Preparation, Properties, and Reactions of Metal-Containing Heterocycles, XCIII[◇]

Diosma[5.*n*.5.*n*]ortho-, -meta-, and -paracyclophanes (*n* = 0–2)☆

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The reaction of the *ortho-*, *meta-*, and *para*-bis(triflates) $[(F_3CSO_2OCH_2CH_2C_6H_4)_2(CH_2)_n]$ with $n = 0$ (*ortho*: **1a**), $n = 0, 1$ (*meta*: **1b**, **d**), and $n = 0-2$ (*para*: **1c**, **e**, **g**) with $[Os(CO)_4]^{2-}$ results in the formation of the diosma[5.*n*.5.*n*]-ortho-, -meta-, and -paracyclophanes with $n = 0$ (ortho: **2a**), $n = 0, 1$ (meta: **2b**, **d**), and $n = 0-2$ (para: **2c**, **e**, **g**). On reaction of the bis(triflates) **1a**, **b** with the dianionic $[Fe(CO)_4]^{2-}$ the corresponding ferracyclophanes are formed only in situ. Carbon monoxide insertion into the Fe–C σ bonds of the ferracycles affords the ketones **6a**, **b**. The structures of **2a** and **2e** were investigated by X-ray structural analysis. Compounds **2a** and **2e** crystallize in the space group $P2_1/c$ with $Z = 8$ and $P\bar{1}$ with $Z = 2$, respectively.

Metallacycloalkanes with at least two metal-carbon σ bonds serve as model compounds in transition metal-catalyzed or mediated organic syntheses, where they appear as reactive intermediates[1–3]. An easy access to metallacycloalkanes has been opened by the bis(triflate) route[2,4–9], which is a variant of cationic alkylation[8]. The excellent and inert leaving group $F_3CSO_2O^-$ stabilizes carbenium-like atoms at the ends of a hydrocarbon chain[10], thereby enabling an electrophilic attack of the terminal carbon atoms at a basic metal center. For instance, metallacycloalkanes of iron, ruthenium, and osmium with various ring sizes are available by the reaction of the corresponding bivalent metalates $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os) with alkanediylbis(trifluoromethanesulfonates)[4,5,7–9]. The use of bistriflates with a xylidene framework leads to metallacyclophanes as products following the bistriflate route[4,5]. Thus, a connection was established between the chemistry of metallacycloalkanes and that of cyclophanes. Cyclophane chemistry is undergoing rapid development and has produced a multitude of architecturally impressive molecules, with features related to structure and functionalization, that are able to embed guest molecules[11]. The specific integration of heteroatoms (N, O, S) leads to cyclophane frameworks with special complexation qualities, suitable for molecular recognition.

The introduction of a tetracarbonyl transition metal moiety has an influence on the structure of the metallacyclophane because of the steric requirement. Simultaneously, a new reactive center is obtained that is capable of inserting carbon monoxide into the M–C σ bonds. A cyclic ketone is formed easily by reductive elimination of the organometallic fragment[12,13].

In this article we describe the preparation and properties of diosma[5.*n*.5.*n*]ortho-, -meta-, and -paracyclophanes with *n* = 0–2 and the reaction of the corresponding ferracyclophanes with carbon monoxide.

Results and Discussion

Diosmacyclophanes

The diosma[5.*n*.5.*n*]cyclophanes (*n* = 0–2) **2a–g**, being made of two equivalent $-[CH_2]_2-C_6H_4-[CH_2]_n-C_6H_4-[CH_2]_2-Os(CO)_4-$ building blocks, are formed by treating the corresponding bis(triflates) **1a–g**[14] with a suspension of the metal Lewis base $[Os(CO)_4]^{2-}$ in dimethyl ether at −30 °C (Scheme 1). The reaction proceeds successfully only in dimethyl ether because of the low solubility and the weak nucleophilicity of the $[Os(CO)_4]^{2-}$ dianion[15]. Within three days a bright yellow solution containing **2a–g** and a yellow-brown precipitate were obtained from the pale yellow $Na_2[Os(CO)_4]$ suspension. The latter consists of metal-containing oligomers and sodium triflate. The osmacyclophanes **2a–g** are rather stable in air and can be handled at room temperature without decomposition. The osmium–carbon σ bond is thermally quite stable. This observation is in agreement with the stability of other 5d transition metal–carbon σ bonds[13c].

