10.

5.3.8 1-(4-Bromobutyl)-4-(4′-tetrahydropyranyloxybutyl)benzene (3h)

Yield 52.7 g (95%), colorless, airstable oil. ^1H NMR ($CDCl_3$): δ 7.09 (s, 4H, $CH_{arom.}$), 4.57 (t, $^3J_{HH}$ = 3.5 Hz, 1H, OCHO), 3.90–3.72 (m, 2H, CH_2O), 3.53–3.38 (m, 4H, CH_2O, CH_2Br), 2.64–2.57 (m, 4H, $CH_2C_{arom.}$), 1.93–1.50 (m, 14H, $CH_2CH_2CH_2$,

$OCH_2CH_2CH_2CH_2CHO$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.9, 138.9 (s, $C_{arom.}$), 128.3, 128.1 (s, $CH_{arom.}$), 98.7 (s, OCHO), 67.3 (s, $OCHOCH_2$), 62.1 (s, CH_2OTHP), 35.2, 34.4, 33.6, 32.1, 30.6, 29.8, 29.3, 28.1, 25.4, 19.5 (s, CH_2). EI-MS: *m/z* 368.1/370.2 ($^{79}Br/^{81}Br$) [M^+]. Anal. Calcd for $C_{19}H_{29}BrO_2$: C, 61.79; H, 7.91 Found: C, 62.17; H, 8.45.

5.4 General Procedure for the Preparation of 4a–h

A solution of the starting materials **3a–h (**140 mmol) in THF (100 mL) was added to a suspension of NaCp · dioxane (30.7 g, 174 mmol) in THF (500 mL). The mixture was stirred for 12 h at room temperature and then concentrated to a volume of 100 mL. To this suspension diethyl ether (1.0 L) was added. This mixture was washed with water until the water layer remained colorless. The organic layer was separated, dried with anhydrous magnesium sulfate and filtered. Subsequently the solvent was evaporated under reduced pressure and the remaining oil was directly used for the preparation of the bis(alcohols) **6a-h**.

5.5 General Procedure for the Preparation of the Bis(alcohols) 6a–h

n-BuLi (70 mL, 110.0 mmol, 1.6 M in *n*-hexane) was added dropwise to a solution of **4a–h** (100.0 mmol) in *n*-hexane (400 mL) at –10 °C. The resulting suspension was stirred at room temperature for 30 min. Subsequently the precipitate was filtered (P3), washed two times with *n*-hexane (200 mL) and diethyl ether (50 mL) and dried under reduced pressure. The intermediary occurring lithium salts were dissolved in THF (300 mL), then $FeCl_2 \cdot 1.44$ THF (11.53 g, 50.0 mmol) was added and the reaction mixture was refluxed for 12 h. Subsequent the solvent was evaporated under reduced pressure, and the residue was dissolved in diethyl ether and washed three times with water (300 mL). Then the organic layer was separated and the solvent was removed in vacuo. The residue **5a-h** was dissolved in ethanol (1.0 L) and PPTS[54] (2.5 g, 9.9 mmol) was added and the solution was heated under reflux for

12 h, to remove the protecting group. After concentration of the reaction mixture to ca 100 mL, the residue was diluted in diethyl ether (1.0 L) and washed five times with water (300 mL). The organic layer was separated, dried over magnesium sulfate, filtered (P2), and evaporated to dryness. Finally the product was purified by column chromatography on silica gel ($d = 10$ cm, $l = 40$ cm, diethyl ether).

5.5.1 1,1´-Bis[2-{2-(2-hydroxyethyl)phenyl}ethyl]ferrocene (6a)

Yield 6.3 g (26%), yellow, air-stable oil. ^{1}H NMR (CDCl$_3$): δ 7.17 (s, 8H, CH$_{\text{arom.}}$), 4.02 (m,[55] 8H, C_5H_4), 3.78 (t, $^3J_{\text{HH}} = 7.1$ Hz, 4H, CH_2OH), 2.90–2.81 (m, 8H, CH$_2$C$_{\text{arom.}}$), 2.63–2.57 (m, 4H, C$H_2C_5H_4$). ^{13}C{^{1}H} NMR: δ 140.4, 135.8 (s, C$_{\text{arom.}}$), 129.8, 129.4, 126.6, 126.1 (s, CH$_{\text{arom.}}$), 88.6 (s, C_4H_4C), 68.8, 68.0 (s, C_4H_4C), 63.2 (s, CH$_2$OH) 35.7, 34.4, 31.4 (s, CH$_2$). FD-MS: *m/z* 482.3 [M$^+$]. CV: $E°$ –83 mV. Anal. Calcd for $C_{30}H_{34}FeO_2$: C, 74.69; H, 7.10. Found: C, 74.64; H, 7.36.

5.5.2 1,1´-Bis[2-{3-(2-hydroxyethyl)phenyl}ethyl]ferrocene (6b)

Yield 4.1 g (17%), yellow, air-stable oil. ^{1}H NMR (CDCl$_3$): δ 7.18–6.92 (m, 8H, CH$_{\text{arom.}}$), 3.94 (m,[55] 8H, C_5H_4), 3.73 (t, $^3J_{\text{HH}} = 6.6$ Hz, 4H, CH_2OH.), 2.77–2.71 (m, 8H, CH$_2$C$_{\text{arom.}}$), 2.56–2.49 (m, 4H, C$H_2C_5H_4$), 1.64 (s, 2H, OH). ^{13}C{^{1}H} NMR: δ 142.3, 138.4 (s, C$_{\text{arom.}}$), 129.2, 128.5, 126.4 (s, CH$_{\text{arom.}}$), 88.5 (s, C_4H_4C), 68.7, 67.9 (s, C_4H_4C), 63.6 (s, CH$_2$OH), 39.1, 37.7, 31.6 (s, CH$_2$). FD-MS: *m/z* 482.3 [M$^+$]. CV: $E°$ –88 mV. Anal. Calcd for $C_{30}H_{34}FeO_2$: C, 74.69; H, 7.10. Found: C, 75.13; H, 7.21.

5.5.3 1,1´-Bis[2-{4-(2-hydroxyethyl)phenyl}ethyl]ferrocene (6c)

Yield 5.1 g (21%), orange, air-stable solid, mp 67 °C. ^{1}H NMR (CDCl$_3$): δ 7.13 (s, 8H, CH$_{\text{arom.}}$), 4.03 (s, 8H, C_5H_4), 3.83 (t, $^3J_{\text{HH}} = 6.6$ Hz, 4H, CH_2OH), 2.86–2.75 (m, 8H,

$CH_2C_{arom.}$), 2.61–2.54 (m, 4H, C*H*$_2C_5H_4$), 1.60 (s, 2H, OH). $^{13}C\{^1H\}$ NMR: δ 140.2, 135.8 (s, $C_{arom.}$), 128.9, 128.5 (s, $CH_{arom.}$), 88.5 (s, C_4H_4*C*), 68.9, 68.1 (s, *C*$_4H_4C$), 63.7 (s, CH_2OH), 38.7, 37.2, 31.6 (s, CH_2). FD-MS: *m/z* 482.0 [M^+]. CV: *E*° –95 mV. Anal. Calcd for $C_{30}H_{34}FeO_2$: C, 74.69; H, 7.10. Found: C, 74.63; H, 6.77.

5.5.4 1,1′-Bis[3-{3-(3-hydroxypropyl)phenyl}propyl]ferrocene (6d)

Yield 4.8 g (18%), yellow, air-stable oil. ^1H NMR ($CDCl_3$): δ 7.16–6.93 (m, 8H, $CH_{arom.}$), 3.88 (s, 8H, C_5H_4), 3.58 (t, $^3J_{HH}$ = 6.5 Hz, 4H, C*H*$_2OH$), 2.63–2.29 (m, 8H, $CH_2C_{arom.}$), 2.26 (t, $^3J_{HH}$ = 7.7 Hz, 4H, C*H*$_2C_5H_4$), 1.86–1.67 (m, 8H, CH_2C*H*$_2CH_2$), 1.58 (s, 2H, OH). $^{13}C\{^1H\}$ NMR: δ 142.5, 141.7 (s, $C_{arom.}$), 128.6, 128.3, 125.9, 125.7 (s, $CH_{arom.}$), 88.8 (s, C_4H_4*C*), 68.6, 67.7 (s, *C*$_4H_4C$), 62.2 (s, CH_2OH), 35.7, 34.2, 32.7, 32.0, 28.9 (s, CH_2). FD-MS: *m/z* 538.2 [M^+]. CV: *E*° –98 mV. Anal. Calcd for $C_{34}H_{42}FeO_2$: C, 75.83; H, 7.86. Found: C, 76.12; H, 7.75.

5.5.5 1,1′-Bis[3-{4-(3-hydroxypropyl)phenyl}propyl]ferrocene (6e)

Yield 5.7 g (21%), yellow, air-stable oil. ^1H NMR ($CDCl_3$): δ 7.11 (s, 8H, $CH_{arom.}$), 3.95 (s, 8H, C_5H_4), 3.65 (t, $^3J_{HH}$ = 6.3 Hz, 4H, C*H*$_2OH$), 2.70–2.56 (m, 8H, $CH_2C_{arom.}$), 2.33 (t, $^3J_{HH}$ = 7.7 Hz, 4H, C*H*$_2C_5H_4$), 1.93–1.74 (m, 8H, CH_2C*H*$_2CH_2$), 1.54 (s, 2H, OH). $^{13}C\{^1H\}$ NMR: δ 139.9, 139.0 (s, $C_{arom.}$), 128.4, 128.3 (s, $CH_{arom.}$), 88.8 (s, C_4H_4*C*), 68.5, 67.7 (s, *C*$_4H_4C$), 62.2 (s, CH_2OH), 35.3, 34.2, 32.7, 31.6, 28.8 (s, CH_2). FD-MS: *m/z* 538.2 [M^+]. CV: *E*° –105 mV. Anal. Calcd for $C_{34}H_{42}FeO_2$: C, 75.83; H, 7.86. Found: C, 75.75; H, 8.08.

