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Synthesis, Structure, and Electrochemistry of Osmametallocenophanes with Different Ring Size[†,1]

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The reaction of the bis(triflates) $[\eta^5\text{-}C_5H_4(CH_2)_nOTf]_2M$ ($n = 3$, M = Fe (**4a**), Ru (**5a**); $n = 4$, M = Fe (**4b**), Ru (**5b**); $n = 6$, M = Fe (**4c**), Ru (**5c**)), which are obtained from the bis(alcohols) $[\eta^5\text{-}C_5H_4(CH_2)_nOH]_2M$ (**2a**−**c**, **3a**−**c**) and $(CF_3SO_2)_2O$ in the presence of pyridine, with $Na_2[Os(CO)_4]$ in dimethyl ether results in the formation of the novel osmametallocenophanes $[\eta^5\text{-}C_5H_4(CH_2)_nOs(CO)_4(CH_2)_nC_5H_4\text{-}\eta^5]M$ (**6a**−**c**, **7a**−**c**). The structures of **6b** ($n = 4$, M = Fe) and **7c** ($n = 6$, M = Ru) were investigated by X-ray structural analyses. In a similar way the bis(rhenium) complexes $[\eta^5\text{-}C_5H_4(CH_2)_nRe(CO)_5]_2M$ (**8a**−**c**, **9a**−**c**) were made accessible from the bis(triflates) **4a**−**c** and **5a**−**c** and $Na[Re(CO)_5]$ in THF. The dependence of the redox behavior of the metallocene unit in the osmametallocenophanes **6a**−**c** and **7b,c** on the metal−metal distance was examined by means of cyclic voltammetry. The obtained results were compared with those of the bis(alcohols) **2a**−**c** and **3a**−**c** and the bis(rhenium) complexes **8a**−**c** and **9a**−**c**. The ferrocenes are characterized by a reversible one-electron oxidation, whereas the ruthenocenes feature an irreversible two-electron process accompanied by a chemical reaction. A consistent through-space effect of the spacer-bound substituents on the redox potential is observed in the case of the ferrocenes.

Introduction

Metallocenophanes which belong to a variant of cyclophanes show interesting structural and physical features.[2] Usually they are classified in three categories: intramolecularly bridged mononuclear systems in which the two cyclopentadienyl rings are linked with one[2a] or several hydrocarbon chains ("super phanes"),[2b] intermolecularly bridged mononuclear compounds connected with other aromatic rings,[2c] and polynuclear species.[2d] Of particular interest is the influence of structural deformations on the properties of metallocenophanes,[3] the intervalence transfer of electrons in binuclear moieties, and the electric conductivity. In subsequent studies one or even several methylene groups in metallocenophanes were replaced by heteroatoms such as oxygen,[4] sulfur,[5] silicon,[6] and others.[7] The background of these investigations included the impact on the redox behavior of the metal center, the stereochemistry, and the access of new monomers for ROP syntheses.[6a,7b]

Of considerable interest is the introduction of additional metals in the proximity of the redox-active metallocene unit. On the basis of the possible interaction of the two metal centers, new interesting features are to be expected. The additional metal can be introduced by several strategies. One prominent way is the combination of macrocycles such as crown ethers or cryptands with metallocenes.[8] These functionalized macrocycles are able to include cationic and anionic[9] guest species. Since the incorporated metals are capable of perturbing the redox properties of the metallocene subcomponent, such systems are potentially valuable for the detection and quantitative estimation of the guests by electrochemical techniques.[10] Furthermore the electrochemical

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[†] Dedicated to Professor Jochen Ellermann on the occasion of his 65th birthday.

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oxidation of the metallocene subunit reduces the cation binding capacity of the ligand subcomponent, which is switched from a high to a low binding state, and in an ideal case the cation will be released.[11] Upon reduction, the cation complexation ability is restored.[12] This characteristic is the fundamental principle of a redox switch[13] and has been employed successfully for the transportation of cations through a membrane.[14]

Another approach for the construction of heterobimetallic metallocenophanes proceeds from donor groups such as thiols[15] or phosphines[16] to bind transition metal fragments. It has been demonstrated that the reversible redox-active chelating ligand class of the 1,1′-bis(diphenylphosphino)metallocenes is able to tune the electron density in a pendant metal complex species without changing the coordination sphere. Thus, the reactivity of the metal fragment can be controlled.[17]

A further possibility to integrate transition metals within the framework of metallocenes is the formation of metal−carbon σ bonds.[18] They are generated by the bis(triflate) route,[19,20] a variant of the cationic alkylation. The excellent and inert leaving group $CF_3SO_2O^-$ stabilizes carbenium-like carbon atoms at the ends of a hydrocarbon chain,[21] thereby enabling an electrophilic attack of the terminal carbon atoms at a basic metal center. For this reason the simultaneous formation of two or more metal−carbon σ bonds in combination with the bivalent metalates $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os) proceeds under very mild conditions. By employing the bis(triflate) method, we were able to obtain for the first time metallacyclophanes with either one or two transition metals in the ring skeleton.[20a,22] The $M(CO)_4$ groups not only exert an influence on the structure of metallacyclophanes but also create reactive centers.[23,24]

Replacing the aromatic rings in metallacyclophanes with metallocenes affords access to the chemistry of metallametallocenophanes. In this paper we describe the synthesis and selected structures of novel osmametallocenophanes with iron and ruthenium as metal centers in the metallocene moiety. The influence of the metal−metal distance in the osmametallocenophanes on the redox potential of the metallocene unit is examined by cyclic voltammetry, and the results are compared with the electrochemical behavior of the 1,1′-bis(ω-hydroxyalkyl)metallocenes and 1,1′-bis(ω-pentacarbonylrhenioalkyl)metallocenes.

Results and Discussion

Synthesis. With some exceptions symmetrically substituted 1,1′-bis(ω-hydroxyalkyl)metallocenes are hitherto scarcely described in the literature.[25] The known representatives have attracted interest as monomers for the generation of metal-containing polymers and were obtained by classical synthetic steps.[25,26] For the general synthesis of such substituted metallocenes with a different chain length of the alkane moiety and different metals in the metallocene unit an alternative method was developed starting from the readily available tetrahydropyran (THP)-protected cyclopentadienylalkyl alcohols **1a**−**c** (Scheme 1). The reaction of **1a**−**c** with $FeCl_2(THF)_{1.44}$[27] or $RuCl_3(H_2O)_x$ by well-known procedures[28] with subsequent deprotection of the intermediates affords the bis(alcohols) **2a**−**c** and **3a**−**c**. **2b** was already known and was obtained in a different way.[25a] The conversion of **2a**−**c** and **3a**−**c** to the bis(triflates) **4a**−**c** and **5a**−**c** in dichloromethane with trifluoromethanesulfonic acid anhydride in the presence of pyridine is achieved with excellent yields.[29] The yellow (**4a**−**c)** and colorless (**5a**−**c**) bis(triflates) are easily soluble in common organic solvents and can be stored below −30 °C.

If solutions of **4a**−**c** and **5a**−**c** in diethyl ether are treated with a suspension of the sodium salt of the organometallic Lewis base $[Os(CO)_4]^{2-}$ in dimethyl ether, within 3 days bright yellow solutions containing the osmametallocenophanes **6a**−**c** and **7a**−**c** and buff-colored precipitates were obtained. In contrast to **6b,c** and **7b,c** the yields of the 10-membered cycles **6a** (ca. 1%) and **7a** (only traces) are very poor. Recently it was demonstrated that the yields of mononuclear osmacycloalkanes with a ring size between eight and 11 tend to zero, because these rings suffer from a strong H/H repulsion between CH_2 groups across the ring.[30] These transannular interactions account for the fact that the ring-closure reactions to give medium-sized osmacycloalkanes[31] are not successful. Below and above a ring

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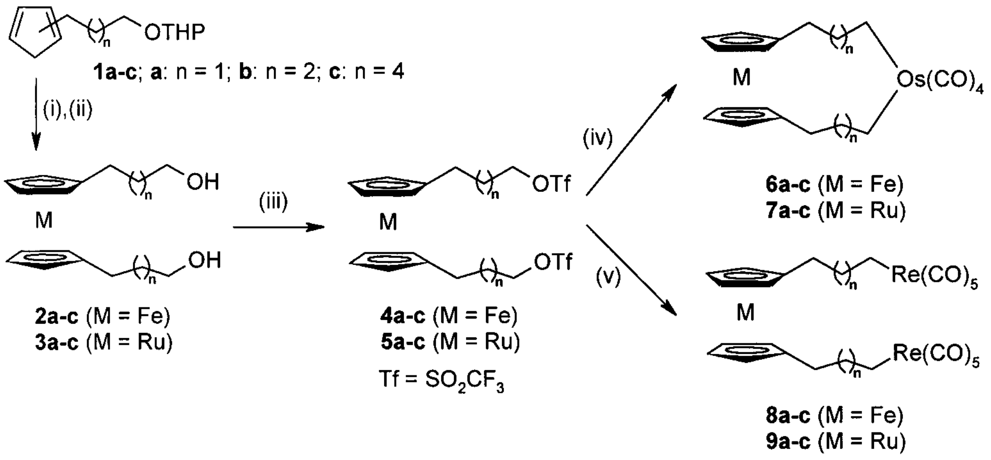
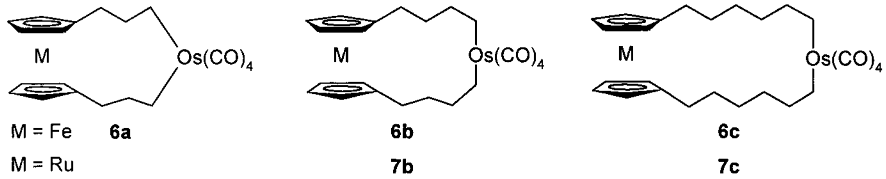
Scheme 1



Reagents: (i) M = Fe: 1) n-BuLi. 2) $FeCl_2$, THF, reflux. M = Ru: $RuCl_3 \cdot x\,H_2O$, Zn, norbornene, EtOH. (ii) EtOH, H_2O, H_3PO_4. (iii) Py, Tf_2O, CH_2Cl_2, -30 °C. (iv) $Na_2[Os(CO)_4]$, Me_2O, -22 °C. (v) $Na[Re(CO)_5]$, THF.