In the case of the bis(triflate) **1f** the formation of the diosma[5.2.5.2]orthocyclophane **2f** was also accompanied by the occurrence of the eleven-membered osmacycle **3f**[4] (Figure 1). According to the method of cationic alkylation with bis(triflates), the generation of "monomeric" osma[5.*n*]cyclophanes obviously requires a spatial proximity of the carbon atoms carrying the triflate groups. Only *ortho*-**1f** meets this condition, whereas a stretched arrangement is present in the case of the *para*-bis(triflates) **1c**, **e**, **g**. Cyclization to a "mononuclear" osma[5.*n*]paracyclophane is therefore impossible. In addition, the preferred formation

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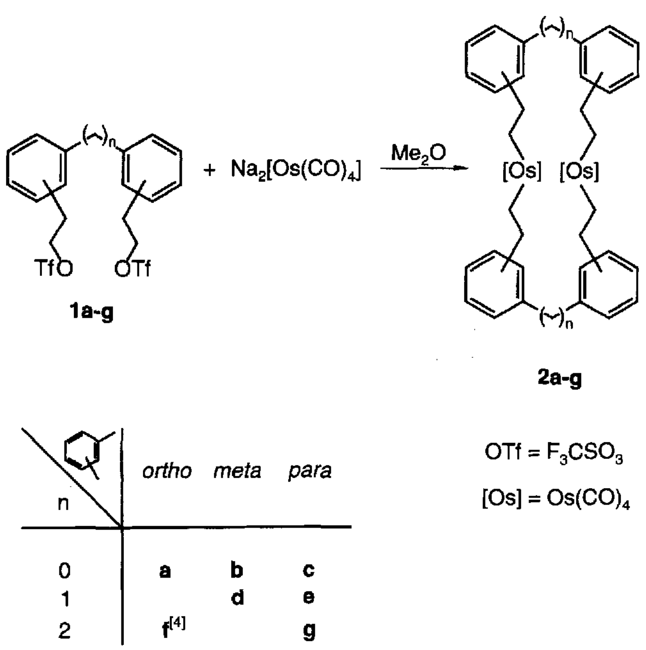
Scheme 1

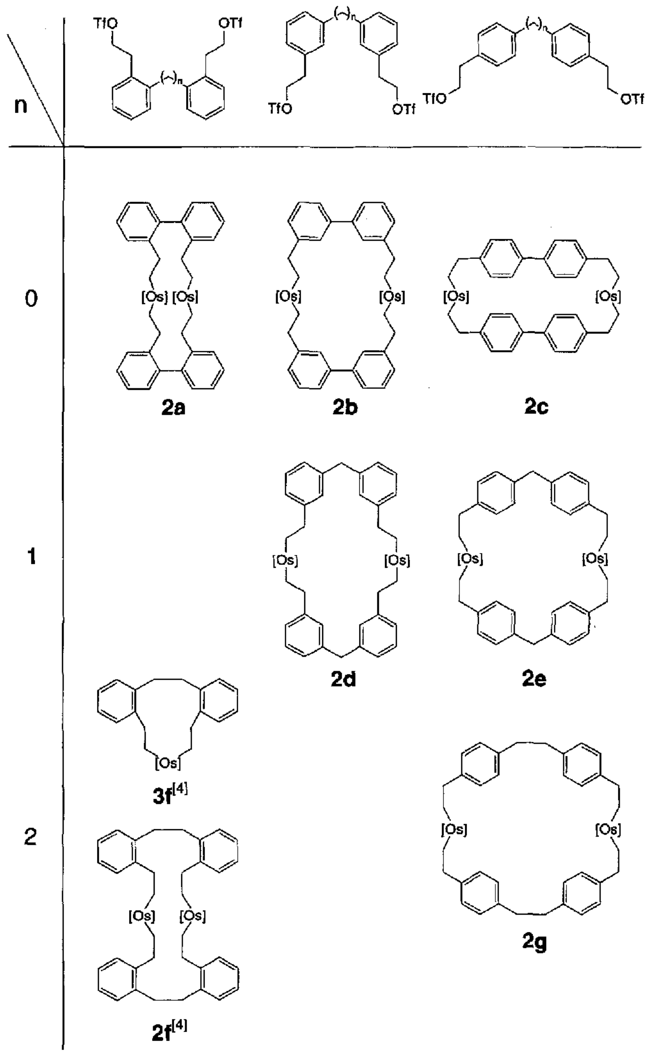


n	*ortho*	*meta*	*para*
0	a	b	c
1		d	e
2	f[4]		g

OTf = F_3CSO_3

[Os] = $Os(CO)_4$

Figure 1. Osmacyclophanes **2a**–**g** from the reaction between the bis(triflates) **1a**–**g** and $Na_2[Os(CO)_4]$