5.5.6 1,1′-Bis[4-{2-(4-hydroxybutyl)phenyl}butyl]ferrocene (6f)

Yield 8.0 g (27%), yellow, air-stable oil. ^1H NMR ($CDCl_3$): δ 7.13 (s, 8H, $CH_{arom.}$), 3.97 (s, 8H, C_5H_4), 3.65 (s broad, 4H, C*H*$_2OH$), 2.67–2.59 (m, 8H, $CH_2C_{arom.}$), 2.35 (t, $^3J_{HH}$ =

6.6 Hz, 4H, $CH_2C_5H_4$), 1.67–1.58 (m, 18H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR: δ 140.2, 139.9 (s, $C_{arom.}$), 129.1, 129.0, 125.8, 125.8 (s, $CH_{arom.}$), 88.9 (s, C_4H_4C), 68.6, 67.6 (s, C_4H_4C), 62.7 (s, CH_2OH), 32.6, 32.5, 32.3, 31.3, 31.1, 29.3, 27.3 (s, CH_2). FD-MS: *m/z* 594.1 [M^+]. CV: *E*° –108 mV. Anal. Calcd for $C_{38}H_{50}FeO_2$: C, 76.75; H, 8.48. Found: C, 77.09; H, 8.49.

5.5.7 1,1′-Bis[4-{3-(4-hydroxybutyl)phenyl}butyl]ferrocene (6g)

Yield 10.4 g (35%), yellow, air-stable oil. ^1H NMR ($CDCl_3$): δ 7.16–6.91 (m, 8H, $CH_{arom.}$), 3.87 (m,[55] 8H, C_5H_4), 3.56 (t, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2OH), 2.56–2.48 (m, 8H, $CH_2C_{arom.}$), 2.24 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $CH_2C_5H_4$), 1.66–1.44 (m, 18H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR: δ 142.6, 142.2 (s, $C_{arom.}$), 128.5, 128.1, 125.8, 125.7 (s, $CH_{arom.}$), 89.1 (s, C_4H_4C), 68.6, 67.6 (s, C_4H_4C), 62.7 (s, CH_2OH), 35.7, 35.6, 32.3, 31.4, 30.9, 29.2, 27.5 (s, CH_2). FD-MS: *m/z* 594.4 [M^+]. CV: *E*° –104 mV. Anal. Calcd for $C_{38}H_{50}FeO_2$: C, 76.75; H, 8.48. Found: C, 76.71; H, 8.38.

5.5.8 1,1′-Bis[4-{4-(4-hydroxybutyl)phenyl}butyl]ferrocene (6h)

Yield 6.8 g (23%), orange, air-stable solid, mp 48 °C. ^1H NMR ($CDCl_3$): δ 7.08 (s, 8H, $CH_{arom.}$), 3.92 (s, 8H, C_5H_4), 3.62 (t, $^3J_{HH}$ = 6.1 Hz, 4H, CH_2OH), 2.62–2.54 (m, 8H, $CH_2C_{arom.}$), 2.29 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $CH_2C_5H_4$), 1.72–1.47 (m, 16H, $CH_2CH_2CH_2$), 1.34 (s, 2H, OH). $^{13}C\{^1H\}$ NMR: δ 140.0, 139.5 (s, $C_{arom.}$), 128.3 (s, $CH_{arom.}$), 89.2 (s, C_4H_4C), 68.6, 67.7 (s, C_4H_4C), 62.8 (s, CH_2OH), 35.3, 35.2, 32.3, 31.4, 30.8, 29.2, 27.6 (s, CH_2). FD-MS: *m/z* 594.4 [M^+]. CV: *E*° –110 mV. Anal. Calcd for $C_{38}H_{50}FeO_2$: C, 76.75; H, 8.48. Found: C, 76.99; H, 8.24.

5.6 General Procedure for the Preparation of the Bis(triflates) 7a–h

To a solution of the corresponding alcohol **6a–h** (2.0 mmol) and pyridine (0.35 mL, 4.3 mmol) in 10 mL of dichloromethane at –30 °C, a mixture of trifluoromethanesulfonic acid anhydride (0.68 mL, 4.2 mmol) and 10 mL of dichloromethane was added within 15 min. The reaction mixture was stirred for a further 20 min at –30 °C, then washed with water and purified by column chromatography with activated silica gel (d = 2.5 cm, l = 10 cm, CH_2Cl_2, –30 °C). Finally the solvent was evaporated under reduced pressure at –30 °C.

5.6.1 1,1´-Bis[2-{2-(2-trifluoromethylsulfonyloxyethyl)phenyl}ethyl]ferrocene (7a)

Yield 806 mg (54%), yellow oil, dec 20 °C. ^{1}H NMR (CD_2Cl_2): δ 7.25–7.19 (m, 8H, $CH_{arom.}$), 4.63 (t, $^3J_{HH}$ = 7.4 Hz, 4H, CH_2OTf), 4.09 (m,[55] 8H, C_5H_4), 3.12 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $TfOCH_2C\mathit{H}_2C_{arom.}$), 2.87–2.81 (m, 4H, $C_5H_4CH_2C\mathit{H}_2C_{arom.}$), 2.63–2.57 (m, 4H, $C\mathit{H}_2C_5H_4$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.8, 132.6 (s, $C_{arom.}$), 129.9, 127.7, 126.5 (s, $CH_{arom.}$), 118.7 (q, $^1J_{FC}$ = 319.3 Hz, CF_3), 89.0 (s, $C_4H_4\mathit{C}$), 77.3 (s, CH_2OTf), 69.6, 68.9 (s, C_4H_4C), 34.4, 32.5, 31.5 (s, CH_2). ^{19}F NMR (CD_2Cl_2): δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 937, 1147, 1215, 1246, 1419. FD-MS: *m/z* 746.1 [M^+].

5.6.2 1,1´-Bis[2-{3-(2-trifluoromethylsulfonyloxyethyl)phenyl}ethyl]ferrocene (7b)

Yield 730 mg (49%), yellow oil, dec 20 °C. ^{1}H NMR (CD_2Cl_2): δ 7.34–7.09 (m, 8H, $CH_{arom.}$), 4.74 (t, $^3J_{HH}$ = 6.9 Hz, 4H, CH_2OTf), 4.07 (m,[55] 8H, C_5H_4), 3.13 (t, $^3J_{HH}$ = 6.9 Hz, 4H, $TfOCH_2C\mathit{H}_2C_{arom.}$), 2.90–2.83 (m, 4H, $C_5H_4CH_2C\mathit{H}_2C_{arom.}$), 2.72–2.66 (m, 4H, $C\mathit{H}_2C_5H_4$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.0, 135.0 (s, $C_{arom.}$), 129.3, 128.8, 127.6, 126.5 (s, $CH_{arom.}$), 118.8 (q, $^1J_{FC}$ = 320.0 Hz, CF_3), 88.6 (s, $C_4H_4\mathit{C}$), 77.8 (s, CH_2OTf), 68.9, 68.1 (s, C_4H_4C), 37.7, 35.6, 31.7 (s, CH_2). ^{19}F NMR (CD_2Cl_2): δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 942, 1147, 1215, 1246, 1419. FD-MS: *m/z* 745.6 [M^+].

5.6.3 1,1′-Bis[2-{4-(2-trifluoromethylsulfonyloxyethyl)phenyl}ethyl]ferrocene (7c)

Yield 746 mg (50%), yellow oil, dec 20 °C. ^{1}H NMR (CD_2Cl_2): δ 7.15 (s, 8H, $CH_{arom.}$), 4.70 (t, $^3J_{HH}$ = 6.9 Hz, 4H, CH_2OTf), 4.07 (s, 8H, C_5H_4), 3.10 (t, $^3J_{HH}$ = 6.9 Hz, 4H, $TfOCH_2CH_2C_{arom.}$), 2.83–2.76 (m, 4H, $C_5H_4CH_2CH_2C_{arom.}$), 2.63–2.57 (m, 4H, $CH_2C_5H_4$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 141.6, 132.5 (s, $C_{arom.}$), 129.0, (s, $CH_{arom.}$), 118.7 (q, $^1J_{FC}$ = 319.3 Hz, CF_3), 88.6 (s, C_4H_4C), 77.9 (s, CH_2OTf), 68.9, 68.1 (s, C_4H_4C), 37.3, 35.3, 31.6 (s, CH_2). ^{19}F NMR (CD_2Cl_2): δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 939, 1147, 1214, 1246, 1419. FD-MS: *m/z* 745.8 [M$^+$].

5.6.4 1,1′-Bis[3-{3-(3-trifluoromethylsulfonyloxypropyl)phenyl}propyl]ferrocene (7d)

Yield 930 mg (58%), yellow oil, dec 20 °C. ^{1}H NMR (CD_2Cl_2): δ 7.25–7.00 (m, 8H, $CH_{arom.}$), 4.55 (t, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2OTf), 3.96 (s, 8H, C_5H_4), 2.73 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $TfOCH_2CH_2C_{arom.}$), 2.61 (t, $^3J_{HH}$ = 7.9 Hz, 4H, $C_5H_4CH_2CH_2C_{arom.}$), 2.34 (t, $^3J_{HH}$ = 7.7 Hz, 4H, $CH_2C_5H_4$), 2.19–2.08 (m, 4H, $TfOCH_2CH_2CH_2C_{arom.}$), 1.86–1.73 (m, 4H, $C_5H_4CH_2CH_2CH_2C_{arom.}$). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): δ 143.1, 139.8 (s, $C_{arom.}$), 128.6, 126.6, 125.7 (s, $CH_{arom.}$), 118.7 (q, $^1J_{FC}$ = 319.4 Hz, CF_3), 88.9 (s, C_4H_4C), 77.3 (s, CH_2OTf), 68.7, 67.9 (s, C_4H_4C), 35.7, 32.9, 31.1, 30.9, 29.0 (s, CH_2). ^{19}F NMR (CD_2Cl_2): δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 932, 1148, 1215, 1247, 1419. FD-MS: *m/z* 802.0 [M$^+$].