Chart 1



size of eight and 11, respectively, the yields increase markedly, which is in agreement with the results presented here (Experimental Section). Because of the very low yield of the 10-membered osmarutheno-cenophane **7a**, this compound could only be detected in the field desorption mass spectrum (30 °C) showing the molecular peak at $m/z = 617.7$.

The yellow (**6a**–**c**) and colorless (**7b,c**) (Chart 1) osmametallocenophanes are readily soluble in all organic solvents and are thermally rather stable. Their molecular composition was corroborated by FD mass spectra displaying in each case the molecular peak. Between 2130 and 2000 cm^{-1} the IR spectra of **6a**–**c** and **7b,c** exhibit four CO absorptions, which is consistent with the presence of *cis*-$Os(CO)_4$ arrangements.

In contrast to previous results[20a,b,22] compounds with only one $Os(CO)_4$ unit (in the following referred to as mononuclear) were obtained. This finding may be rationalized by the following course of reaction: In a first step the bivalent Lewis base $[Os(CO)_4]^{2-}$ attacks one carbocation-like center of the bis(triflate) according to a nucleophilic substitution type to give an open chain intermediate ("monomer"). In a second S_N type reaction either this "monomeric" intermediate can undergo an intramolecular ring closure, or it reacts intermolecularly with a second bis(triflate) to give a "dimer"; alternatively it is able to attack a second $[Os(CO)_4]^{2-}$ anion. The possibility mentioned last is suppressed by the low solubility of $Na_2[Os(CO)_4]$ in dimethyl ether and hence the low concentration of the Lewis base. Because of the free rotation of the cyclopentadienyl ligands in the "monomer", the two reaction centers are likely to find each other, leading to a ring closure in an intramolecular S_N type reaction. Once the "dimer" is formed, it will react to oligomeric or polymeric species, since with increasing chain length the probability of the chain termini approaching each other decreases (negative $\Delta S^{\ddagger}$ value).[32]

To study the dependence of the redox behavior of the metallocene moiety on the number of metalcarbonyl fragments, the open chain metallocene-bridged complexes **8a**–**c** and **9a**–**c** containing two $Re(CO)_5$ building blocks were made accessible from the bis(triflates) **4a**–**c**/**5a**–**c** and $Na[Re(CO)_5]$ in THF at −10 °C (Scheme 1). These complexes containing three metal atoms in the molecule are fairly air-stable and dissolve readily in organic solvents of medium polarity. Their composition was confirmed by FD mass spectra. In the IR spectra of **8a**–**c** and **9a**–**c** three sharp absorptions between 2130 and 1980 cm^{-1} are ascribed to terminal CO ligands, which is consistent with a local C_{4v} symmetry of the $Re(CO)_5$ units.

Considerable similarities are established in the ^1H and $^{13}C\{^1H\}$ NMR spectra of all mentioned ferrocene and ruthenocene derivatives **2a**–**c** to **9a**–**c**. For the protons of the cyclopentadienyl groups, signals are obtained that vary from a broad singlet to an AA′XX′ pattern with centers lying between 3.91 and 3.99 and 4.33 and 4.42 ppm, respectively. Further signals with chemical shifts varying from 2.23 to 2.41 and 2.08 to 2.25 ppm for the ferrocenes and ruthenocenes, respectively, are ascribed to the protons of the CH_2 groups adjacent to the cyclopentadienyl rings. Functional groups X in the position opposite to the metallocene subcomponent and in close vicinity to methylene units exert the greatest influence on the chemical shifts of these methylene protons. Depending on the electron-donating

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or -withdrawing ability of X, ^{1}H chemical shifts range from 0.95 [X = Re(CO)$_5$], 1.02 [X = Os(CO)$_4$], 3.60 (X = OH) to 4.46 (X = OTf). Much less affected are the β-methylene protons. ^{1}H signals between 1.20 and 1.72 ppm are attributed to the remaining protons in the molecules. In particular the ^{1}H NMR spectra of the rhenium complexes **8a**−**c** and **9a**−**c** exhibit complex multiplets corresponding to AA′MM′ and AA′MM′XX′ spin systems for the α- and β-methylene protons, respectively, suggesting a hindered rotation of $C_\alpha-C_\beta$ bonds and an anti periplanar position of the bulky Re(CO)$_5$ fragment and the γ-methylene group.[33] This anti position is also favored in the solid state and was verified by an X-ray structural analysis.[34] In the case of the osmametallocenophanes **6a**−**c** and **7b,c** this situation is different for the small rings **6a,b** and **7b**. While in the region of the α- and β-methylene protons the ^{1}H NMR spectra of **6c** and **7c** are comparable with those of the rhenium species **8a**−**c** and **9a**−**c**, the spectra of **6a,b** and **7b** display virtual triplets and quintets for these protons, respectively.

Unlike the ^{13}C signals of the α-methylene carbon atoms which experience a remarkable low-field shift in the ^{13}C{^{1}H} NMR spectra of the bis(alcohols) and bis(triflates) **2a**−**c**, **3a**−**c** and **4a**−**c**, **5a**−**c**, the corresponding resonances in the spectra of the osmium- and rhenium-containing species **6a**−**c**, **7b**,**c** and **8a**−**c**, **9a**−**c** are high-field shifted. However, in the case of the osmametallocenophanes **6a**−**c** and **7b**,**c** the position of these ^{13}C resonances shows a marked dependence on the ring size with a downfield shift in the sequence −7.8 (**6a**) → −6.4 (**6b**) → −3.6 ppm (**6c**) and −6.5 (**7b**) → −4.3 ppm (**7c**) . This observation is consistent with earlier results obtained for osmacycloalkanes with different ring size.[31] Three ^{13}C signals between 91 and 66 and 93 and 68 ppm are assigned to the cyclopentadienyl carbon atoms in the spectra of the ferrocenes and ruthenocenes **2a**−**c** to **9a**−**c**. The one at lowest field is ascribed to the quaternary C atoms, and the remaining two resonances are attributed to the tertiary C atoms. Interestingly the sequence of the chemical shifts of the cyclopentadienyl tertiary C atoms in the spectra of the ferrocenes (C3′/C4′ > C2′/C5′) is different from that in the spectra of the ruthenocenes (C2′/C5′ > C3′/C4′). The sequence of the corresponding proton signals in the ^{1}H NMR spectra (H2′/H5′ > H3′/H4′) is the same on going from the ferrocenes to the ruthenocenes.[35]

Crystal Structures of 6b and 7c. To get more detailed structural information about the osmametallocenophanes, X-ray structural analyses were performed with the examples of the 12- and 16-membered cycles **6b** and **7c**. The ORTEP drawings are depicted in Figures 1 and 2 with a listing of selected bond distances and angles. Although the crystal structures of both osmametallocenophanes are of restricted quality, they can be used for a brief discussion. The two cyclopentadienyl rings are almost parallel, the angle δ at the metal (ring center−metal−ring center) was found to be 178.9° in **6b** and 178.8° in **7c**. The resulting dihedral angle (tilt angle α) between the planar cyclopentadienyl rings is 1.7° in **6b** and 2.5° in **7c**. The rings deviate from an eclipsed orientation by ca. 8.2° (**6b**) and 11.2° (**7c**). A similar situation is found in the structure of **9a**.[34] Both torsion angles which are defined by the atoms Os(1)−C(22/13)−C(21/12)−C(20/11) in **6b** are −166.4° and 75.2°, whereas in the 16-membered ring **7c** they are almost 180° (Os(1)−C(22/11)−C(21/10)−C(20/9) 175.6°, 179.3°), suggesting a more flexible situation in **7c**. The metal−osmium distances are 6.65 Å (**6b**) and 8.33 Å (**7c**).

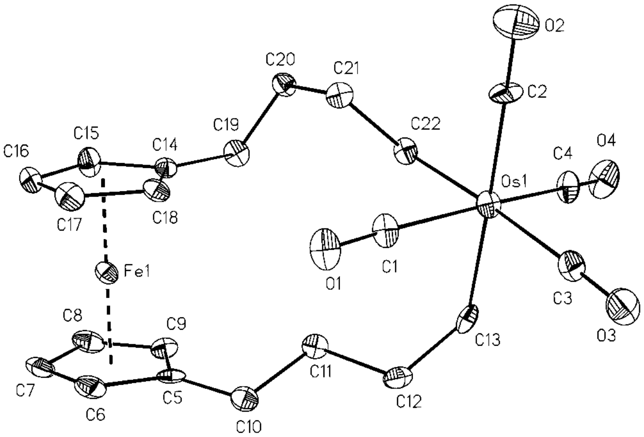

Figure 1. ORTEP plot of **6b**. Selected interatomic distances (Å) and angles (deg): Fe1−Cp1 1.651, Fe1−Cp2 1.655, Os1−C22 2.21(2), Os1−C13 2.19(2), Fe1−Os1 6.65, C22−Os1−C13 87.4(7), Cp1−Fe−Cp2 178.9, tilt angle α 1.7, Os1−C22/13−C21/12−C20/11 −166.4/75.2, mean staggering angle τ 8.2, C5−Cp1−Cp2−C14 63.7.