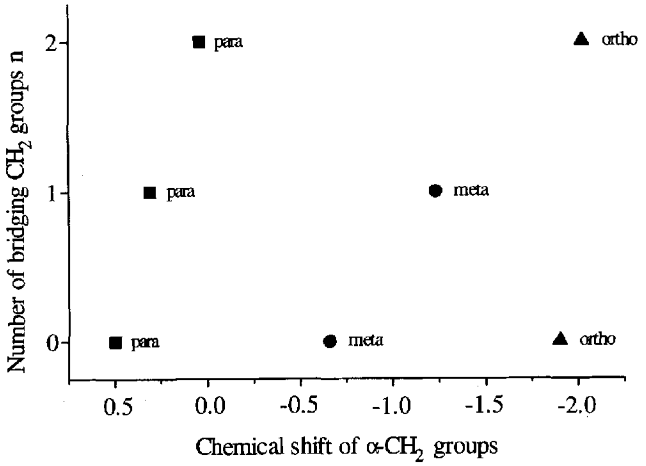
of "dinuclear" osmacyclophanes can be explained by an entropy effect[16]. Nevertheless, the yield of the dimeric species **2a**–**e**, **g** is rather low. This disadvantage is attributed to difficult purification steps: half of the crude product is lost during work-up. Moreover, in addition to the desired diosmacycles **2a**–**e**, **g** trinuclear and oligonuclear species are also formed during the reaction of the corresponding bis(triflates) **1a**–**e**, **g** with $Na_2[Os(CO)_4]$. "Trimeric" osmacycles were detected in the field desorption mass spectra in the case of the *para* compounds **e** and **g** {FD-MS, 32°C, *m/z*: 1531.7 [M^+] (e), 30°C, *m/z*: 1615.8 [M^+] (g)}. The IR spectra of the insoluble reaction residue still reveals CO absorptions that are characteristic of *cis*-$Os(CO)_4$ fragments [IR (KBr): $\tilde{\nu}$ = 2124 cm^{-1}, 2044, 2031, 2002 (CO)].

The molecular composition of the diosmacycles **2a**, **b**, **d**, **e**, **g** was corroborated by FD mass spectra showing in each case the molecular peak. In the spectrum of **2c** only the $M^+ - Os(CO)_4$ peak was observed. The isotopic distribution of the observed molecular peaks is in agreement with the calculated isotopic pattern. Whereas the heterocycles **2a**–**c**, **e** are colorless, **2d**, **g** are yellow. These compounds are all soluble in chlorinated hydrocarbons. They are less soluble in diethyl ether and *n*-pentane. In the region between 2130 and 2000 cm^{-1} the IR spectra of **2a**–**e**, **g** exhibit four CO absorptions, consistent with the presence of a *cis*-$Os(CO)_4$ unit.

In the ^1H-NMR spectra of **2a**–**e**, **g** the protons of the methylene groups between the aromatic rings and the metal give rise to a complex multiplet structure caused by the hindered rotation of these groups in the cyclic system. An AB system in the low-field part of the ^1H-NMR spectra of the diosmaparacyclophanes **2c**, **e**, **g** is assigned to the aromatic protons. The coupling constant $^3J_{AB}$ could be determined only in the case of **2c** (8.3 Hz). The difference of the chemical shifts $\Delta = \delta_A - \delta_B$ decreases with the increase of the number of bridging methylene groups between the aromatic rings. As a consequence, the intensity of the external signals of the AB spectrum becomes so low that $^3J_{AB}$ for **2e**, **g** could not be determined.