5.6.5 1,1′-Bis[3-{4-(3-trifluoromethylsulfonyloxypropyl)phenyl}propyl]ferrocene (7e)

Yield 1076 mg (67%), yellow oil, dec 20 °C. ^{1}H NMR (CD_2Cl_2): δ 7.14 (s, 8H, $CH_{arom.}$), 4.56 (t, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2OTf), 3.98 (s, 8H, C_5H_4), 2.74 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $TfOCH_2CH_2C_{arom.}$), 2.62 (t, $^3J_{HH}$ = 7.7 Hz, 4H, $C_5H_4CH_2CH_2C_{arom.}$), 2.35 (t, $^3J_{HH}$ = 7.7 Hz, 4H, $CH_2C_5H_4$), 2.19–2.08 (m, 4H, $TfOCH_2CH_2CH_2C_{arom.}$), 1.87–1.75 (m, 4H, $C_5H_4CH_2CH_2CH_2C_{arom.}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.8, 137.1 (s, $C_{arom.}$), 128.7, 128.3 (s,

$CH_{arom.}$), 118.8 (q, $^1J_{FC}$ = 319.3 Hz, CF_3), 89.2 (s, C_4H_4C), 77.3 (s, CH_2OTf), 68.8, 68.0 (s, C_4H_4C), 35.4, 32.9, 30.9, 30.7, 28.9 (s, CH_2). ^{19}F NMR: δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 931, 1148, 1215, 1247, 1419. FD-MS: *m/z* 801.7 [M^+].

5.6.6 1,1´-Bis[4-{2-(4-trifluoromethylsulfonyloxybutyl)phenyl}butyl]ferrocene (7f)

Yield 1407 mg (82%), yellow oil, dec 20 °C. ^1H NMR (CD_2Cl_2): δ 7.13 (s, 8H, $CH_{arom.}$), 4.57 (t, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2OTf), 3.98 (s, 8H, C_5H_4), 2.70–2.59 (m, 8H, $CH_2C_{arom.}$), 2.35 (t, $^3J_{HH}$ = 6.7 Hz, 4H, $CH_2C_5H_4$), 1.95–1.85 (m, 4H, $TfOCH_2CH_2$), 1.76–1.53 (m, 12H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.6, 139.1 (s, $C_{arom.}$), 129.4, 129.1, 126.2, 125.9 (s, $CH_{arom.}$), 118.7 (q, $^1J_{FC}$ = 319.4 Hz, CF_3), 89.7 (s, C_4H_4C), 78.1 (s, CH_2OTf), 69.0, 68.2 (s, C_4H_4C), 32.6, 31.8, 31.4, 31.3, 29.3, 29.2, 26.7 (s, CH_2). ^{19}F NMR (CD_2Cl_2): δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 933, 1148, 1215, 1247, 1419. FD-MS: *m/z*: 858.0 [M^+].

5.6.7 1,1´-Bis[4-{3-(4-trifluoromethylsulfonyloxybutyl)phenyl}butyl]ferrocene (7g)

Yield 1184 mg (69%), yellow oil, dec 20 °C. ^1H NMR (CD_2Cl_2): δ 7.22–6.97 (m, 8H, $CH_{arom.}$), 4.55 (t, $^3J_{HH}$ = 6.1 Hz, 4H, CH_2OTf), 3.95 (s, 8H, C_5H_4), 2.66–2.55 (m, 8H, $CH_2C_{arom.}$), 2.32 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $CH_2C_5H_4$), 1.90–1.51 (m, 16H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 143.1, 141.4 (s, $C_{arom.}$), 128.6, 128.3, 126.2, 125.7 (s, $CH_{arom.}$), 118.7 (q, $^1J_{FC}$ = 319.4 Hz, CF_3), 90.2 (s, C_4H_4C), 78.1 (s, CH_2OTf), 69.2, 68.3 (s, C_4H_4C), 35.8, 35.0, 31.6, 31.0, 29.2, 28.8, 26.9 (s, CH_2). ^{19}F NMR: δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 934, 1148, 1214, 1247, 1418. FD-MS: *m/z* 857.7 [M^+].

5.6.8 1,1′-Bis[4-{4-(4-trifluoromethylsulfonyloxybutyl)phenyl}butyl]ferrocene (7h)

Yield 1270 mg (74%), yellow oil, dec 20 °C. ^{1}H NMR (CD_2Cl_2): δ 7.10 (s, 8H, $CH_{arom.}$), 4.55 (t, $^3J_{HH}$ = 6.1 Hz, 4H, CH_2OTf), 3.96 (s, 8H, C_5H_4), 2.66–2.56 (m, 8H, $CH_2C_{arom.}$), 2.31 (t, $^3J_{HH}$ = 7.4 Hz, 4H, $CH_2C_5H_4$), 1.90–1.47 (m, 16H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.6, 138.6 (s, $C_{arom.}$), 128.5, 128.3 (s, $CH_{arom.}$), 118.7 (q, $^1J_{FC}$ = 319.4 Hz, CF_3), 90.2 (s, C_4H_4C), 78.1 (s, CH_2OTf), 69.2, 68.3 (s, C_4H_4C), 35.4, 34.6, 31.6, 30.9, 29.1, 28.8, 27.0 (s, CH_2). ^{19}F NMR (CD_2Cl_2): δ –75.7 (s, CF_3). IR (CCl_4, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 933, 1148, 1215, 1247, 1419. FD-MS: *m/z* 858.3 [M^+].

5.7 General Procedure for the Preparation of the Osmacycloferrocenophanes 8a–h and Diosmacycloferrocenophanes 9a–h

A solution of the bis(triflates) **7a–h** (1.0 mmol) in 10 and 90 mL of diethyl and dimethyl ether at –80 °C, respectively, was added dropwise within 4h to a suspension of $Na_2[Os(CO)_4]$ (348.2 mg, 1.0 mmol) in 100 mL of refluxing dimethyl ether. Stirring and refluxing this mixture for 3d afforded a yellow clear solution and a yellow-brown precipitate. After evaporation of the solvents the residue was extracted three times with 200 mL of *n*-pentane. The insoluble components were filtered off (P4), and the solvent was evaporated under reduced pressure leaving the crude products, which were purified by column chromatography on silica gel (*l* = 20 cm, *n*-pentane/Et_2O 50:1 (**8a–h**); *n*-pentane/Et_2O 25:1 (**9a–h**)). Recrystallization from *n*-pentane at –80 °C afforded the analytically pure osmacycloferrocenophanes **8a–h** and diosmacycloferrocenophanes **9a–h**.

5.7.1 11,11,11,11-Tetracarbonyl-11-osma[2]orthocyclo[5]orthocyclo[2](1,1′)ferrocenophane (8a)

Yield 113 mg (15%), yellow, air-stable crystals, mp 151 °C. ^{1}H NMR (CD_2Cl_2): δ 7.21–7.01 (m, 8H, $CH_{arom.}$), 4.02 (m,[56] 8H, C_5H_4), 3.10 (m,[57] N = 17.8 Hz, 4H, $OsCH_2C\mathit{H}_2C_{arom.}$), 2.91–2.84 (m, 4H, $C_5H_4CH_2C\mathit{H}_2C_{arom.}$), 2.70–2.64 (m, 4H, $C\mathit{H}_2C_5H_4$), 1.41 (m,[58] N = 17.6 Hz, 4H, CH_2Os). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 180.4 (s, $OsCO_{ax.}$), 172.5 (s, $OsCO_{eq.}$), 147.4, 140.5 (s, $C_{arom.}$), 131.4, 130.8, 127.7, 127.2 (s, $CH_{arom.}$), 90.4 (s, $C_4H_4\mathit{C}$), 70.6, 68.7 (s, C_4H_4C), 42.7, 36.1, 33.6 (s, CH_2), –0.8 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2124, 2045, 2035, 2012. FD-MS: *m/z* 752.0 [M$^+$]. CV: *E*° –72 mV. Anal. Calcd for $C_{34}H_{32}FeO_4Os$: C, 54.40; H, 4.30. Found: C, 54.08; H, 4.04.

5.7.2 11,11,11,11-Tetracarbonyl-11-osma[2]metacyclo[5]metacyclo[2](1,1′)ferrocenophane (8b)

Yield 173 mg (23%), yellow, air-stable crystals, mp 122 °C. ^{1}H NMR (CD_2Cl_2): δ 7.21–6.94 (m, 8H, $CH_{arom.}$), 4.03 (m,[56] 8H, C_5H_4), 3.03 (m,[57] N = 17.9 Hz, 4H, $OsCH_2C\mathit{H}_2C_{arom.}$), 2.82–2.66 (m, 8H, $CH_2C_{arom.}$, $C\mathit{H}_2C_5H_4$), 1.40 (m,[58] N = 17.9 Hz, 4H, CH_2Os). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 178.2 (s, $OsCO_{ax.}$), 171.1 (s, $OsCO_{eq.}$), 142.8, 142.5 (s, $C_{arom.}$), 128.2, 127.3, 125.8, 125.3 (s, $CH_{arom.}$), 89.0 (s, $C_4H_4\mathit{C}$), 69.3, 67.3 (s, C_4H_4C), 43.6, 38.5, 32.1 (s, CH_2), 0.7 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2126, 2044, 2040, 2012. FD-MS: *m/z* 752.0 [M$^+$]. CV: *E*° –87 mV. Anal. Calcd for $C_{34}H_{32}FeO_4Os$: C, 54.40; H, 4.30. Found: C, 54.37; H, 3.89.

5.7.3 11,11,11,11-Tetracarbonyl-11-osma[2]paracyclo[5]paracyclo[2](1,1′)ferrocenophane (8c)

Yield 128 mg (17%), yellow, air-stable crystals, dec 172 °C. ^{1}H NMR (CD_2Cl_2): δ 7.10–7.00 (m, 8H, $CH_{arom.}$), 4.07 (m,[56] 8H, C_5H_4), 3.19–3.15 (m, 4H, $OsCH_2CH_2C_{arom.}$), 2.56–2.49 (m, 4H, $C_5H_4CH_2CH_2C_{arom.}$), 2.15–2.08 (m, 4H, $CH_2C_5H_4$), 1.30–1.26 (m, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 176.2 (s, $OsCO_{ax.}$), 171.4 (s, $OsCO_{eq.}$), 142.8, 140.7 (s, $C_{arom.}$), 128.8, 128.1 (s, $CH_{arom.}$), 88.2 (s, C_4H_4C), 68.3, 67.2 (s, C_4H_4C), 41.2, 39.3, 33.0 (s, CH_2), 1.8 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2128, 2050, 2036, 2001. FD-MS: *m/z* 751.7 [M^+]. CV: $E°$ –89 mV. Anal. Calcd for $C_{34}H_{32}FeO_4Os$: C, 54.40; H, 4.30. Found: C, 54.20; H, 4.25.