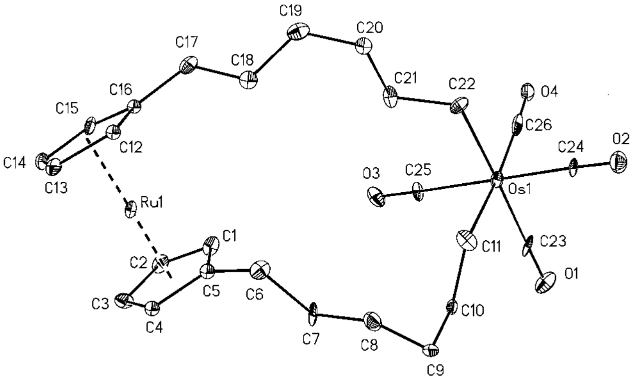

Figure 2. ORTEP plot of **7c**. Selected interatomic distances (Å) and angles (deg): Ru1−Cp1 1.812, Ru1−Cp2 1.839, Os1−C11 2.25(2), Os1−C22 2.26(3), Ru1−Os1 8.33, Cp1−Ru1−Cp2 178.8.2, tilt angle α 2.5, C20/9−C21/10−C22/11−Os1 175.6/179.3, C22−Os1−C11 82.0(10), mean staggering angle τ 11.

Redox Behavior of Compounds 2a−c, 3a−c, 6a−c, 7b,c, 8a−c, and 9a−c. The influence of substituents bound by alkyl spacers on the redox potentials $E°$ of the metallocene moiety is reflected in cyclic voltammograms of **2a**−**c**, **6a**−**c** and **8a**−**c**, recorded in acetonitrile solutions (see Figure 3a for the example of **6b**). All cyclic voltammograms of the ferrocene derivatives are similar in shape to that of the unsubstituted parent molecule. **2a**−**c**, **6a**−**c**, and **8a**−**c** are oxidized in a one-electron process to the corresponding ferrocenium cations. Elec-

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(34) Krebs, I. Ph.D. Dissertation, University of Tübingen, Germany, 1998. Structure of **9a**: formula $C_{26}H_{20}O_{10}Re_2Ru$, fw = 965.89, colorless, cryst dimens, 0.30 × 0.10 × 0.10, cryst syst, monoclinic, space group, $P2_1/n$, $a = 6.582(4)$ Å, $b = 40.57(2)$ Å, $c = 10.576(4)$ Å, $\beta = 92.77(2)°$, $V = 2821(2)$ Å^3, $Z = 4$, $d_{calcd} = 2.274$ g cm^{-3}, $T = -100$ °C, $F(000) = 1800$ e, μ(Mo Kα) = 9.143 mm^{-1}, 2θ limits 4−50°, no. of reflns measd = 7350, no. of unique data with $I \geq 2\sigma(I) = 1149$, no. of variables = 173, $S = 1.99$, R1 = 0.043, wR2 = 0.111.

(35) Hall, D. C.; Sharpe, N. W. *Organometallics* **1990**, *9*, 952.

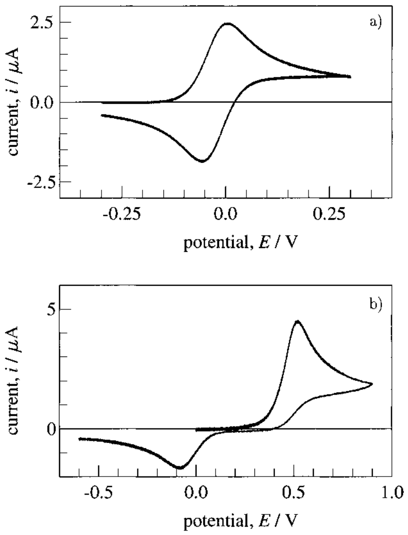

Figure 3. Cyclic voltammograms of (a) 5,5,5,5-tetracarbonyl-5-osma-[9]ferrocenophane (**6b**) in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate, $c = 2 \times 10^{-4}$ mol/L, $v = 100$ mV/s, (b) 5,5,5,5-tetracarbonyl-5-osma-[9]-ruthenocenophane (**7b**) in acetonitrile/0.1 M tetrabutylammonium hexafluorophosphate, $c = 2 \times 10^{-4}$ mol/L, $v = 100$ mV/s.

Table 1. Formal Potentials of Ferrocenes 2a−c, 8a−c, and 6a−c, versus Fc/Fc$^+$

compound	$E_{1/2}$, mV
2a	−97
2b	−118
2c	−123
8a	−142
8b	−133
8c	−124
6a	−130
6b	−126
6c	−108

trochemical and chemical reversibility was established by the following features of the curves: (i) peak potential separations are 50−70 mV (scan rate $v = 10-10000$ mV/s, 59 mV theoretical), (ii) i_{pc}/i_{pa} ratios are 1.0 ± 0.1, (iii) i_{pa} vs $v^{1/2}$ plots are linear, and (iv) $(E_{pa} + E_{pc})/2$ values are constant over the entire range of the scan rate. Only a single oxidation/reduction peak couple was observed in the potential window. Since cyclic voltammograms of butane-1,4-diylbis(pentacarbonylrhenium)[36] and 1,1,1,1-tetracarbonyl-1-osmacyclohexane[20d] do not show voltammetric signals within the potential range investigated, the peaks were assigned to the Fe(II)/Fe(III) redox couple.

The compounds **2a**−**c**, **6a**−**c**, and **8a**−**c** are oxidized at $E°$ values between −98 and −142 mV (Experimental Section, Table 1, and Figure 4) ($E°(\text{fc/fc}^+) = 0$ mV).[37] Hence, all substituents make oxidation of the ferrocene derivatives easier as compared to ferrocene itself. This is reasonable in view of the inductive electron-donating effect of alkyl groups and has also been reported for other alkyl ferrocenes in various solvents, e.g., 1,1′-dimethylferrocene ($E° = -98$ to -115 mV)[38] and 1,1′-diethylferrocene ($E° = -113$ to -117 mV)[38c,d,39] and higher homologues.[38d]

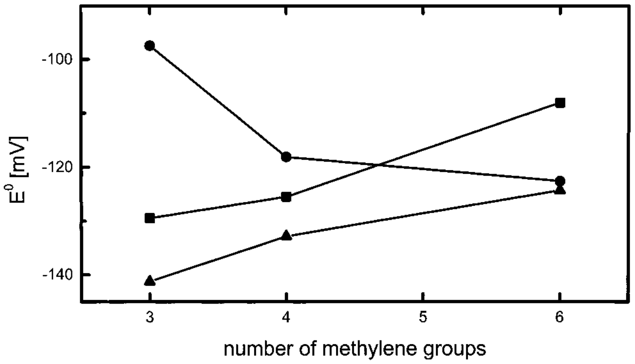

Figure 4. Redox potentials [mV] of **2a**−**c**, **6a**−**c**, and **8a**−**c** as a function of the number of methylene groups; (●) 1,1′-Bis(ω-hydroxyalkyl)ferrocenes **2a**−**c**, (▲) 1,1′-bis(ω-pentacarbonylrhenioalkyl)ferrocenes **8a**−**c**, (■) osmaferrocenophanes **6a**−**c**.

On the other hand, the electron-withdrawing CH_2OH substituent shifts $E°$ to more positive values. For 1,1′-bis(1-hydroxymethyl)ferrocene, in which the ferrocene and OH groups are separated by only a single CH_2 unit, formal potentials of +70 mV[38a] in aqueous solution, +22 mV[4b] in CH_3CN, and +60 mV[38d] were reported. The $E°$ values of the bis(alcohols) **2a**−**c** with a larger distance between the OH group and the Fe center are again negative and decrease with increasing spacer length. The difference between the propyl derivative **2a** and the butyl derivative **2b** is larger (21 mV) than that between **2b** and **2c** (5 mV).

Also, in the rhenium complexes **8a**−**c**, the influence of the substituents becomes smaller with increasing length of the spacer, but the effect of the electron rich rhenium carbonyl fragment on $E°$ is opposite that of the hydroxy functionality. Consequently, the $E°$ values of both series of compounds converge at the limiting value of an unsubstituted dialkyl ferrocene with long chain length. With six methylene groups in the spacer between the ferrocene and the OH or $Re(CO)_5$ moieties the effects of the latter substituents essentially disappear.