In the $^{13}C\{^1H\}$-NMR spectra of the osmacycles **2a**–**g** the α-ring carbon atoms show a remarkable high-field shift compared with that of the bis(triflates) **1a**–**g**. If the number of bridging CH_2 groups *n* is constant, the high-field shift increases in the sequence para < meta < ortho. If compounds with the same substitution pattern but a larger ring size are compared with each other, e.g., the diosmaparacyclophanes **2c**, **e**, **g**, the high-field shift increases with the number *n* (0 < 1 < 2) of bridging methylene units between the two aromatic rings. The smaller the ring strain, the more the signal of the α-CH_2 groups is shifted to higher field (Figure 2). Because of the *para* substitution of the aromatic rings in **2c**, **e**, **g** in the $^{13}C\{^1H\}$-NMR spectra only four $^{13}C\{^1H\}$ resonances occur for the aromatic ring carbon atoms compared with six signals for the same atoms observed in the $^{13}C\{^1H\}$-NMR spectra of the ortho- and metacyclophanes **2a**, **b**, **d**.

Figure 2. Dependence of the chemical shift of the α-CH_2 groups of the diosmacyclophanes **2a–g** on the ring size



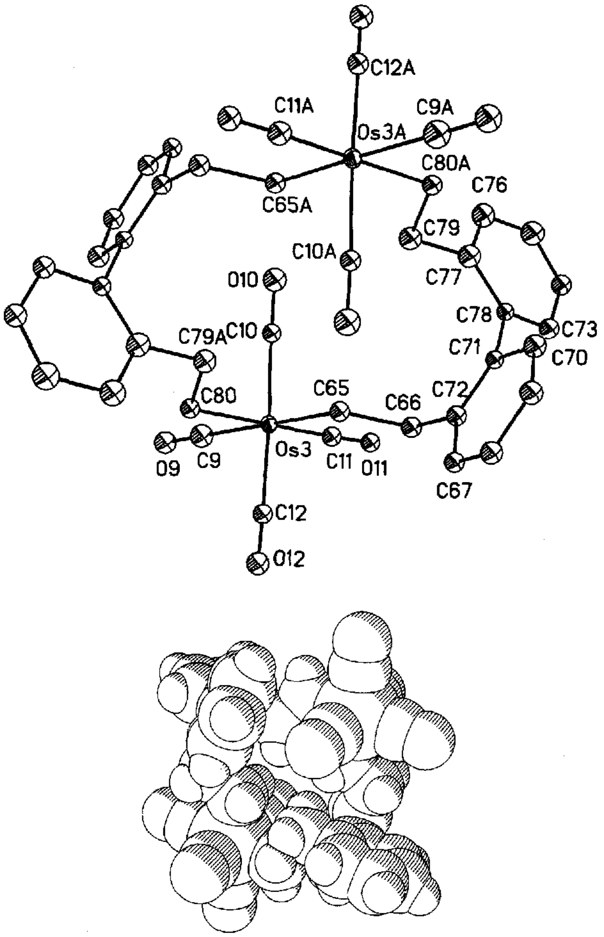
Structures of 2a and 2e

Since the discovery of crown ethers by Pedersen[17] in 1967 the chemistry of synthetic hosts for specific complexation of organic and inorganic guest molecules has developed rapidly[18]. The investigations on synthetic cyclophanes as hosts in particular have contributed to an understanding of the complexation of neutral organic guest molecules in aqueous and organic solvents. The structure of complexes containing enclosed benzene, toluene, *p*-xylene, durene, napthalene, anisole, and *p*-nitrophenol have been proved by their X-ray crystal structures. In addition to arenes chloroform, dichloromethane, 1,2-dichloroethane, carbon disulfide, and acetonitrile have also been found to be embedded in the non-polar cavities of cyclophanes.

The introduction of a transition metal complex fragment into the ring framework of a cyclophane effects the geometrical properties of the cavity formed by the metallacyclophane. In addition, an interaction between the transition metal fragment and the guest molecule could appear, which would be of special interest particularly for the development of synthetic enzymes[19].