5.7.4 13,13,13,13-Tetracarbonyl-13-osma[3]metacyclo[7]metacyclo[3](1,1′)ferrocenophane (8d)

Yield 163 mg (20%), yellow, air-stable crystals, mp 61.3 °C. ^{1}H NMR (CD_2Cl_2): δ 7.21–6.97 (m, 8H, $CH_{arom.}$), 3.93 (m,[56] 8H, C_5H_4), 2.64–2.56 (m, 8H, $CH_2C_{arom.}$), 2.28 (t,$^3J_{HH}$ = 7.5 Hz, 4H, $CH_2C_5H_4$), 2.12–1.99 (m, 4H, $OsCH_2CH_2CH_2C_{arom.}$), 1.91–1.79 (m, 4H, $C_5H_4CH_2CH_2CH_2C_{arom.}$), 1.01 (m,[58] N = 17.0 Hz, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 178.9 (s, $OsCO_{ax.}$), 171.1 (s, $OsCO_{eq.}$), 142.3 (s, $C_{arom.}$), 128.6, 128.1, 126.0, 125.8 (s, $CH_{arom.}$), 89.2 (s, C_4H_4C), 68.6, 67.3 (s, C_4H_4C), 42.4, 39.1, 35.6, 32.3, 28.2 (s, CH_2), –3.9 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2125, 2039, 2009. FD-MS: *m/z* 808.5 [M^+]. CV: $E°$ –101 mV. Anal. Calcd for $C_{38}H_{40}FeO_4Os$: C, 56.57; H, 5.00. Found: C, 56.42; H, 4.64.

5.7.5 13,13,13,13-Tetracarbonyl-13-osma[3]paracyclo[7]paracyclo[3](1,1′)ferrocenophane (8e)

Yield 183 mg (23%), yellow, air-stable crystals, mp 127.5 °C. ^{1}H NMR (CD_2Cl_2): δ 7.14–7.06 (m, 8H, $CH_{arom.}$), 3.95 (m,[56] 8H, C_5H_4), 2.66–2.53 (m, 8H, $CH_2C_{arom.}$), 2.32 (t, $^3J_{HH}$

= 8.0 Hz, 4H, C*H*$_2$C$_5$H$_4$), 2.08–1.82 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 0.96 (m,[58] N = 17.3 Hz, 4H, CH$_2$Os). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 178.8 (s, OsCO$_{ax.}$), 171.0 (s, OsCO$_{eq.}$), 139.6, 139.4 (s, C$_{arom.}$), 128.5, 128.2 (s, CH$_{arom.}$), 89.3 (s, C$_4$H$_4$*C*), 68.7, 67.1 (s, *C*$_4$H$_4$C), 41.6, 38.2, 35.2, 31.8, 28.0 (s, CH$_2$), –5.5 (s, CH$_2$Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2125, 2040, 2009. FD-MS: *m/z* 808.4 [M$^+$]. CV: *E*° –102 mV. Anal. Calcd for $C_{38}H_{40}FeO_4Os$: C, 56.57; H, 5.00. Found: C, 56.31; H, 4.99.

5.7.6 15,15,15,15-Tetracarbonyl-15-osma[4]orthocyclo[9]orthocyclo[4](1,1′)ferrocenophane (8f)

Yield 173 mg (20%), yellow, air-stable crystals, mp 90.3 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.16–7.08 (m, 8H, CH$_{arom.}$), 3.97 (m,[56] 8H, C$_5$H$_4$), 2.70–2.64 (m, 8H, CH$_2$C$_{arom.}$), 2.37 (t, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*$_2$C$_5$H$_4$), 1.97–1.85 (m, 4H, CH$_2$C*H*$_2$CH$_2$Os), 1.67–1.51 (m, 12H, CH$_2$C*H*$_2$CH$_2$), 1.14–1.07 (m,[58] N = 17.3 Hz, 4H, CH$_2$Os). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 179.5 (s, OsCO$_{ax.}$), 171.2 (s, OsCO$_{eq.}$), 141.0, 140.6 (s, C$_{arom.}$), 129.4, 129.3, 125.8, 125.7 (s, CH$_{arom.}$), 89.2 (s, C$_4$H$_4$*C*), 68.7, 67.6 (s, *C*$_4$H$_4$C), 38.8, 38.7, 32.8, 32.4, 31.7, 31.2, 29.1 (s, CH$_2$), –3.2 (s, CH$_2$Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2124, 2039, 2010. FD-MS: *m/z* 863.7 [M$^+$]. CV: *E*° –93 mV. Anal. Calcd for $C_{42}H_{48}FeO_4Os$: C, 58.46; H, 5.61. Found: C, 58.23; H, 5.35.

5.7.7 15,15,15,15-Tetracarbonyl-15-osma[4]metacyclo[9]metacyclo[4](1,1′)ferrocenophane (8g)

Yield 226 mg (26%), yellow, air-stable crystals, mp 82.1 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.14–6.98 (m, 8H, CH$_{arom.}$), 3.93 (m,[56] 8H, C$_5$H$_4$), 2.65–2.57 (m, 8H, CH$_2$C$_{arom.}$), 2.33 (t, $^3J_{HH}$ = 7.7 Hz, 4H, C*H*$_2$C$_5$H$_4$), 1.83–1.51 (m, 16H, CH$_2$C*H*$_2$CH$_2$), 1.04 (m,[58] N = 17.0 Hz, 4H, CH$_2$Os). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 179.3 (s, OsCO$_{ax.}$), 171.2 (s, OsCO$_{eq.}$), 143.1, 142.7 (s,

$C_{arom.}$), 128.5, 128.1, 125.8 (s, $CH_{arom.}$), 89.4 (s, $C_4H_4\mathit{C}$), 68.9, 67.4 (s, C_4H_4C), 38.7, 37.7, 35.7, 35.2, 31.7, 31.0, 29.3 (s, CH_2), –3.1 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2125, 2040, 2008. FD-MS: *m/z* 863.7 [M^+]. CV: *E*° –103 mV. Anal. Calcd for $C_{42}H_{48}FeO_4Os$: C, 58.46; H, 5.61. Found: C, 58.31; H, 5.21.

5.7.8 15,15,15,15-Tetracarbonyl-15-osma[4]paracyclo[9]paracyclo[4](1,1′)ferrocenophane (8h)

Yield 232 mg (27%), yellow, air-stable crystals, mp 73.3 °C. ^1H NMR (CD_2Cl_2): *δ* 7.09 (s, 8H, $CH_{arom.}$), 3.89 (m,[56] 8H, C_5H_4), 2.63–2.57 (m, 8H, $CH_2C_{arom.}$), 2.25 (t, $^3J_{HH}$ = 7.7 Hz, 4H, $C\mathit{H}_2C_5H_4$), 1.72–1.46 (m, 16H, $CH_2C\mathit{H}_2CH_2$), 0.97–0.91 (m, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 179.0 (s, $OsCO_{ax.}$), 171.2 (s, $OsCO_{eq.}$), 140.1, 139.7 (s, $C_{arom.}$), 128.5, 128.3 (s, $CH_{arom.}$), 89.4 (s, $C_4H_4\mathit{C}$), 68.5, 67.2 (s, C_4H_4C), 37.6, 36.5, 35.1, 34.2, 31.4, 29.9, 28.7 (s, CH_2), –4.0 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2125, 2040, 2008. FD-MS: *m/z* 863.7 [M^+]. CV: *E*° –110 mV. Anal. Calcd for $C_{42}H_{48}FeO_4Os$: C, 58.46; H, 5.61. Found: C, 58.53; H, 5.61.

5.7.9 11,11,11,11,43,43,43,43-Octacarbonyl-11,43-diosma[2]orthocyclo[5]orthocyclo[2]-(1,1′)ferroceno[2]orthocyclo[5]orthocyclo[2](1,1′)ferrocenophane (9a)

Yield 17 mg (2%), pale yellow, air-stable crystals, mp 152°C. ^1H NMR (CD_2Cl_2): *δ* 7.15–7.09 (m, 16H, $CH_{arom.}$), 3.93 (s, 16H, C_5H_4), 2.95 (m,[57] N = 17.9 Hz, 8H, $OsCH_2C\mathit{H}_2C_{arom.}$), 2.91–2.84 (m, 8H, $C_5H_4CH_2C\mathit{H}_2C_{arom.}$), 2.61–2.54 (m, 8H, $C\mathit{H}_2C_5H_4$), 1.24 (m,[58] N = 17.9 Hz, 8H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 179.1 (s, $OsCO_{ax.}$), 171.0 (s, $OsCO_{eq.}$), 146.0, 139.0 (s, $C_{arom.}$), 129.3, 128.7, 126.2, 125.7 (s, $CH_{arom.}$), 88.5 (s, $C_4H_4\mathit{C}$), 68.6, 68.1 (s, C_4H_4C), 41.3, 34.5, 31.7 (s, CH_2), –1.4 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *ν*(CO) 2124, 2045, 2038, 2012. FD-MS: *m/z* 1496 (5%), 1497 (15%), 1498 (53%), 1499 (61%), 1500

(76%), 1501 (83%), 1502 (100%), 1503 (86%), 1504 (58%), 1505 (35%), 1506 (10%); Calcd 1496 (14%), 1497 (25%), 1498 (47%), 1499 (58%), 1500 (82%), 1501 (82%), 1502 (100%), 1503 (62%), 1504 (63%), 1505 (39%), 1506 (15%) [M^+ (isotopic distribution)]. Anal. Calcd for $C_{68}H_{64}Fe_2O_8Os_2$: C, 54.40; H, 4.30. Found: C, 54.22; H, 4.35

5.7.10 11,11,11,11,43,43,43,43-Octacarbonyl-11,43-diosma[2]metacyclo[5]metacyclo[2]-(1,1′)ferroceno[2]metacyclo[5]metacyclo[2](1,1′)ferrocenophane (9b)