Although the substituents in compounds **2a**−**c** and **8a**−**c** are separated from the redox-active center in all molecules by more than three σ bonds, there is still an appreciable and consistent effect on $E°$. The OH substituent attenuates the electron-donating properties of the alkyl chain, while the $Re(CO)_5$ group increases the electron density at the $FeCp_2$ unit. Similar effects of substituents on the redox potentials of ferrocenes were explained by a Coulombic through-space interaction,[12] which possibly also causes the $E°$ shifts observed in the present series of compounds. Due to the length of the alkyl spacer, direct electronic interactions are highly unlikely, since in ferrocenecarboxyclic acids two methylene groups already decrease the influence of the COOH substituent on the ferrocene redox potential strongly.[40]

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The redox potentials of the osmaferrocenophanes **6a**−**c** (Figure 4) show a trend similar to that of the rhenium complexes **8a**−**c**, but they are shifted slightly to more positive values. Even for a large distance between the Fe and the Os center, the $E°$ values do not converge to the dialkyl limiting value, in contrast to those of the OH and $Re(CO)_5$ derivatives **2a**−**c** and **8a**−**c** discussed before. Consistent with this observation, the trimethylene bridge in [3]ferrocenophane causes a positive shift of $E°$ relative to 1,1′-diethylferrocene.[5e] Considerable effects of the number n of methylene groups in bridged ferrocenes on $E°$ were reported,[41] and the redox potentials shifted to less positive values with increasing n ($n = 3$, 4, 5). Unfortunately, the latter $E°$ values[41] cannot be referred to the $E°(\mathrm{fc/fc^+})$ standard, and a limiting value similar to that in the case of the dialkyl substituted ferrocenes cannot be defined. At least for bridges with $n = 3$, tilting of the Cp rings alters the electronic structure of the ferrocenium ions,[42] an effect that should strongly decrease with increasing n. Indeed, X-ray results for **2a**[43] and **6b** (present work) show that the Cp ligands are essentially coplanar. It is thus improbable that ring tilting plays an important role in the compounds investigated here, and the observed shifts must be due to some other effect that cannot be identified on the basis of the data available.

The cyclic voltammograms of the ruthenocenes **9a**−**c** and **7b,c** (see Figure 3b for the example of **7b**) recorded in acetonitrile solutions are different in shape from those of the ferrocene derivatives **2a**−**c**, **6a**−**c,** and **8a**−**c**. They show an oxidation wave between +350 and +500 mV and a smaller reduction wave between −50 and −250 mV. The oxidation potential increases and the reduction potential decreases with increasing scan rate. The oxidation is easier than the corresponding reaction of ruthenocene (+0.59 V vs fc/fc$^+$).[44] Products of the oxidation of **3a**−**c** seem to decrease the activity of the surface of the platinum electrode, and after a few cycles the peaks disappear. Linearity of i_{pa} vs $v^{1/2}$ plots, however, shows that the oxidation and reduction processes are diffusion controlled.

In contrast to the isoelectronic ferrocene, the electrochemical behavior of ruthenocene in acetonitrile cannot be described by a simple electron transfer.[44,45] Rather, it exhibits an irreversible two-electron oxidation process that is accompanied by coordination of one donor solvent molecule in an ECE reaction sequence. The shape and behavior of the cyclic voltammograms of **9a**−**c** and **7b,c** suggest a similar mechanism for these substituted compounds. The oxidation peak potential for **7b**,**c** linearly depends on log(v) with a slope of 35 mV (**7b**) and 31 mV (**7c**), in accordance with the assumption of a fast (pseudo) first-order chemical reaction[46] of the primary oxidation product. Formal potentials cannot be estimated from these voltammograms.

Conclusion

Recently it was demonstrated that the bis(triflate) route is a successful method for the access of metallacyclophanes provided with metal−carbon σ bonds.[19,20] Replacing the aromatic units with metallocenes leads to the novel heterobimetallic osmametallocenophanes with either an iron (**6a**−**c**) or a ruthenium center (**7a**−**c**). In contrast to previous results[20,22,31] reporting on di- and trinuclear metallacyclophanes and metallacycloalkanes, the formation of metallametallocenophanes with only one tetracarbonyl osmium fragment is preferred. However, main products are still oligo- and polymeric species. The yields of the osmametallocenophanes strongly depend on the ring size, varying between 1 and 22%. The very poor yields of the 10-membered rings **6a** and **7a** are attributed to the ring strain energies of medium-sized rings, which is in agreement with previous results.[30,31] On the basis of the torsion angles in **6b** and **7c** which are derived from X-ray structural investigations, the 16-membered ring **7c** is more flexible than the 14-membered cycle **6b**.

To investigate the influence of the metal−metal distances in the osmametallocenophanes **6a**−**c** and **7b,c** on the redox behavior of the metallocene unit, cyclic voltammograms were recorded. They were compared with corresponding cyclic voltammograms of the bis(alcohols) **2a**−**c** and **3a**−**c** and bis(rhenium) complexes **8a**−**c** and **9a**−**c**. All ferrocenes and ruthenocenes described herein are characterized by reversible one-electron and irreversible two-electron oxidation processes accompanied by fast (pseudo) first-order chemical reactions, respectively. The redox potentials of the ferrocene bis(alcohols) **2a**−**c** and the ferrocene bis(rhenium) complexes **8a**−**c** depend on the spacer length. This effect is attributed to a Coulombic through-space interaction and decreases with increasing spacer length, and the $E°$ values converge at the limiting value of a ferrocene with two unsubstituted long alkyl chains. The $E°$ values of the osmaferrocenophanes **6a**−**c** show a trend similar to those of the bis(rhenium) complexes **8a**−**c**, but they are shifted to slightly more positive values. Hence, the Coulombic through-space interaction seems also to be important in **6a**−**c**, but additional effects may be present. On the basis of the structural investigation of the osmaferrocenophane **6b**, however, ring tilting is excluded as a probable reason for the additional potential shift.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. NMR spectra were recorded at 250.13 MHz (^{1}H NMR), 62.90 MHz (^{13}C NMR), and 235.33 MHz (^{19}F

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(42) Dong, T.-Y.; Lee, S.-H. *J. Organomet. Chem.* **1995**, *487*, 77.

(43) Krebs, I. Ph.D. Dissertation, University of Tübingen, Germany, 1998. Structure of **2a**: formula $C_{16}H_{22}FeO_2$, fw = 302.19, color, yellow, cryst dimens 0.35 × 0.18 × 0.15, cryst syst, triclinic, space group, $P\bar{1}$, $a = 10.692(3)$ Å, $b = 10.863(3)$ Å, $c = 14.361(5)$ Å, $\alpha = 89.33(2)°$, $\beta = 74.51(2)°$, $\gamma = 63.16(2)°$, $V = 1422.7(7)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.411$ g cm^{-3}, $T = -100$ °C, $F(000) = 640$ e, μ(Mo Kα) = 1.055 mm^{-1}, 2θ limits 4−54°, no. of reflns measd = 13058, no. of unique data with $I \geq 2\sigma(I) = 5427$, no. of variables = 344, $S = 1.631$, R1 = 0.037, wR2 = 0.088.

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NMR) with $CDCl_3$ as solvent at 20 °C, if not stated otherwise. ^1H and ^{13}C chemical shifts were measured relative to $CDCl_3$. The assignment of the signals has been supported by DEPT-135, homonuclear, and heteronuclear correlation spectra. Elemental analyses were performed with a Carlo Erba 1106 analyzer; F and S analyses were carried out according to Schöniger[47] and determined as described by Brunisholz and Michod[48] and Wagner,[49] respectively. Rhenium, ruthenium and osmium were determined with a Varian AA20.

$Os_3(CO)_{12}$,[50] $Na_2[Os(CO)_4]$,[51] $Re_2(CO)_{10}$,[52] $FeCl_2(THF)_{1.44}$,[27] the 2-{[ω-(1,3-cyclopentadien-1-yl)alkyl]oxy}tetrahydro-2*H*-pyrans **1a**−**c**,[53] and tetrabutylammonium hexafluorophosphate[54] were synthesized according to literature methods.

General Procedure for the Preparation of the 1,1′-Bis(ω-hydroxyalkyl)ferrocenes 2a−c. *n*-BuLi (70 mL, 110.0 mmol, 1.6 M in *n*-hexane) was added dropwise to a solution of **1a**−**c** (100.0 mmol) in *n*-hexane (400 mL) at −10 °C. The resulting suspension was stirred at room temperature for 30 min. The precipitate was filtered (P3), washed with *n*-hexane (2 × 100 mL) and diethyl ether (100 mL), and dried under reduced pressure. The intermediary occurring lithium salts were dissolved in THF (300 mL), and $FeCl_2 \cdot 1.44THF$ (50.0 mmol, 11.53 g) was added to this solution. The reaction mixture was refluxed for 12 h, and subsequently THF was removed at reduced pressure and the residue was dissolved in diethyl ether (300 mL). The resulting solution was washed with water (3 × 100 mL). After removing diethyl ether under reduced pressure the residue was dissolved in ethanol (70%, 500 mL) and phosphoric acid (85%, 10 mL), and the solution was refluxed for 12 h. Then ethanol was replaced by diethyl ether (300 mL). The resulting solution was washed with water (3 × 100 mL). After evaporating diethyl ether the crude product was purified by column chromatography on silica gel ($d = 10$ cm, $l = 40$ cm, CH_2Cl_2/ethyl acetate = 1:1).

1,1′-Bis(3-hydroxypropyl)ferrocene (2a): yield 32%, air-stable orange crystals, mp 49.7 °C. ^1H NMR: δ 3.93 (s, 8H, C_5H_4), 3.59 (t, $^3J_{HH} = 6.3$ Hz, 4H, CH_2OH), 2.34 (t, $^3J_{HH} = 7.7$ Hz, 4H, $C_5H_4CH_2$), 1.76−1.63 (m, 6H, $C_5H_4CH_2CH_2$, OH). $^{13}C\{^1H\}$ NMR: δ 88.5 (s, C_4H_4C), 68.6, 67.8 (s, C_4H_4C), 62.5 (s, CH_2OH), 34.0 (s, $C_5H_4CH_2CH_2$), 25.6 (s, $C_5H_4CH_2$). IR (KBr, cm^{-1}): ν(OH) 3340 (br). MS (EI, 70 kV), *m/z*: 302 [M^+]. CV: *E*° −97 mV. Anal. Calcd (found) for $C_{16}H_{22}FeO_2$: C, 63.57 (63.78); H, 7.28 (7.36); Fe, 18.54 (18.39).