Concerning the possibility of the formation of metallacyclophane-guest complexes the structures of the diosmacyclophanes **2a** and **2e** are described with regard to the shape and the size of the cavity. Although the crystal structure of **2a** is of poor quality[20] it can nevertheless be used for a discussion of the structure. One of the independent molecules of structure **2a** with an inversion center is depicted in Figure 3 (top). Cyclophanes with one and two biphenyl units have been investigated regarding their lowest energy conformation[21]. Thus, twist angles of the biphenyl system are observed that cover the whole possible range of 0–90°. In the centrosymmetric diosmacyclophane **2a**, the two least-square planes of the aromatic rings C67 to C72 and C73 to C78 of the biphenyl fragment display a twist angle of 85.2°. The distance of the parallel best planes, determined by the atoms C67 to C72 and C67A to C72A, is 7.1 Å. In the case of the parallel best planes containing the carbon atoms C73 to C78 and C73A to C78A the distance is 3.6 Å. The two best planes fixed by the atoms Os3, C9, C11, C65, C80, and Os3A, C9A, C11A, C65A, C80A are shifted vertically by 3.9 Å. The osmium atoms Os3 and Os3A are separated from each other by 7.3 Å. Because of the *ortho* substitution of the biphenyl unit a compact conformation is found in the structure of the diosmacyclophane **2a** in which the CO groups C10–O10 and C10A–O10A are bent[22] toward the remaining "cavity" [C10–Os3–C12 (166.9(7)°)]. The space-filling drawing of **2a** (Figure 3, bottom) clearly shows that the interior of the cyclophane framework is too small for inclusion of a guest molecule. In addition, the shielding CO units hinder entrance into the cavity.

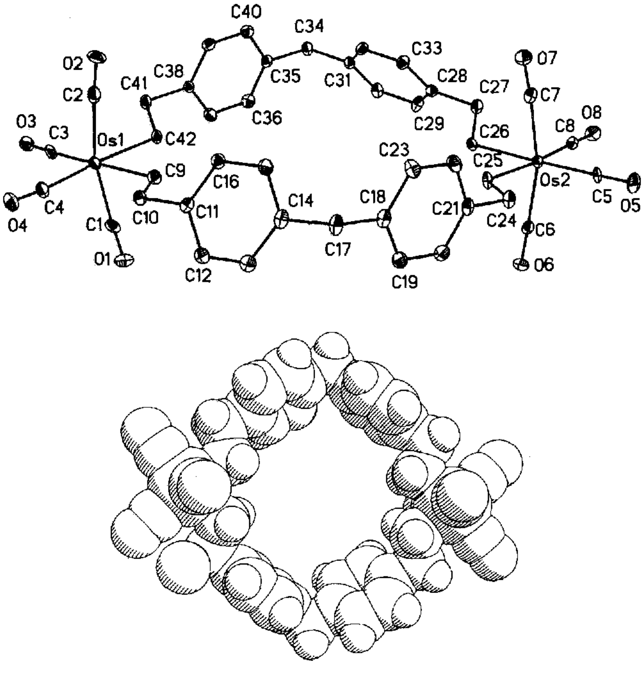
Figure 3. Top: ORTEP plot of the molecular structure of compound **2a**. – Bottom: Space-filling representation of compound **2a**



The solid-state structure of **2e** (Figure 4) reveals that the conformation can be described by a rhombohedron in which the vertices are occupied by the atoms Os1, Os2, C17, and C34. The distances Os1–Os2 (12.3 Å) and C17–C34 (12.2 Å) are similar. At the same time the molecule adopts a "dished" conformation with the planes of the aromatic rings inclined from a rectangular arrangement. This inclination is determined by the torsion angles C9–C10–C11–C16 (62.6°), C25–C24–C21–C22 (89.6°), C26–C27–C28–C33 (74.5°), and C42–C41–C38–C37

(76.3°). As expected, the distance between the facing carbon atoms of the aromatic rings at the upper brim of the "dish" is greater [C12−C30 and C13−C29 (11.6 Å), C19−C37 and C20−C36 (10.5 Å)] than the corresponding distance at the bottom [(C16−C32 and C15−C33 (8.9 Å), C23−C39 and C22−C40 (10.1 Å)]. The expansion of the interior along the Os1−Os2 axis is defined by the distances C9−C25 and C42−C26 and is calculated for both to be 9.0 Å. Despite this dishing of the molecule, inspection of the space-filling representation of the diosmacyclophane **2e** (Figure 4, bottom) reveals that there is still a significant free passage through the center of the macrocycle. The maximum and minimum cavity clear pathways are approximately 8.5 and 5.0 Å, respectively. The molecules are arranged in such a way as to produce a continuous channel. This structure is similar to that observed for the 1,6,20,25-tetraaza[6.1.6.1]-paracyclophane[23] and *N*,*N'*,*N''*,*N'''*-tetramethyl-2,11,20,29-tetraaza[3.3.3.3]paracyclophane[24], which both form stable complexes with durene and 1,4-dioxane in the solid state. However, the diosmacyclophane **2e** meets those requirements, concerning the size of the cavity and the packing of the molecules, of being capable of including a wide range of guest species. Future investigations will examine this assumption.