Yield 7 mg (1%), pale yellow, air-stable crystals, mp 124°C. ^1H NMR (CD_2Cl_2): δ 7.21–6.96 (m, 16H, $CH_{arom.}$), 3.98 (m,[56] 16H, C_5H_4), 2.96 (m,[57] N = 17.6 Hz, 8H, $OsCH_2C\mathit{H}_2C_{arom.}$), 2.79–2.73 (m, 8H, $C_5H_4CH_2C\mathit{H}_2C_{arom.}$), 2.63–2.56 (m, 8H, $C\mathit{H}_2C_5H_4$), 1.30-1.20 (m, 8H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 178.8 (s, $OsCO_{ax.}$), 171.0 (s, $OsCO_{eq.}$), 148.2, 142.4 (s, $C_{arom.}$), 128.2, 127.9, 125.6, 125.3 (s, $CH_{arom.}$), 88.7 (s, $C_4H_4\mathit{C}$), 68.8, 67.8 (s, C_4H_4C), 44.1, 37.7, 31.7 (s, CH_2), –0.7 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2125, 2045, 2039, 2011. FD-MS: *m/z* 1496 (20%), 1497 (15%), 1498 (39%), 1499 (45%), 1500 (66%), 1501 (63%), 1502 (100%), 1503 (62%), 1504 (57%), 1505 (23%), 1506 (8%); Calcd 1496 (14%), 1497 (25%), 1498 (47%), 1499 (58%), 1500 (82%), 1501 (82%), 1502 (100%), 1503 (62%), 1504 (63%), 1505 (39%), 1506 (15%) [M^+ (isotopic distribution)].[59]

5.7.11 11,11,11,11,43,43,43,43-Octacarbonyl-11,43-diosma[2]paracyclo[5]paracyclo[2]-(1,1′)ferroceno[2]paracyclo[5]paracyclo[2](1,1′)ferrocenophane (9c)

Yield 16 mg (2%), pale yellow, air-stable crystals, mp 163°C. ^1H NMR (CD_2Cl_2): δ 7.14–7.07 (m, 16H, $CH_{arom.}$), 3.99 (m,[56] 16H, C_5H_4), 2.97 (m,[57] N = 17.9 Hz, 8H, $OsCH_2C\mathit{H}_2C_{arom.}$), 2.79–2.71 (m, 8H, $C_5H_4CH_2C\mathit{H}_2C_{arom.}$), 2.66–2.60 (m, 8H, $C\mathit{H}_2C_5H_4$), 1.30-1.20 (m,[58] N = 17.9 Hz, 8H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 178.7 (s, $OsCO_{ax.}$), 171.0 (s, $OsCO_{eq.}$), 145.8, 139.5 (s, $C_{arom.}$), 128.3, 127.6 (s, $CH_{arom.}$), 88.9 (s, $C_4H_4\mathit{C}$), 68.9, 67.5 (s, C_4H_4C), 43.8, 37.3, 31.7 (s, CH_2), –0.7 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *v*(CO) 2128, 2050, 2036, 2001. FD-MS: *m/z* 1496 (16%), 1497 (36%), 1498 (55%), 1499 (78%), 1500 (85%), 1501 (80%), 1502 (100%), 1503 (50%), 1504 (77.3%), 1505 (47%), 1506 (15%); Calcd 1496 (14%), 1497 (25%), 1498 (47%), 1499 (58%), 1500 (82%), 1501 (82%), 1502 (100%), 1503 (62%), 1504 (63%), 1505 (39%), 1506 (15%) [M^+ (isotopic distribution)]. Anal. Calcd for $C_{68}H_{64}Fe_2O_8Os_2$: C, 54.40; H, 4.30. Found: C, 54.10; H, 3.93.

5.7.12 13,13,13,13,49,49,49,49-Octacarbonyl-13,49-diosma[3]metacyclo[7]metacyclo[3]-(1,1′)ferroceno[3]metacyclo[7]metacyclo[3](1,1′)ferrocenophane (9d)

Yield 10 mg (1 %), pale yellow, air-stable crystals, mp 60.4 °C. ^1H NMR (CD_2Cl_2): δ 7.21–6.98 (m, 16H, $CH_{arom.}$), 3.95 (m,[56] 16H, C_5H_4), 2.63-2.53 (m, 16H, $CH_2C_{arom.}$), 2.37–2.28 (m, 8H, $C\mathit{H}_2C_5H_4$), 2.09–1.96 (m, 8H, $CH_2C\mathit{H}_2CH_2$), 1.88–1.75 (m, 8H, $CH_2C\mathit{H}_2CH_2$), 1.04 (m,[58] N = 17.0 Hz, 8H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.2 (s, $OsCO_{ax.}$), 171.0 (s, $OsCO_{eq.}$), 142.6, 142.5 (s, $C_{arom.}$), 128.7, 128.1, 125.8, 125.7 (s, $CH_{arom.}$), 89.0 (s, $C_4H_4\mathit{C}$), 68.6, 67.7 (s, C_4H_4C), 43.0, 40.6, 35.8, 32.8, 28.8 (s, CH_2), –3.2 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): *v*(CO) 2125, 2039, 2009. FD-MS: *m/z* 1608 (15%), 1609 (27%), 1610 (52%), 1611 (59%), 1612 (76%), 1613 (81%), 1614 (100%), 1615 (61%), 1616 (49%), 1617 (25%), 1618 (15%); Calcd 1608 (14%), 1609 (24%), 1610 (45%), 1611 (58%), 1612 (81%), 1613 (83%), 1614 (100%), 1615 (66%), 1616 (64%), 1617 (41%), 1618 (18%) [M^+ (isotopic distribution)].[59]

5.7.13 13,13,13,13,49,49,49,49-Octacarbonyl-13,49-diosma[3]paracyclo[7]paracyclo[3]-(1,1′)ferroceno[3]paracyclo[7]paracyclo[3](1,1′)ferrocenophane (9e)

Yield 15 mg (2 %), pale yellow, air-stable crystals, mp 127°C. ^1H NMR (CD_2Cl_2): δ 7.09 (s, 16H, $CH_{arom.}$), 3.93 (m,[56] 16H, C_5H_4), 2.61-2.52 (m, 16H, $CH_2C_{arom.}$), 2.28 (t, $^3J_{HH}$ =

7.85 Hz, 8H, C*H*$_2$C$_5$H$_4$), 2.07–1.94 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 1.85–1.73 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 1.30-1.20 (m,[58] N = 17.9 Hz, 8H, CH$_2$Os). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 179.2 (s, OsCO$_{ax.}$), 171.1 (s, OsCO$_{eq.}$), 139.9, 139.6 (s, C$_{arom.}$), 128.3 (s, CH$_{arom.}$), 89.1 (s, C$_4$H$_4$*C*), 68.7, 67.5 (s, *C*$_4$H$_4$C), 42.5, 40.5, 35.3, 32.6, 28.6 (s, CH$_2$), –3.3 (s, CH$_2$Os). IR (*n*-pentane, cm^{-1}): *v*(CO) 2125, 2039, 2009. FD-MS: *m/z* 1608 (20%), 1609 (33%), 1610 (65%), 1611 (62%), 1612 (89%), 1613 (61%), 1614 (100%), 1615 (73%), 1616 (38%), 1617 (29%), 1618 (14%); Calcd 1608 (14%), 1609 (24%), 1610 (45%), 1611 (58%), 1612 (81%), 1613 (83%), 1614 (100%), 1615 (66%), 1616 (64%), 1617 (41%), 1618 (18%) [M$^+$ (isotopic distribution)]. Anal. Calcd for $C_{76}H_{80}Fe_2O_8Os_2$: C, 56.57; H, 5.00. Found: C, 56.70; C, 56.63; H, 4.74.

5.7.14 15,15,15,15,55,55,55,55-Octacarbonyl-15,55-diosma[4]orthocyclo[9]orthoyclo[4]-(1,1´)ferroceno[4]orthocyclo[9]orthocyclo[4](1,1´)ferrocenophane (9f)

Yield < 0.5%.IR (*n*-pentane, cm^{-1}): *v*(CO) 2124, 2039, 2011. FD-MS: *m/z* 1720 (17%), 1721 (23%), 1722 (47%), 1723 (66%), 1724 (85%), 1725 (87%), 1726 (100%), 1727 (57%), 1728 (55%), 1729 (36%), 1730 (15%); Calcd 1720 (13%), 1721 (24%), 1722 (44%), 1723 (57%), 1724 (80%), 1725 (84%), 1726 (100%), 1727 (70%), 1728 (65%), 1729 (44%), 1730 (20%) [M$^+$ (isotopic distribution)].[59,60]

5.7.15 15,15,15,15,55,55,55,55-Octacarbonyl-15,55-diosma[4]metacyclo[9]metayclo[4]-(1,1´)ferroceno[4]orthocyclo[9]orthocyclo[4](1,1´)ferrocenophane (9g)

Yield < 0.5%.IR (*n*-pentane, cm^{-1}): *v*(CO) 2124, 2039, 2009. FD-MS: *m/z* 1720 (22%), 1721 (21%), 1722 (44%), 1723 (55%), 1724 (73%), 1725 (87%), 1726 (100%), 1727 (54%), 1728 (46%), 1729 (36%), 1730 (18%); Calcd 1720 (13%), 1721 (24%), 1722 (44%), 1723 (57%), 1724 (80%), 1725 (84%), 1726 (100%), 1727 (70%), 1728 (65%), 1729 (44%), 1730 (20%) [M$^+$ (isotopic distribution)].[59,60]

5.7.16 15,15,15,15,55,55,55,55-Octacarbonyl-15,55-diosma[4]paracyclo[9]paracyclo[4]-(1,1´)ferroceno[4]paracyclo[9]paracyclo[4](1,1´)ferrocenophane (9h)

Yield 15 mg (2 %), pale yellow, air-stable crystals, mp 65 °C. ^{1}H NMR (CD_2Cl_2): δ 7.09 (s, 16H, $CH_{arom.}$), 3.93 (m,[56] 16H, C_5H_4), 2.59 (t, $^3J_{HH}$ = 7.54 Hz, 16H, $CH_2C_{arom.}$), 2.31 (t, $^3J_{HH}$ = 7.54 Hz, 8H, $C\mathit{H}_2C_5H_4$), 1.85–1.53 (m, 32H, $CH_2C\mathit{H}_2CH_2$), 1.04-0.98 (m, 8H, CH_2Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.5 (s, $OsCO_{ax.}$), 171.2 (s, $OsCO_{eq.}$), 140.4, 139.9 (s, $C_{arom.}$), 128.3 (s, $CH_{arom.}$), 89.4 (s, $C_4H_4\mathit{C}$), 68.7, 67.5 (s, C_4H_4C), 38.6, 38.2, 35.3, 35.0, 31.6, 30.8, 29.1 (s, CH_2), –3.1 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2124, 2039, 2009. FD-MS: *m/z* 1720 (15%), 1721 (25%), 1722 (34%), 1723 (77%), 1724 (87%), 1725 (92%), 1726 (100%), 1727 (60%), 1728 (52%), 1729 (40%), 1730 (5%); Calcd 1720 (13%), 1721 (24%), 1722 (44%), 1723 (57%), 1724 (80%), 1725 (84%), 1726 (100%), 1727 (70%), 1728 (65%), 1729 (44%), 1730 (20%) [M$^+$ (isotopic distribution)]. Anal. Calcd for $C_{84}H_{96}Fe_2O_8Os_2$: C, 58.46; H, 5.61. Found: C, 58.56 ; H, 5.23.