1,1′-Bis(4-hydroxybutyl)ferrocene (2b): yield 36%, air-stable brown oil. ^1H NMR: δ 3.94 (s, 8H, C_5H_4), 3.56 (t, $^3J_{HH} = 6.0$ Hz, 4H, CH_2OH), 2.26 (t, $^3J_{HH} = 7.1$ Hz, 4H, $C_5H_4CH_2$), 1.72 (s, 2H, OH), 1.6−1.4 (m, 8H, $C_5H_4CH_2(CH_2)_2$). $^{13}C\{^1H\}$ NMR: δ 89.1 (s, C_4H_4C), 68.8, 67.9 (s, C_4H_4C), 62.7 (s, CH_2OH), 32.6, 29.1, 27.2 (s, $C_5H_4(CH_2)_3$). IR (KBr, cm^{-1}): ν(OH) 3340 (br). MS (EI, 70 kV), *m/z*: 330.1 [M^+]. CV: *E*° −118 mV. Anal. Calcd (found) for $C_{18}H_{26}FeO_2$: C, 65.47 (65.57); H, 7.93 (7.85); Fe, 16.91 (17.01).

1,1′-Bis(6-hydroxyhexyl)ferrocene (2c): yield 40%, air-stable orange crystals, mp 40.4 °C. ^1H NMR: δ 3.94 (s, 8H, C_5H_4), 3.61 (t, $^3J_{HH} = 6.4$ Hz, 4H, CH_2OH), 2.28 (t, $^3J_{HH} = 7.4$ Hz, 4H, $C_5H_4CH_2$), 1.6−1.2 (m, 8H, $C_5H_4CH_2(CH_2)_4$). $^{13}C\{^1H\}$ NMR: δ 89.2 (s, C_4H_4C), 68.0, 69.0 (s, C_4H_4C), 63.0 (s, CH_2OH), 37.7 (s, CH_2CH_2OH), 31.1 (s, $C_5H_4CH_2CH_2$), 29.5, 29.3 (s, $C_5H_4CH_2CH_2(CH_2)_2$), 29.2 (s, $C_5H_4CH_2$). IR (KBr, cm^{-1}): ν(OH) 3320 (br). MS (EI, 70 kV), *m/z*: 386.1 [M^+]. CV: *E*° −123 mV. Anal. Calcd (found) for $C_{22}H_{34}FeO_2$: C, 68.39 (68.43); H, 8.87 (8.78); Fe, 14.45 (14.21).

General Procedure for the Preparation of the 1,1′-Bis(ω-hydroxyalkyl)ruthenocenes 3a−c. A solution of **1a**−**c** (50.0 mmol) and norbornene (9.42 g, 100.0 mmol) in EtOH (100 mL) was cooled to −35 °C. Upon addition of $RuCl_3 \cdot xH_2O$ (40.05% Ru, 6.31 g, 25.0 mmol) and zinc dust (40.0 g, 611.0 mmol) the red solution first turned blue and then green. The well-stirred suspension was warmed to room temperature within 2 h and then poured into a saturated solution of $NaHCO_3$ (100 mL). Extraction of the solution with diethyl ether (3 × 100 mL) and concentration in vacuo gave a residue from which the THP protecting group was removed as described above. The crude product was purified by chromatography on a silica gel column. Eluent CH_2Cl_2/ethyl acetate = 1:1.

1,1′-Bis(3-hydroxypropyl)ruthenocene (3a): yield 28%, white cream, air-stable solid, mp 94.1 °C. ^1H NMR: δ 4.42 (m,[55] 8H, C_5H_4), 3.65 (t, $^3J_{HH} = 6.4$ Hz, 4H, CH_2OH), 2.27−2.21 (m, 4H, $C_5H_4CH_2$), 1.85 (s, 2H, OH), 1.77−1.65 (m, 4H, $C_5H_4CH_2CH_2$). $^{13}C\{^1H\}$ NMR: δ 92.6 (s, C_4H_4C), 77.6, 70.2 (s, C_4H_4C), 63.1 (s, CH_2OH), 34.8 (s, $C_5H_4CH_2CH_2$), 25.7 (s, $C_5H_4CH_2$). IR (KBr, cm^{-1}): ν(OH) 3268 (br). MS (EI, 70 kV), *m/z* : 348.2 [M^+]. Anal. Calcd (found) for $C_{16}H_{22}O_2Ru$: C, 55.32 (55.14); H, 6.38 (6.39); Ru, 29.09 (28.98).

1,1′-Bis(4-hydroxybutyl)ruthenocene (3b): yield 33%, cream-brown, air-stable oil. ^1H NMR: δ 4.35 (m,[55] 8H, C_5H_4), 3.56 (t, $^3J_{HH} = 6.1$ Hz, 4H, CH_2OH), 2.24 (s, 2H, OH), 2.12 (t, $^3J_{HH} = 7.4$ Hz, 4H, $C_5H_4CH_2$), 1.52−1.45 (m, 8H, $CH_2CH_2CH_2$-OH). $^{13}C\{^1H\}$ NMR: δ 92.5 (s, C_4H_4C), 71.1, 69.5 (s, C_4H_4C), 62.5 (s, CH_2OH), 32.5 (s, CH_2CH_2OH), 28.7 (s, $C_5H_4CH_2$), 27.7 (s, $C_5H_4CH_2CH_2$). IR (KBr, cm^{-1}): ν(OH) 3316 (br). MS (EI, 70 kV), *m/z*: 376.3 [M^+]. Anal. Calcd (found) for $C_{18}H_{26}O_2Ru$: C, 57.58 (57.98); H, 6.98 (6.91); Ru, 26.92 (27.15).

1,1′-Bis(6-hydroxyhexyl)ruthenocene (3c): yield 25%, colorless, air-stable solid, mp 52.3 °C. ^1H NMR: δ 4.35 (m,[55] 8H, C_5H_4), 3.59 (t, $^3J_{HH} = 6.5$ Hz, 4H, CH_2OH), 2.10 (t, $^3J_{HH} = 7.6$ Hz, $C_5H_4CH_2$), 1.56−1.26 (m, 18H, $C_5H_4CH_2(CH_2)_4CH_2OH$). $^{13}C\{^1H\}$ NMR: δ 92.8 (s, C_4H_4C), 71.1, 69.5 (s, C_4H_4C), 62.97 (s, CH_2OH), 31.65 (s, $C_5H_4CH_2$), 32.7, 29.4, 28.9, 25.6 (s, $C_5H_4CH_2(CH_2)_4CH_2OH$). IR (KBr, cm^{-1}): ν(OH) 3270 (br). MS (EI, 70 kV), *m/z*: 432.1 [M^+]. Anal. Calcd (found) for $C_{22}H_{32}O_2Ru$: C, 60.94 (61.18); H, 8.37 (8.01); Ru, 23.31 (23.69).

General Procedure for the Preparation of the 1,1′-Bis(ω-(trifluoromethylsulfonyloxy)alkyl)metallocenes 4a−c, 5a−c. The corresponding alcohol **2a**−**c**, **3a**−**c** (2.0 mmol) and pyridine (0.17 mL, 2.15 mmol) were dissolved in 5 mL of CH_2Cl_2, and the mixture was cooled to −30 °C. Trifluoromethanesulfonic acid anhydride (0.34 mL, 2.1 mmol) dissolved in 5 mL of CH_2Cl_2 was added dropwise within 15 min to the reaction mixture, which was subsequently stirred for 20 min. Finally it was extracted with water (3 × 30 mL). The product was purified by column chromatography with activated silica gel ($d = 2.5$ cm, $l = 10$ cm, CH_2Cl_2, −30 °C). The eluent was removed under reduced pressure at −30 °C.

1,1′-Bis(3-(trifluoromethylsulfonyloxy)propyl)ferrocene (4a): yield 89%, yellow-brown oil, dec 20 °C. ^1H NMR: δ 4.46 (t, $^3J_{HH} = 6.3$ Hz, 4H, CH_2OTf), 3.97 (m,[55] 8H, C_5H_4), 2.41 (t, $^3J_{HH} = 7.4$ Hz, 4H, $C_5H_4CH_2$), 1.98−1.87 (m, 4H, $C_5H_4CH_2CH_2$). $^{13}C\{^1H\}$ NMR: δ 118.6 (q, $^1J_{CF} = 314.5$ Hz, CF_3), 87.0 (s, C_4H_4C), 76.9 (s, CH_2OTf), 69.3, 69.0 (s, C_4H_4C), 31.3 (s, CH_2CH_2OTf), 25.4 (s, $C_5H_4CH_2$). ^{19}F NMR: δ −75.2 (s, CF_3). IR (CH_2Cl_2, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 929, 1144, 1204, 1245, 1411. MS (FD, 30 °C), *m/z*: 565.8 (100). Anal. Calcd (found) for $C_{18}H_{20}F_6FeO_6S_2$: C, 38.18 (38.19); H, 3.56 (3.61); F, 20.13 (19.82); Fe, 9.86 (9.95); S, 11.32 (11.25).