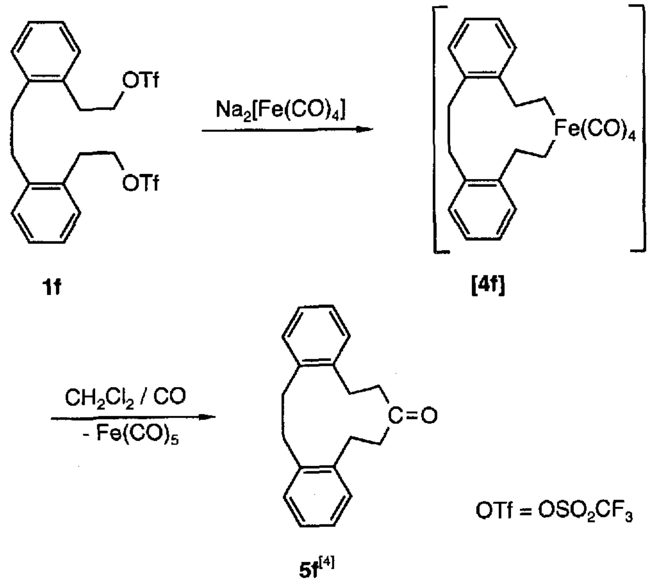
Figure 4. Top: ORTEP plot of the molecular structure of compound **2e**. − Bottom: Space-filling representation of compound **2e**. − Selected bond lengths [A] and angles [°]: Os1−C9 2.215(9), Os1−C42 2.223(8), Os2−C25 2.209(8), Os2−C26 2.213(8), C9−C10 1.532(11), C41−C42 1.518(12), C24−C25 1.536(12), C26−C27 1.530(12), C10−C11 1.514(11), C38−C41 1.520(10), C21−C24 1.518(10), C27−C28 1.525(12), C14−C17 1.521(12), C17−C18 1.508(10), C31−C34 1.526(11), C34−C35 1.518(11); C1−Os1−C2 166.0(4), C6−Os2−C7 165.2(3), C9−Os1−C42 81.9(3), C25−Os2−C26 82.8(3), Os1−C9−C10 118.5(6), Os1−C42−C41 117.0(5), Os2−C25−C24 117.5(5), Os2−C26−C27 115.7(5), C9−C10−C11 113.2(7), C38−C41−C42 110.9(7), C21−C24−C25 111.7(7), C26−C27−C28 112.2(7), C14−C17−C18 113.4(7), C31−C34−C35 113.1(7)



Reaction of Diferra[5.*n*.5.*n*]cyclophanes with Carbon Monoxide

Cyclization of functionalized, large hydrocarbon chains is still a difficult task in organic synthesis[25]. In particular, the derivatization of large rings is hardly possible by employing "classical" methods[26]. The thermally induced decomposition of osma-, ruthena-, and ferracycloalkanes in the presence of carbon monoxide results in the insertion of the latter into the M−C σ bond, followed by reductive elimination of the metal fragment to leave cyclic ketones of various ring sizes[7]. Metal-containing cyclic ketones should be expected as intermediates of this reaction which, however, are extremely unstable and generally cannot be detected or even isolated. This behavior is revealed in particular by ferracyclophanes even below −40 °C without any additional carbon monoxide, which stems from a partial decarbonylation of the $Fe(CO)_4$ groups. The resulting products are macrocyclic ketones (oxocyclophanes) being formed in a facile way. Thermolysis of comparable ruthena- and osmacyclophanes results only in the formation of the stable clusters $M_3(CO)_{12}$ and unidentified products[4]. The remarkable stability of osmium−carbon σ bonds establishes the employment of osmacyclophanes as model compounds for detailed structural and spectroscopic investigations. This property was also found by Moss et al., who reported on the rates of the alkyl migration in complexes of iron, ruthenium, and osmium[27]. The marked reactivity of ferracyclophanes with regard to carbon monoxide insertion is a promising tool for more favorable access to cyclic ketones with large ring size. Referring to the above-mentioned synthetic possibility the bis(triflate) method should offer an easy approach for macrocycles functionalized with keto groups.