6 Crystallographic Analysis

Single crystals of **8b**, **8c**, **8e**, **9a**, and **9h** suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane and toluene into a solution of **8b**,**c**,**e** or **9a,h** in dichloromethane and slow evaporation of dichloromethane. Selected crystals were mounted on a P4 Siemens four-circle diffractometer. Graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) was used for the measurement of intensity data in the ω-scan mode. An empirical absorption correction was applied for **8b**, **8e**, **9a** but not for **8c**, **9h**. All structures were solved by direct methods with the SHELXS-86 program.[61] Refinement was carried out with full-matrix least-squares methods based on F^2 in SHELXL-97[62] with anisotropic thermal parameters for all non hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model.

In **8c**, the asymmetric unit contains half a molecule of dichloromethane that is disordered about the center of inversion and was included in the refinement using isotropic thermal parameters. In **9h** the unit cell contains an additional *n*-hexane molecule disordered about the center of inversion and ill defined. It was included in the refinement using isotropic thermal parameters and C–C distance restraints. Crystal data and a summary of data collection and refinement details are given in Table 2.

Table 2. Crystal Data and Summary of Data Collection and Refinement for **8b**, **8c**, **8e**, **9a**, and **9h**

	8b	**8c · 0.5 CH_2Cl_2**	**8e**	**9a**	**9h · *n*-hexane**
formula	$C_{34}H_{32}FeO_4Os$	$C_{34.5}H_{33}ClFeO_4Os$	$C_{38}H_{40}FeO_4Os$	$C_{68}H_{64}Fe_2O_8Os_2$	$C_{90}H_{110}Fe_2O_8Os_2$
fw	750.65	793.11	806.75	1501.29	1811.88
cryst size, mm^3	0.25×0.45×0.25	0.6×0.15×0.04	0.2×0.6×0.4	0.50×0.40×0.10	0.5×0.08×0.08
temp, K	173(2)	173(2)	173(2)	173(2)	173(2)
crystal syst	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_12_12_1$	$Pbca$	$P\overline{1}$
a, Å	6.195(3)	6.2833(17)	8.857(2)	14.646(4)	6.6774(19)
b, Å	41.882(12)	16.437(3)	11.944(3)	12.629(7)	11.1945(16)
c, Å	11.053(3)	29.161(4)	31.810(8)	32.278(9)	29.219(4)
α, deg					93.038(8)
β, deg	95.84(3)	92.244(17)			92.63(2)
γ, deg					104.982(9)
V, $Å^3$	2852.9(18)	3009.4(10)	3365.0(15)	5970(4)	2102.9(7)
Z	4	4	4	4	1
d_{calcd}, g/cm^3	1.748	1.750	1.592	1.670	1.431
μ(Mo Kα), mm^{-1}	4.996	4.827	4.242	4.774	3.402
F(000), e	1480	1564	1608	2960	918
θ range, deg	2.09–27.52	2.44–27.50	2.13–27.52	2.22–27.52	2.06–27.50
index ranges	$-8 \leq h \leq 8$	$-1 \leq h \leq 6$	$-4 \leq h \leq 11$	$-19 \leq h \leq 19$	$-8 \leq h \leq 1$
	$-54 \leq k \leq 54$	$-21 \leq k \leq 1$	$-15 \leq k \leq 15$	$-16 \leq k \leq 16$	$-14 \leq k \leq 14$
	$-14 \leq l \leq 14$	$-37 \leq l \leq 37$	$-10 \leq l \leq 41$	$-1 \leq l \leq 41$	$-37 \leq l \leq 37$
no. of data collected	22663	8653	15908	26143	12141
max./min. transmission	0.7262/0.3184		0.8199/0.3536	0.762/0.362	
R_{int}	0.0773	0.0470	0.0355	0.0585	0.0430
no. of unique data/restraints/params	6100/0/362	6264/2/374	7715/0/398	6587/0/362	9664/14/446
GOF on F^2	1.192	1.007	1.072	1.013	1.018
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0361, 0.0839	0.0463, 0.0974	0.0273, 0.0668	0.0308, 0.0685	0.0666, 0.1363
R1, wR2 (all data)	0.0430, 0.0902	0.0758, 0.1091	0.0296, 0.0678	0.0500, 0.0756	0.1299, 0.1621
largest diff. peak, hole e/ $Å^3$	1.832, –1.901	1.719, –1.731	1.198, –1.037	0.825, –0.949	2.061, –1.243

$R1 = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]]^{0.5}$; $w = [\exp(5(\sin^2 \theta/\lambda^2)]/[\sigma^2(F_o^2) + bP + (aP)^2]$; $P = [F_o^2 + 2 F_c^2]/3$

Table 3. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for **8b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	4228(1)	6934(1)	10520(1)	21(1)
Fe(1)	7762(1)	5484(1)	6234(1)	19(1)
O(1)	7610(7)	7471(1)	10953(4)	53(1)
O(2)	1117(6)	7329(1)	8731(3)	36(1)
O(3)	1917(7)	7122(1)	12755(3)	48(1)
O(4)	1688(6)	6319(1)	9760(3)	37(1)
C(1)	6303(8)	7285(1)	10797(4)	31(1)
C(2)	2250(7)	7179(1)	9371(4)	26(1)
C(3)	2720(8)	7046(1)	11928(4)	32(1)
C(4)	2627(7)	6540(1)	10104(3)	26(1)
C(5)	6299(7)	6796(1)	9080(3)	25(1)
C(6)	6012(7)	6990(1)	7899(4)	23(1)
C(7)	7460(7)	6898(1)	6934(3)	20(1)
C(8)	9125(7)	6673(1)	7110(3)	22(1)
C(9)	10448(6)	6598(1)	6196(3)	20(1)
C(10)	10111(8)	6759(1)	5097(4)	29(1)
C(11)	8501(10)	6986(1)	4911(4)	36(1)
C(12)	7186(8)	7056(1)	5815(4)	31(1)
C(13)	12190(7)	6345(1)	6386(4)	25(1)
C(14)	11357(6)	6019(1)	6786(3)	22(1)
C(15)	9524(6)	5887(1)	5950(3)	18(1)
C(16)	7265(6)	5962(1)	5976(3)	21(1)
C(17)	6046(7)	5787(1)	5038(4)	25(1)
C(18)	7523(7)	5602(1)	4423(3)	26(1)
C(19)	9658(7)	5662(1)	4980(3)	24(1)
C(20)	6691(7)	6666(1)	11733(4)	28(1)
C(21)	5910(8)	6439(1)	12691(4)	34(1)
C(22)	4759(7)	6146(1)	12184(3)	26(1)
C(23)	5746(7)	5945(1)	11388(4)	28(1)
C(24)	4763(8)	5667(1)	10926(4)	30(1)
C(25)	2740(8)	5585(1)	11273(4)	35(1)
C(26)	1732(9)	5780(2)	12058(4)	37(1)
C(27)	2719(8)	6059(1)	12500(4)	32(1)
C(28)	5865(10)	5455(1)	10067(4)	37(1)
C(29)	6313(9)	5622(1)	8885(4)	30(1)
C(30)	7009(7)	5389(1)	7963(3)	25(1)
C(31)	5606(7)	5214(1)	7083(4)	27(1)
C(32)	6913(8)	5016(1)	6416(4)	29(1)
C(33)	9122(8)	5063(1)	6865(4)	29(1)
C(34)	9189(7)	5294(1)	7822(4)	28(1)

Table 4. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for **8c**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	998(1)	3170(1)	563(1)	24(1)
Fe(1)	7886(2)	3537(1)	3602(1)	22(1)
O(1)	3722(9)	3373(3)	1473(2)	34(1)
O(2)	3321(10)	1544(3)	411(2)	43(1)
O(3)	4090(9)	4170(4)	-12(2)	48(2)
O(4)	-2225(10)	2917(4)	-239(2)	55(2)
C(1)	2648(12)	3328(4)	1153(2)	27(2)
C(2)	2475(11)	2138(5)	475(2)	27(2)
C(3)	3005(13)	3809(4)	207(2)	33(2)
C(4)	-973(13)	3012(4)	41(2)	33(2)
C(5)	-1579(12)	2584(4)	944(2)	31(2)
C(6)	-1176(13)	1748(4)	1161(2)	33(2)
C(7)	388(12)	1775(4)	1566(2)	28(2)
C(8)	-116(12)	2235(5)	1951(2)	32(2)
C(9)	1299(11)	2317(4)	2323(2)	29(2)
C(10)	3309(12)	1953(4)	2327(2)	26(2)
C(11)	3753(12)	1464(4)	1950(2)	26(2)
C(12)	2327(12)	1382(4)	1581(2)	26(2)
C(13)	4974(12)	2079(4)	2714(2)	30(2)
C(14)	4142(12)	2347(4)	3168(2)	31(2)
C(15)	5924(11)	2528(4)	3516(2)	25(2)
C(16)	8091(12)	2301(4)	3502(2)	30(2)
C(17)	9148(13)	2528(4)	3917(2)	35(2)
C(18)	7668(13)	2906(5)	4197(2)	36(2)
C(19)	5649(12)	2913(4)	3949(2)	30(2)
C(20)	-941(12)	4290(4)	670(3)	31(2)
C(21)	157(14)	5101(4)	753(3)	41(2)
C(22)	1553(13)	5136(4)	1190(2)	29(2)
C(23)	3682(12)	5372(4)	1186(2)	28(2)
C(24)	4948(12)	5392(4)	1583(2)	26(2)
C(25)	4140(12)	5179(4)	2005(2)	26(2)
C(26)	2000(12)	4958(4)	2013(2)	31(2)
C(27)	748(12)	4933(4)	1613(2)	30(2)
C(28)	5567(13)	5180(4)	2438(2)	32(2)
C(29)	5728(13)	4355(4)	2677(2)	33(2)
C(30)	7253(11)	4366(4)	3084(2)	24(2)
C(31)	6878(12)	4718(4)	3522(2)	32(2)
C(32)	8786(13)	4684(4)	3792(3)	36(2)
C(33)	10373(12)	4318(4)	3524(3)	35(2)
C(34)	9426(12)	4131(4)	3093(3)	35(2)
Cl(60)	-2229(12)	773(5)	-64(2)	92(2)
Cl(61)	969(17)	-433(6)	146(3)	124(3)
C(60)	-190(30)	200(10)	-287(5)	55(5)