1,1′-Bis(4-(trifluoromethylsulfonyloxy)butyl)ferrocene (4b): yield 91%, yellow-brown oil, dec 20 °C. ^1H NMR:

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δ 4.46 (t, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2OTf), 3.93 (m,[55] 8H, C_5H_4), 2.31 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $C_5H_4C\mathit{H}_2$), 1.82−1.71 (m, 4H, $C\mathit{H}_2CH_2OTf$), 1.61−1.48 (m, 4H, $C_5H_4CH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR: δ 118.6 (q, $^1J_{CF}$ = 321 Hz, CF_3), 87.9 (s, $C_4H_4\mathit{C}$), 77.6 (s, CH_2OTf), 68.7, 68.0 (s, C_4H_4C), 28.7 (s, $\mathit{C}H_2CH_2OTf$), 28.5 (s, $C_5H_4\mathit{C}H_2$), 26.7 (s, $C_5H_4CH_2\mathit{C}H_2$). ^{19}F NMR: δ −75.3 (s, CF_3). IR (CH_2Cl_2, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 932, 1145, 1207, 1245, 1411. MS (FD, 30 °C), *m/z*: 594.0 [M^+]. Anal. Calcd (found) for $C_{20}H_{24}F_6FeO_6S_2$: C, 40.42 (40.74); H, 4.07 (3.99); F, 19.18 (19.43); Fe, 9.39 (9.51); S, 10.79 (10.43).

1,1′-Bis(6-(trifluoromethylsulfonyloxy)hexyl)ferrocene (4c): yield 93%, yellow-brown oil, dec 20 °C. ^1H NMR: δ 4.46 (t, $^3J_{HH}$ = 6.4 Hz, 4H, CH_2OTf), 3.99 (m,[55] 8H, C_5H_4), 2.18 (t, $^3J_{HH}$ = 7.1 Hz, 4H, $C_5H_4C\mathit{H}_2$), 1.79−1.69 (m, $C\mathit{H}_2CH_2OTf$), 1.45−1.31 (m, 12H, $C_5H_4CH_2(C\mathit{H}_2)_3$). $^{13}C\{^1H\}$ NMR: δ 118.6 (q, $^1J_{CF}$ = 319.0 Hz, CF_3), 90.7 (s, $C_4H_4\mathit{C}$), 77.9 (s, CH_2OTf), 69.8, 68.9 (s, C_4H_4C), 29.2 (s, $C_5H_4\mathit{C}H_2$), 30.8 (s, $C_5H_4CH_2\mathit{C}H_2$), 28.6 (s, $\mathit{C}H_2CH_2CH_2OTf$), 29.2 (s, $\mathit{C}H_2CH_2OTf$), 24.9 (s, $C_5H_4CH_2CH_2\mathit{C}H_2$). ^{19}F NMR: δ −75.3 (s, CF_3). IR (CH_2Cl_2, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 936, 1146, 1211, 1245, 1412. MS (FD, 30 °C), *m/z*: 650.3 [M^+]. Anal. Calcd (found) for $C_{24}H_{32}F_6FeO_6S_2$: C, 44.31 (44.24); H, 4.96 (4.75); F, 17.52 (17.31); Fe, 8.58 (8.35); S, 9.86 (9.69).

1,1′-Bis(3-(trifluoromethylsulfonyloxy)propyl)ruthenocene (5a): yield 92%, colorless oil, dec 20 °C. ^1H NMR: δ 4.46 (t, $^3J_{HH}$ =6.2 Hz, 4H, CH_2OTf), 4.38 (m,[55] 8H, C_5H_4), 2.27−2.21 (m, 4H, $C_5H_4C\mathit{H}_2$), 1.98−1.85 (m, $C_5H_4CH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR: δ 119.0 (q, ^1J = 319.5 Hz, CF_3) 90.7 (s, $C_4H_4\mathit{C}$), 77.0 (s, CH_2OTf), 71.6, 70.8 (s, C_4H_4C), 31.8 (s, $C_5H_4CH_2\mathit{C}H_2$), 25.2 (s, $C_5H_4\mathit{C}H_2$). ^{19}F NMR: δ −75.2 (s, CF_3). IR (CH_2Cl_2, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 930, 1145, 1205, 1246, 1412. MS (FD, 30 °C), *m/z*: 612.0 [M^+]. Anal. Calcd (found) for $C_{18}H_{20}F_6O_6RuS_2$: C, 35.35 (35.18); H, 3.29 (3.61); F, 18.64 (19.01); Ru, 16.53 (16.26); S, 10.49 (10.24).

1,1′-Bis(4-(trifluoromethylsulfonyloxy)butyl)ruthenocene (5b): yield 91%, colorless oil, dec 20 °C. ^1H NMR: δ 4.47 (t, $^3J_{HH}$ = 6.3 Hz, 4H, CH_2OTf), 4.36 (m,[55] 8H, C_5H_4), 2.15 (t, $^3J_{HH}$ = 7.7 Hz, 4H, $C_5H_4C\mathit{H}_2$), 1.84−1.73 (m, 4H, $C\mathit{H}_2CH_2OTf$), 1.58−1.45 (m, 4H, $C_5H_4CH_2C\mathit{H}_2$). $^{13}C\{^1H\}$ NMR: δ 118.6 (q, $^1J_{CF}$ = 314.5 Hz, CF_3), 91.5 (s, $C_4H_4\mathit{C}$), 77.6 (s, CH_2OTf), 71.1, 69.9 (s, C_4H_4C), 29.4 (s, $C_5H_4\mathit{C}H_2$), 28.8 (s, $\mathit{C}H_2CH_2OTf$), 27.3 (s, $C_5H_4CH_2\mathit{C}H_2$). ^{19}F NMR: δ −75.3 (s, CF_3). IR (CH_2Cl_2, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 937, 1146, 1213, 1245, 1412. MS (FD, 30 °C), *m/z*: 639.4 [M^+]. Anal. Calcd (found) for $C_{20}H_{26}F_6RuO_6S_2$: C, 37.44 (37.76); H, 4.08 (3.87); F, 17.77 (18.15); Ru, 15.75 (15.96); S, 10.00 (9.85).

1,1′-Bis(6-(trifluoromethylsulfonyloxy)hexyl)ruthenocene (5c); yield 94%, colorless oil, dec 20 °C. ^1H NMR: δ 4.46 (t, $^3J_{HH}$ = 6.4 Hz, 4H, CH_2OTf), 4.33 (m,[55] 8H, C_5H_4), 2.11−2.05 (m, 4H, $C_5H_4C\mathit{H}_2$), 1.78−1.70 (m, 4H, $C\mathit{H}_2CH_2OTf$), 1.6−1.2 (m, 12H, $C_5H_4CH_2(C\mathit{H}_2)_3$). $^{13}C\{^1H\}$ NMR: δ 118.6 (q, $^1J_{CF}$ = 320.0 Hz, CF_3), 92.3 (s, $C_4H_4\mathit{C}$), 77.6 (s, CH_2OTf), 71.0, 69.6 (s, C_4H_4C), 31.4 (s, $C_5H_4CH_2\mathit{C}H_2$), 29.7 (s, $C_5H_4CH_2CH_2\mathit{C}H_2$), 29.1 (s, $\mathit{C}H_2CH_2OTf$), 28.9 (s, $C_5H_4\mathit{C}H_2$), 24.9 (s, $\mathit{C}H_2CH_2CH_2OTf$). ^{19}F NMR: δ −75.3 (s, CF_3). IR (CH_2Cl_2, cm^{-1}): ν(CH_2, CF_3, SO_2, SOC) 937, 1146, 1212, 1245, 1412. MS (FD, 30 °C), *m/z*: 695.6 [M^+]. Anal. Calcd (found) for $C_{24}H_{32}F_6O_6RuS_2$: C, 41.44 (41.73); H, 4.64 (4.55); F, 16.39 (16.06); Ru, 14.53 (14.57); S, 9.22 (9.39).

General Procedure for the Preparation of the Osmametallocenophanes 6a−c, 7a−c. To a suspension of $Na_2[Os(CO)_4]$ (348.2 mg, 1.0 mmol) in dimethyl ether (500 mL) was added a solution of the bis(triflates) **4a−c, 5a−c** (1.0 mmol) in 10 mL of diethyl ether at −70 °C. Stirring and refluxing of this mixture for 4 days at −22 °C gave a clear yellow solution and a yellow-brown precipitate. The solvent was allowed to bubble off through a mercury valve, and the residue was extracted with *n*-pentane (3 × 200 mL). The insoluble components were filtered off (D4), and the solvent was evaporated under reduced pressure, leaving the crude products, which were purified by column chromatography on silica gel (*d* = 2.5 cm, *l* = 30 cm, *n*-pentane/Et_2O = 100:1). Twice repeated recrystallization from *n*-pentane at −80 °C afforded the analytically pure osmametallocenophanes **6a−c** and **7b**,**c**.

4,4,4,4-Tetracarbonyl-4-osma-[7]ferrocenophane (6a): yield ca. 1%. ^1H NMR: δ 3.96 (m,[55] 8H, C_5H_4), 2.23 (t, $^3J_{HH}$ = 6.4 Hz, $C_5H_4C\mathit{H}_2$), 2.08 (m, 4H, $C_5H_4CH_2C\mathit{H}_2$), 1.44 (t, $^3J_{HH}$ = 7.7 Hz, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR: δ 179.2 (s, $OsCO_{ax}$), 170.4 (s, $OsCO_{eq}$), 91.2 (s, $C_4H_4\mathit{C}$), 66.0, 68.8 (s, C_4H_4C), 33.2 (s, $C_5H_4CH_2\mathit{C}H_2$), 32.4 (s, $C_5H_4\mathit{C}H_2$), −7.8 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2124, 2043, 2033, 2011. MS (FD, 30 °C), *m/z*: 572.8. CV: *E*° −130 mV. Because of the poor yield of **6a**, no further characterization was possible.

5,5,5,5-Tetracarbonyl-5-osma-[9]ferrocenophane (6b): yield 18%, yellow, air-stable crystals, dec 95.8 °C. ^1H NMR: δ 3.95 (m,[55] 8H, C_5H_4), 2.39 (t, $^3J_{HH}$ = 6.8 Hz, 4H, $C_5H_4C\mathit{H}_2$), 1.98−2.07 (m, 4H, $C\mathit{H}_2CH_2Os$), 1.62−1.54 (m, 4H, $C_5H_4CH_2C\mathit{H}_2$), 1.24 (t, $^3J_{HH}$ = 7.7 Hz, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR: δ 179.0 (s, $OsCO_{ax}$), 170.6 (s, $OsCO_{eq}$), 90.2 (s, $C_4H_4\mathit{C}$), 69.5, 66.5 (s, C_4H_4C), 26.5 (s, $C_5H_4\mathit{C}H_2$), 34.3 (s, $C_5H_4CH_2\mathit{C}H_2$), 35.3 (s, $\mathit{C}H_2CH_2Os$), −6.4 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2124, 2045, 2032, 2010. MS (FD, 30 °C), *m/z*: 600.4 [M^+]. CV: *E*° −126 mV. Anal. Calcd (found) for $C_{22}H_{24}FeO_4Os$: C, 44.15 (44.07); H, 4.04 (4.01); Fe, 9.33 (9.20), Os, 31.78 (31.40).

7,7,7,7-Tetracarbonyl-7-osma-[13]ferrocenophane (6c): yield 22%, yellow, air-stable crystals, dec 79.9 °C. ^1H NMR: δ 3.91 (m,[55] 8H, C_5H_4), 2.25 (t, $^3J_{HH}$ = 7.84 Hz, 4H, $C_5H_4C\mathit{H}_2$), 1.84−1.69 (m, 4H, $C\mathit{H}_2CH_2Os$), 1.59−1.32 (m, 12H, $C_5H_4CH_2(C\mathit{H}_2)_3$), 1.02 (m,[56] *N* = 17.2 Hz, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR: δ 179.2 (s, $OsCO_{ax}$), 171.4 (s, $OsCO_{eq}$), 90.1 (s, $C_4H_4\mathit{C}$), 69.3, 67.3 (s, C_4H_4C), 36.2 (s, $\mathit{C}H_2CH_2Os$), 35.1 (s, $\mathit{C}H_2CH_2CH_2Os$), 29.7 (s, $C_5H_4CH_2\mathit{C}H_2$), 29.3 (s, $C_5H_4\mathit{C}H_2$), 28.3 (s, $C_5H_4CH_2CH_2\mathit{C}H_2$), −3.6 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2125, 2043, 2038, 2009. MS (FD, 30 °C), *m/z*: 655.5 [M^+]. CV: *E*° −108 mV. Anal. Calcd (found) for $C_{26}H_{32}FeO_4Os$: C, 47.71 (47.31); H, 4.93 (4.87); Fe, 8.53 (8.19); Os, 29.06 (29.45).

5,5,5,5-Tetracarbonyl-5-osma-[9]ruthenocenophane (7b): yield 17%, colorless, air-stable crystals, dec 124.7 °C. ^1H NMR: δ 4.42 (m,[55] 8H, C_5H_4), 2.27 (t, $^3J_{HH}$ = 6.8, 4H, $C_5H_4C\mathit{H}_2$), 2.04−1.92 (m, 4H, $C\mathit{H}_2CH_2Os$), 1.57−1.46 (m, 4H, $C_5H_4CH_2C\mathit{H}_2$), 1.18 (t, ^3J = 7.7 Hz 4H, CH_2Os). $^{13}C\{^1H\}$ NMR: δ 178.9 (s, $OsCO_{ax}$), 170.6 (s, $OsCO_{eq}$), 94.3 (s, $C_4H_4\mathit{C}$), 71.9, 68.7 (s, C_4H_4C), 35.9 (s, $C_5H_4CH_2\mathit{C}H_2$), 35.4 (s, $\mathit{C}H_2CH_2Os$), 26.7 (s, $C_5H_4\mathit{C}H_2$), −6.5 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2124, 2044, 2039, 2010. MS (FD, 30 °C), *m/z*: 643.6 [M^+]. Anal. Calcd (found) for $C_{22}H_{24}O_4OsRu$: C, 41.05 (41.37); H, 3.76 (3.84); Os, 29.55 (29.71); Ru, 15.70 (15.55).

7,7,7,7-Tetracarbonyl-7-osma-[13]ruthenocenophane (7c): yield 21%, colorless, air-stable crystals, dec 74.5 °C. ^1H NMR: δ 4.39 (s, 8H, C_5H_4), 2.19−2.13 (m, 4H, $C_5H_4C\mathit{H}_2$), 1.85−1.72 (m, 4H, $C\mathit{H}_2CH_2Os$), 1.46−1.44 (m, 8H, $C_5H_4CH_2(C\mathit{H}_2)_2$), 1.44−1.35 (m, 4H, $C\mathit{H}_2CH_2CH_2Os$), 1.04 (m,[56] *N* =17.1 Hz, 4H, CH_2Os). $^{13}C\{^1H\}$ NMR: δ 178.8 (s, $OsCO_{ax}$), 170.9 (s, $OsCO_{eq}$), 93.6 (s, $C_4H_4\mathit{C}$), 71.3, 69.0 (s, C_4H_4C), 35.5 (s, $\mathit{C}H_2CH_2Os$), 34.7 (s, $\mathit{C}H_2CH_2CH_2Os$), 30.3, 27.9 (s, $C_5H_4CH_2(\mathit{C}H_2)_2$), 28.7 (s, $C_5H_4\mathit{C}H_2$), −4.3 (s, CH_2Os). IR (*n*-pentane, cm^{-1}): ν(CO) 2124, 2043, 2037, 2009. MS (FD, 30 °C), *m/z*: 701.7 [M^+]. Anal. Calcd (found) for $C_{26}H_{32}RuO_4Os$: C, 44.67 (44.92); H, 4.61 (4.65); Ru, 14.44 (14.21); Os, 27.18 (26.92).

General Procedure for the Preparation of 1,1′-Bis(ω-(pentacarbonylrhenio)alkyl)metallocenes 8a−c, 9a−c. A solution of $Re_2(CO)_{10}$ (326.3 mg, 0.50 mmol) in THF (50 mL) was stirred for 3 h over sodium amalgam (0.6%) at 20 °C. The orange solution of essentially $Na[Re(CO)_5]$ was transferred into a Schlenk tube and cooled to −10 °C, and the bis(triflates) **4a−c** and **5a−c** (0.50 mmol) were added. After stirring at −10 °C for 30 min the reaction mixture was allowed to warm to 20 °C, and the solvent was removed under vacuum. The residue

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[56] m: high-field part of an AA′MM′ pattern.

was extracted with CH_2Cl_2 (2 × 50 mL). The insoluble components were filtered off (D4), the solvent was removed, and the crude product was purified by column chromatography on silica gel ($d = 2.5$ cm, $l = 30$ cm, *n*-pentane/Et_2O 100:1). The final products were recrystallized two times from *n*-pentane at −50 °C.

1,1′-Bis(3-(pentacarbonylrhenio)propyl)ferrocene (8a): yield 58%, yellow powder, dec 122.8 °C. ^1H NMR: δ 3.96 (s, 8H, C_5H_4), 2.28 (t, $^3J_{HH} = 7.6$ Hz, 4H, $C_5H_4CH_2$), 1.99−1.86 (m, 4H, $C_5H_4CH_2CH_2$), 0.97 (m,[56] $N = 17.2$ Hz, 4H, CH_2Re). $^{13}C\{^1H\}$ NMR: δ 185.6 (s, $ReCO_{cis}$), 181.2 (s, $ReCO_{trans}$), 89.0 (s, C_4H_4C), 68.8, 67.4 (s, C_4H_4C), 41.0 (s, $C_5H_4CH_2CH_2$), 37.2 (s, $C_5H_4CH_2$), −9.1 (s, CH_2Re). IR (*n*-pentane, cm^{-1}): ν(CO) 1984, 2010, 2124. MS (FD, 30 °C), *m/z*: 919.4 [M^+]. CV: $E°$ −142 mV. Anal. Calcd (found) for $C_{26}H_{29}FeO_{10}Re_2$: C, 33.92 (34.24); H, 2.19 (2.22); Fe, 6.07 (5.89); Re, 40.45 (40.21).

1,1′-Bis(4-(pentacarbonylrhenio)butyl)ferrocene (8b): yield 56%, yellow powder, dec 122.4 °C. ^1H NMR: δ 3.9 (s, 8H, C_5H_4), 2.27 (t, $^3J_{HH} = 7.8$ Hz, 4H, $C_5H_4CH_2$), 1.81−1.65 (m, 4H, CH_2CH_2Re), 1.39−1.48 (m, 4H, $C_5H_4CH_2CH_2$), 0.90 (m,[56] $N = 17.1$ Hz, 4H, CH_2Re). $^{13}C\{^1H\}$ NMR: δ 185.9 (s, $ReCO_{cis}$), 181.5 (s, $ReCO_{trans}$), 89.5 (s, C_4H_4C), 68.6, 77.6 (s, C_4H_4C), 39.2 (s, CH_2CH_2Re), 38.9 (s, $C_5H_4CH_2CH_2$), 28.7 (s, $C_5H_4CH_2$), −10.6 (s, CH_2Re). IR (*n*-pentane, cm^{-1}): ν(CO) 1984, 2012, 2124. MS (FD, 30 °C), *m/z*: 947.9 [M^+]. CV: $E°$ −133 mV. Anal. Calcd (found) for $C_{28}H_{24}FeO_{10}Re_2$: C, 35.45 (35.17); H, 2.55 (2.69); Fe, 5.89 (5.97); Re, 39.25 (38.93).