Table 5. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for **8e**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	8270(1)	5158(1)	2875(1)	26(1)
Fe(1)	11320(1)	5319(1)	6378(1)	25(1)
O(1)	9460(5)	7381(3)	3234(1)	44(1)
O(2)	4899(4)	5829(3)	2887(1)	51(1)
O(3)	9387(5)	5729(3)	1985(1)	49(1)
O(4)	7632(6)	2737(3)	2582(1)	59(1)
C(1)	8967(5)	6583(4)	3111(1)	27(1)
C(2)	6128(6)	5565(4)	2863(2)	35(1)
C(3)	8916(6)	5551(4)	2308(1)	32(1)
C(4)	7835(6)	3625(4)	2691(2)	35(1)
C(5)	10637(5)	4731(4)	3015(1)	32(1)
C(6)	11097(6)	3498(4)	2956(1)	30(1)
C(7)	12628(6)	3229(4)	3148(1)	33(1)
C(8)	12586(5)	3260(4)	3626(1)	29(1)
C(9)	11779(7)	2439(4)	3844(1)	35(1)
C(10)	11671(8)	2466(4)	4280(2)	41(1)
C(11)	12350(6)	3300(5)	4508(2)	41(1)
C(12)	13117(6)	4132(5)	4292(2)	43(1)
C(13)	13250(7)	4111(4)	3854(2)	38(1)
C(14)	12205(7)	3318(6)	4988(2)	49(1)
C(15)	10679(7)	3702(6)	5119(2)	57(2)
C(16)	10493(8)	3716(6)	5610(2)	58(2)
C(17)	11564(6)	4545(4)	5808(1)	34(1)
C(18)	11485(6)	5727(4)	5754(1)	34(1)
C(19)	12676(6)	6228(5)	5989(2)	37(1)
C(20)	13506(5)	5357(5)	6183(2)	42(1)
C(21)	12821(6)	4326(5)	6068(2)	39(1)
C(22)	7848(6)	4482(4)	3514(1)	33(1)
C(23)	7784(6)	5314(4)	3877(1)	35(1)
C(24)	7653(6)	4716(4)	4304(1)	37(1)
C(25)	7466(5)	5477(4)	4679(1)	32(1)
C(26)	6350(5)	5263(5)	4976(1)	35(1)
C(27)	6164(6)	5938(5)	5326(2)	39(1)
C(28)	7080(5)	6857(4)	5396(1)	34(1)
C(29)	8214(7)	7069(4)	5099(1)	39(1)
C(30)	8380(7)	6397(4)	4752(1)	39(1)
C(31)	6918(7)	7582(5)	5784(2)	42(1)
C(32)	8122(6)	7314(4)	6123(2)	36(1)
C(33)	7914(5)	6155(4)	6304(2)	35(1)
C(34)	9182(5)	5735(4)	6572(1)	27(1)
C(35)	10281(6)	6371(4)	6796(1)	36(1)
C(36)	11260(6)	5616(6)	7006(1)	46(1)
C(37)	10783(6)	4515(5)	6921(2)	43(1)
C(38)	9511(6)	4594(4)	6651(1)	33(1)

Table 6. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [Å^2 × 10^3] for **9a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	4340(1)	1158(1)	9059(1)	33(1)
Fe(1)	5723(1)	6914(1)	8515(1)	34(1)
O(1)	5863(2)	1004(3)	8401(1)	55(1)
O(2)	2932(2)	-440(3)	8722(1)	68(1)
O(3)	5318(2)	-430(2)	9633(1)	57(1)
O(4)	3077(2)	2105(3)	9723(1)	65(1)
C(1)	5291(3)	1009(3)	8638(2)	42(1)
C(2)	3478(3)	112(3)	8842(2)	46(1)
C(3)	4964(3)	167(3)	9429(1)	43(1)
C(4)	3513(3)	1706(3)	9485(1)	41(1)
C(5)	3640(3)	2279(3)	8638(1)	39(1)
C(6)	3782(3)	2082(4)	8176(1)	46(1)
C(7)	3198(2)	2776(3)	7903(1)	35(1)
C(8)	2324(3)	2404(3)	7806(1)	42(1)
C(9)	1733(2)	2962(4)	7559(1)	48(1)
C(10)	2015(3)	3915(4)	7390(2)	51(1)
C(11)	2877(3)	4288(3)	7483(1)	44(1)
C(12)	3476(2)	3744(3)	7744(1)	37(1)
C(13)	4402(2)	4208(4)	7838(2)	46(1)
C(14)	4385(2)	5114(3)	8143(2)	46(1)
C(15)	5323(2)	5540(3)	8230(1)	34(1)
C(16)	5865(3)	5319(3)	8585(1)	42(1)
C(17)	6722(3)	5795(3)	8533(2)	47(1)
C(18)	6731(3)	6326(3)	8150(2)	49(1)
C(19)	5862(3)	6167(3)	7962(1)	41(1)
C(20)	4636(3)	7916(3)	8563(1)	43(1)
C(21)	5394(3)	8428(3)	8381(2)	50(1)
C(22)	6123(3)	8392(3)	8666(2)	48(1)
C(23)	5827(3)	7860(3)	9026(1)	41(1)
C(24)	4895(3)	7569(3)	8964(1)	37(1)
C(25)	4263(2)	7076(3)	9274(1)	42(1)
C(26)	4701(3)	6397(4)	9609(1)	48(1)
C(27)	3989(3)	5991(3)	9913(1)	40(1)
C(28)	3549(3)	5050(3)	9824(2)	49(1)
C(29)	2855(3)	4662(4)	10075(2)	54(1)
C(30)	2612(3)	5203(4)	10426(2)	49(1)
C(31)	3048(3)	6136(3)	10523(1)	43(1)
C(32)	3735(2)	6548(3)	10269(1)	37(1)
C(33)	4163(3)	7585(3)	10399(1)	43(1)
C(34)	4854(3)	7450(3)	10743(1)	38(1)

Table 7. Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$Å^2$ × 10^3] for **9h**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Os(1)	-1714(1)	5476(1)	5837(1)	62(1)
Fe(1)	7486(1)	-2481(1)	10014(1)	26(1)
C(1)	1109(16)	6439(12)	5762(4)	91(4)
O(1)	2811(14)	6963(11)	5734(3)	132(4)
C(2)	-2913(16)	6136(9)	5322(3)	70(3)
O(2)	-3640(13)	6543(7)	5025(2)	95(2)
C(3)	-1434(18)	4000(10)	5499(3)	80(3)
O(3)	-1203(16)	3152(9)	5294(3)	112(3)
C(4)	-4338(18)	4626(10)	6031(3)	120(7)
O(4)	-5931(13)	4097(9)	6174(3)	100(3)
C(5)	-396(16)	4913(9)	6480(3)	66(3)
C(6)	-833(16)	3512(9)	6533(3)	70(3)
C(7)	200(16)	3184(9)	6966(3)	63(3)
C(8)	-83(15)	1814(9)	6982(3)	65(3)
C(9)	1216(14)	1469(8)	7369(3)	51(2)
C(10)	322(14)	917(9)	7749(3)	63(2)
C(11)	1535(12)	619(8)	8103(3)	51(2)
C(12)	3627(12)	810(6)	8087(2)	40(2)
C(13)	4500(15)	1376(10)	7707(3)	71(3)
C(14)	3331(17)	1695(10)	7357(3)	76(3)
C(15)	4932(12)	451(6)	8462(2)	39(2)
C(16)	4274(12)	-894(7)	8572(2)	41(2)
C(17)	5811(11)	-1235(6)	8908(2)	35(2)
C(18)	5199(10)	-2602(6)	9008(2)	31(2)
C(19)	6755(10)	-2983(6)	9326(2)	29(1)
C(20)	8916(11)	-2400(6)	9402(2)	35(2)
C(21)	9793(11)	-3090(6)	9720(2)	37(2)
C(22)	8177(10)	-4108(6)	9828(2)	33(2)
C(23)	6324(10)	-4034(6)	9588(2)	31(2)
C(24)	2684(10)	2378(6)	9281(2)	29(1)
C(25)	4673(10)	2460(6)	9508(2)	29(1)
C(26)	4443(11)	1431(6)	9785(2)	33(2)
C(27)	2354(10)	715(6)	9733(2)	32(2)
C(28)	1260(10)	1289(6)	9422(2)	30(1)
C(29)	2266(11)	3240(6)	8928(2)	36(2)
C(30)	46(11)	3378(7)	8898(3)	40(2)
C(31)	-259(12)	4256(7)	8528(3)	46(2)
C(32)	-2406(13)	4414(8)	8508(3)	49(2)
C(33)	-2882(13)	5315(7)	8175(3)	45(2)
C(34)	-1504(15)	6473(8)	8134(3)	61(2)
C(35)	-1997(16)	7333(8)	7861(3)	64(3)
C(36)	-3960(16)	7069(9)	7615(3)	59(2)
C(37)	-5294(17)	5916(9)	7654(3)	72(3)
C(38)	-4775(14)	5056(8)	7930(3)	58(2)
C(39)	-4480(20)	8001(9)	7315(3)	91(4)
C(40)	-3070(20)	8253(10)	6930(3)	95(4)
C(41)	-3313(18)	7050(9)	6602(3)	75(3)
C(42)	-1750(20)	7146(11)	6262(3)	88(4)
C(60)	4230(60)	480(40)	5816(14)	400(20)
C(61)	1900(60)	410(40)	5622(14)	370(20)
C(62)	1180(50)	60(40)	5108(14)	340(20)

7 Electrochemical Experiments

Cyclic voltammograms were recorded with a Bioanalytical Systems (BAS, West Lafayette, IN) CV-50 W electrochemical workstation. A Metrohm Pt electrode tip (Filderstadt, Germany) was used as a working electrode. The counter electrode was a Pt wire of 1 mm diameter. A single-unit Haber-Luggin double reference electrode[63] was used. The resulting potential values refer to Ag/Ag^+ (0.01 M in CH_3CN/0.1 M NBu_4PF_6). Ferrocene was used as an external standard. Its potential was determined by separate cyclic voltammetric experiments in acetonitrile. All potentials in the present paper are reported relative to the Fc/Fc^+ standard.[64] A gastight full-glass three-electrode cell was used, its assembly has been described elsewhere.[65] The cell was purged with argon before it was filled with electrolyte. NBu_4PF_6 (0.1 M) was used as supporting electrolyte. Background curves were recorded before adding substrate to the solution and subtracted from the experimental data. The automatic BAS CV-50W *iR*-drop compensation facility was used for all experiments.