1,1′-Bis(6-(pentacarbonylrhenio)hexyl)ferrocen (8c): yield 60%, yellow powder, dec 67.2 °C. ^1H NMR: δ 3.96 (s, 8H, C_5H_4), 2.28 (m, 4H, $C_5H_4CH_2$), 1.65−1.83 (m, 4H, CH_2CH_2Re), 1.38−1.55 (m, 4H, $C_5H_4CH_2CH_2$), 1.31 (m, 4H, $C_5H_4CH_2CH_2CH_2$), 1.30 (m, 4H, $CH_2CH_2CH_2Re$), 0.94 (m,[56] $N = 17.0$ Hz, 4H, CH_2Re). $^{13}C\{^1H\}$ NMR: δ 186.0 ($ReCO_{cis}$), 181.5 ($ReCO_{trans}$), 89.6 (s, C_4H_4C), 68.7, 67.7 (s, C_4H_4C), 39.1 (s, CH_2CH_2Re), 37.3 (s, $CH_2CH_2CH_2Re$), 31.3 (s, $C_5H_4CH_2CH_2$), 29.4 (s, $C_5H_4CH_2CH_2CH_2$), 29.1 (s, $C_5H_4CH_2$), −9.2 (s, CH_2Re). IR (*n*-pentane, cm^{-1}): ν(CO) 1984, 2011, 2124. MS (FD, 30 °C), *m/z*: 1004.2 [M^+]. CV: $E°$ −124 mV. Anal. Calcd (found) for $C_{32}H_{32}FeO_{10}Re_2$: C, 38.25 (38.67); H, 3.21 (3.36); Fe, 5.56 (5.21); Re, 37.06 (37.35).

1,1′-Bis(3-(pentacarbonylrhenio)propyl)ruthenocene (9a): yield 60%, colorless crystals, dec 124.1 °C. ^1H NMR: δ 4.40 (m,[55] 8H, C_5H_4), 2.13 (t, $^3J_{HH} = 7.6$ Hz, 4H, $C_5H_4CH_2$), 1.95−1.82 (m, 4H, $C_5H_4CH_2CH_2$), 0.96 (m,[56] $N = 17.0$ Hz, 4H, CH_2Re). $^{13}C\{^1H\}$ NMR: δ 186.3 (s, $ReCO_{cis}$), 181.8 (s, $ReCO_{trans}$), 93.1 (s, C_4H_4C), 71.6, 69.9 (s, C_4H_4C), 42.1 (s, $C_5H_4CH_2CH_2$), 37.4 (s, $C_5H_4CH_2$), −8.9 (s, CH_2Re). IR (*n*-pentane, cm^{-1}): ν(CO) 1985, 2012, 2124. MS (FD, 30 °C), *m/z*: 965.5 [M^+]. Anal. Calcd (found) for $C_{26}H_{20}O_{10}Re_2Ru$: C, 32.33 (32.62); H, 2.09 (2.24); Re, 38.56 (38.35); Ru, 10.46 (10.31).

1,1′-Bis(4-(pentacarbonylrhenio)butyl)ruthenocene (9b): yield 61%, colorless powder, dec 119.1 °C. ^1H NMR: δ 4.40 (m,[55] 8H, C_5H_4), 2.19−2.13 (m, 4H, $C_5H_4CH_2$), 1.86−1.71 (m, 4H, CH_2CH_2Re), 1.49−1.37 (m, 4H, $C_5H_4CH_2CH_2$), 0.94 (m,[56] $N = 17.0$ Hz, CH_2Re). $^{13}C\{^1H\}$ NMR: δ 186.4 ($ReCO_{cis}$), 181.9 ($ReCO_{trans}$), 93.6 (C_4H_4C), 71.6, 69.9 (C_4H_4C), 39.9 (CH_2CH_2Re), 39.6 ($C_5H_4CH_2CH_2$), 29.0 ($C_5H_4CH_2$), −9.1 (CH_2Re). IR (*n*-pentane, cm^{-1}): ν(CO) 1984, 2011, 2124. MS (FD, 30 °C), *m/z*: 993.9 [M^+]. Anal. Calcd (found) for $C_{28}H_{24}O_{10}Re_2Ru$: C, 33.83 (34.18); H, 2.43 (2.61); Re, 37.47 (37.22); Ru, 10.17 (10.05).

1,1′-Bis(6-(pentacarbonylrhenio)hexyl)ruthenocene (9c): yield 55%, colorless powder, dec 89.7 °C. ^1H NMR: δ 4.39 (m,[55] 8H, C_5H_4), 2.15−2.10 (m, 4H, $C_5H_4CH_2$), 1.66−1.82 (m, 4H, CH_2CH_2Re) 1.45−1.36 (m, 4H, $C_5H_4CH_2CH_2$), 1.20−1.35 (m, 8H, $C_5H_4(CH_2)_2(CH_2)_2$), 0.93 (m,[56] $N = 17.01$ Hz, 4H, CH_2Re). $^{13}C\{^1H\}$ NMR: δ 186.0 (s, $ReCO_{cis}$), 181.5 (s, $ReCO_{trans}$), 93.1 (s, C_4H_4C), 71.1, 69.5 (s, C_4H_4C), 39.1 (s, CH_2CH_2Re), 37.4, 29.1 (s, $C_5H_4(CH_2)_2(CH_2)_2$), 39.1 (s, $C_5H_4CH_2CH_2$), 29.1 (s, $C_5H_4CH_2$), −9.2 (s, CH_2Re). IR (*n*-pentane, cm^{-1}): ν(CO) 1984, 2011, 2124. MS (FD, 30 °C), *m/z*: 1050.1 [M^+]. Anal. Calcd (found) for $C_{32}H_{32}O_{10}Re_2Ru$: C, 36.60 (36.86); H, 3.07 (2.95); Re, 35.47 (35.02); Ru, 9.62 (10.01).

Table 2. Crystal Data and Refinement Details for Compounds 6b and 7c

	compound	
	6b	**7c**
formula	$C_{22}H_{24}FeO_4Os$	$C_{26}H_{32}O_4OsRu$
fw	598.46	699.79
color	yellow	colorless
cryst dimens	0.50 × 0.25 × 0.15	0.30 × 0.20 × 0.20
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	6.1467(12)	5.901(3)
b, Å	43.404(9)	49.915(11)
c, Å	8.187	9.112(2)
β, deg	106.60(3)	108.64(3)
V, Å^3	2093.1(7)	2543.1(13)
Z	4	4
d_{calcd}, g cm^{-3}	1.899	1.828
T, °C	20	−100
F(000), e	1160	1360
μ(Mo Kα), mm^{-1}	6.782	5.613
2θ limits, deg	6−54	4−44
no. of reflns measd	11 744	9064
no. of unique data with $I \geq 2\sigma(I)$	3385	3015
no. of variables	254	260
S	1.23	2.23
R1[a]	0.083	0.090
wR2[b]	0.169	0.206

[a] R1 $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] wR2 $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$.

Crystallographic Analysis. Single crystals of low quality of **6b** and **7c** were obtained from THF and *n*-pentane solutions, respectively. The crystals were mounted on a glass fiber and transferred to a CAD4 (Enraf Nonius) and a P4 (Siemens) diffractometer, respectively, using graphite-monochromated Mo Kα radiation. In the case of **7c** rotation photographs were taken and a photo search was performed to find a suitable reduced cell. The lattice constants of both structures were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters are summarized in Table 2. Intensities were collected with the ω-scan technique. An absorption correction was applied (ψ-scan, maximum and minium transmission: **6b**, 0.64, 0.38; **7c**, 0.71, 0.42). All structures were solved by direct methods[57] and refined by least-squares with anisotropic thermal parameters for all non-hydrogen atoms (based on F^2). The atoms C4, C5, C15, C16, C18, and C20 of **7c** were refined isotropically. All hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 2.424 and −2.513 (**6b**) and 4.422 and −2.840 e Å (**7c**), respectively.

Electrochemical Experiments. All electrochemical experiments were performed with a Bioanalytical Systems (BAS, West Lafayette, IN) CV-50W electrochemical workstation controlled by a standard 80486 personal computer (control program version 2.0). For electroanalytical experiments a Metrohm Pt electrode tip (Filderstadt, Germany) was used as working electrode. The counter electrode was a Pt wire of 1 mm diameter. A single-unit Haber-Luggin double reference-electrode[58] 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 the respective

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(57) Sheldrick, G. M. *SHELXTL V5.03 program*; University of Göttingen, Germany, 1995.

(58) Gollas, B.; Krauss, B.; Speiser, B.; Stahl, H. *Curr. Sep.* **1994**, *13*, 42.

solvent, and all potentials were rescaled to $E°(fc/fc^+)$ (+0.103 V in CH_3CN vs Ag/Ag^+). All potentials in the present paper are reported relative to the fc/fc^+ standard.[37]

For cyclic voltammetry a gastight full-glass three-electrode cell was used: its assembly for the experiments has been described.[54] The cell was purged with argon before it was filled with electrolyte. Background curves were recorded before adding substrate to the solution. These were later subtracted from the experimental data with substrate. The automatic BAS CV-50W *iR*-drop compensation facility was used for all experiments.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **6b** and **7c** (14 pages). Ordering information is given on any current masthead page.

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