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[56] m: AA´XX´ pattern.

[57] m: low field part of an AA´XX´ pattern.

[58] m: high field part of an AA´XX´ pattern.

[59] Due to the very low yield no elemental analyses were available.

[60] Due to the very low yield no ^{1}H and ^{13}C {^{1}H} NMR spectroscopic characterization was possible.

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Summary

Cyclophanes and metallocenophanes represent typical examples in supramolecular chemistry and are provided with several inherent features of general interest. They do not only reveal a multitude of aesthetic structures. In several cases they can be applied for molecular recognition and specific ferrocenophanes are used as redox switches. Due to the steric requirement of transition metal fragments their introduction into the framework of cyclophanes and metallocenophanes affect the geometric parameters of the cavities. At the same time a new reactive center is created that is capable of inserting small molecules, like carbon monoxide, into metal–carbon σ bonds and of reacting with a new ligand if a vacant coordination site is available. For the formation of the Os–C σ bonds advantage of the bis(triflate) method has been taken, which is a variant of the cationic alkylation. This route was found to be the most straightforward and efficient way for the concomitant formation of several metal–carbon σ bonds under very mild conditions. The triflate residue is an excellent and inert leaving group stabilizing carbenium-like carbon atoms at the ends of a hydrocarbon chain, thereby enabling an electrophilic attack of the terminal carbon atoms even at a weakly basic metal center. With regard to this method osmaferrocenophanes, osmacyclophanes and four- to fifty-one-membered multiosmacycloalkanes were obtained by reaction of the corresponding bis(triflates) with $Na_2[Os(CO)_4]$ in dimethyl ether.

Objective of the present work is the synthesis of the novel di- and tetranuclear *ortho*-, *meta*-, and *para*-osmacycloferrocenophanes $[\eta^5\text{-}C_5H_4(CH_2)_nC_6H_4(CH_2)_nOs(CO)_4(CH_2)_nC_6H_4\text{-}(CH_2)_nC_5H_4\text{-}\eta^5]_xFe_x$ (*ortho*, *meta*, *para*: n = 2, 4; *meta*, *para*: n = 3; x = 1, 2) consisting of an extended hydrocarbon skeleton containing additionally two and four transition metal centers,

respectively. Prior to the application of the bis(triflate) method in this work several primary steps had to be elaborated.

These investigations have been started with the synthesis of 1,n-bis(2-hydroxyethyl)benzene (n = 2–4), 1,n-bis(3-hydroxypropyl)benzene (n = 3, 4), and 1,n-bis(4-hydroxybutyl)benzene (n = 2–4). To attain to 1,n-bis(4-hydroxybutyl)benzene (n = 2–4) by hydroboration of 1,n-bis(3-butenyl)benzenes (n = 2–4), a synthetic route for the bis(butenyl)benzenes had to be developed. The reaction of the aromatic bis(alcohols) $HO(CH_2)_nC_6H_4(CH_2)_nOH$ (*ortho*, *meta*, *para*: n = 2, 4; *meta*, *para*: n = 3) with $HBr_{(aq)}$ in toluene afforded the new colorless, highly viscous, aromatic α,ω-bromoalkanols $HO(CH_2)_nC_6H_4(CH_2)_nBr$ (*o*, *m*, *p*: n = 2, 4; *m*, *p*: n = 3) in good yields. Subsequent to purification by column chromatography on silica gel the aromatic α,ω-bromoalkanols were reacted in CH_2Cl_2 with dihydropyran to get the new THP protected aromatic α,ω-bromoalkanols $THPO(CH_2)_nC_6H_4(CH_2)_nBr$ (*o*, *m*, *p*: n = 2, 4; *m*, *p*: n = 3) in almost quantitative yields. They were used without purification for the formation of the THP protected cyclopentadienyl alcohols $THPO(CH_2)_nC_6H_4(CH_2)_nCp$ (*o*, *m*, *p*: n = 2, 4; *m*, *p*: n = 3), which were treated with *n*-BuLi in *n*-hexane and then converted with $FeCl_2 \cdot THF_{1.44}$ in THF to the THP protected ferrocenediylalcohols $[\eta^5\text{-}C_5H_4(CH_2)_nC_6H_4(CH_2)_nOTHP]_2Fe$ (*o*, *m*, *p*: n = 2, 4; *m*, *p*: n = 3). Deprotection of these intermediates succeeded in ethanol with pyridinium-*p*-toluenesulfonate to obtain the ferrocenediylalcohols $[\eta^5\text{-}C_5H_4(CH_2)_nC_6H_4(CH_2)_nOH]_2Fe$ (*o*, *m*, *p*: n = 2, 4; *m*, *p*: n = 3) in moderate to satisfying yields. With the exception of the orange waxy *para* (n = 2, 4) compounds, these materials represent yellow, highly viscous oils, readily soluble in chlorinated hydrocarbons. They were characterized spectroscopically and by elemental analyses. For the formation of the bis(triflates) $[\eta^5\text{-}C_5H_4(CH_2)_nC_6H_4(CH_2)_nOTf]_2Fe$ (*o*, *m*, *p*: n = 2, 4; *m*, *p*: n = 3) the ferrocenediylalcohols were reacted with trifluoromethanesulfonic acid anhydride in the presence of a slight excess of pyridine in CH_2Cl_2 at –30 °C. The yellow heat sensitive compounds are easily soluble in common organic solvents and were identified by their mass, ^1H, $^{13}C\{^1H\}$ NMR, and IR spectra.

The di- and tetranuclear *ortho*-, *meta*-, and *para*-osmacycloferrocenophanes $[\eta^5\text{-}C_5H_4(CH_2)_nC_6H_4(CH_2)_nOs(CO)_4(CH_2)_nC_6H_4(CH_2)_nC_5H_4\text{-}\eta^5]_xFe_x$ (*ortho*, *meta*, *para*: n = 2, 4; *meta*, *para*: n = 3; x = 1; x = 2) consisting of an extended hydrocarbon skeleton and containing additionally two and four transition metal centers, respectively, were obtained by adding the corresponding bis(triflates) to a suspension of the organometallic Lewis base $Na_2[Os(CO)_4]$ in refluxing dimethyl ether within three days. These yellow solids are rather stable to aerial oxygen and can be handled at room temperature without decomposition. Whereas the dinuclear species were isolated in up to 27% yield, the tetranuclear species were obtained in yields of approximately 2%. They were fully characterized if the yields were high enough. The conformation and the solid state structure of these di- and tetranuclear osmacycloferrocenophanes strongly depend on the substitution pattern of the phenylene rings and the number of methylene groups in the chain. For the dinuclear species roughly a boat shaped structure is observed which is more or less distorted. In the case of the *ortho*-diosmacycloferrocenophane with two methylene groups in the alkyl chains the four metal atoms are located at the vertices of a distorted square and the basic cyclophane framework has approximately the shape of a paddle wheel. The four metal atoms in the corresponding *para* compound with four methylene groups in the alkyl chains are positioned at the vertices of a parallelogram and the main cyclophane framework is remarkably stretched. The macrocycles 11,11,11,11-tetracarbonyl-11-osma[2]metacyclo[5]metacyclo[2](1,1′)ferrocenophane, 11,11,11,11-tetracarbonyl-11-osma[2]paracyclo[5]paracyclo[2](1,1′)ferrocenophane, and 13,13,13,13-tetracarbonyl-13-osma[3]paracyclo[7]paracyclo[3](1,1′)ferrocenophane crystallize in the monoclinic and orthorhombic space group $P2_1/n$ and $P2_12_12_1$, respectively, with Z = 4.

The centrosymmetric 11,11,11,11,43,43,43,43-octacarbonyl-11,43-diosma[2]orthocyclo[5]orthocyclo[2](1,1′)ferroceno[2]orthocyclo[5]orthocyclo[2](1,1′)ferrocenophane crystallizes in the orthorhombic space group *P*bca with Z = 4. A further crystal structure could be obtained from the centrosymmetric tetranuclear macrocycle 15,15,15,15,55,55,55,55-octacarbonyl-15,55-diosma[4]paracyclo[9]paracyclo[4](1,1′)ferroceno[4]paracyclo[9]paracyclo[4](1,1′)ferrocenophane, which crystallizes in the triclinic space group $P\overline{1}$ with Z = 1.

The redox potentials of the ferrocenediylalcohols and the dinuclear osmacycloferrocenophanes were investigated by cyclic voltammetry in dependence on the chain lengths of the $(CH_2)_n$-spacers (n = 2–4) and the substitution patterns of the phenylene groups. These data indicate that the OH and $Os(CO)_4$ functional groups have little or no effect on the $E°$ values of the ferrocene unit in these compounds. The main factor for the redox potentials is the number of methylene functions between the ferrocene and phenylene rings and their substitution patterns.

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