Scheme 2



The formation of the cyclic ketone **5f** by treating the reaction product of $Na_2[Fe(CO)_4]$ and the bis(triflate) **1f** in dimethyl ether with carbon monoxide in the presence of dichloromethane (Scheme 2) has been described recently[4].

Because of the promising results of this reaction the behavior of the corresponding ferracyclophanes, formed in situ from the system bis(triflates) **1a–c, e, g**/$Na_2[Fe(CO)_4]$ in dimethyl ether in the presence of carbon monoxide was also investigated.

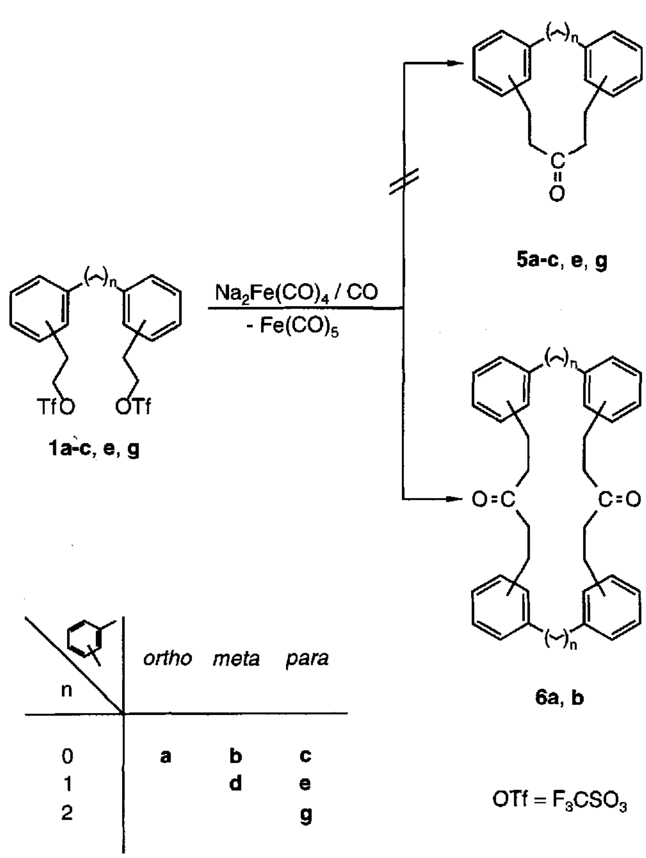
Because of the greater nucleophilicity and hence reactivity of $Na_2[Fe(CO)_4]$ compared with $Na_2[Os(CO)_4]$[15] the reaction takes place even at −60 °C within 2 h, and a clear red-brown dimethyl ether solution is obtained from a beige $Na_2[Fe(CO)_4]$ suspension. To prevent uncontrollable decomposition of the ferracyclophanes formed in situ excess carbon monoxide was immediately bubbled into the solution. In the case of the bis(triflate) **1a**, no "monomeric" cyclic ketone **5a** was detectable, but the appearance of the "dimeric" ketone **6a** was unequivocally confirmed by FD-MS and IR spectroscopy. Reaction of **1b** with $Na_2[Fe(CO)_4]$ as described leads to the generation of the "dimeric" ketone **6b**, which was corroborated by the typical IR absorption of the >C=O groups. Regarding the ring strain, the occurrence of an eleven-membered cyclic ketone **5b** is unlikely. The observed IR absorption has to be assigned to the >C=O stretching vibration of the diketone **6b**. By employment of the bis(triflates) **1c, e, g** in the same way no indications for the formation of either "monomeric" cyclic ketones **5c, e, g** or "dimeric" dioxocyclophanes **6c, e, g** are discernible (Scheme 3). The IR spectra only display >C=O bands which can be traced back to $Fe(CO)_5$ and $Fe_3(CO)_{12}$. Because of the low yields of the diketones **6a** and **6b** no further spectroscopic and analytical data could be obtained.

The reaction of the bis(triflates) **1a–c, e, g** with $[Fe(CO)_4]^{2-}$ in dimethyl ether could also lead to the formation of oligomeric species, as described for the osmacyclophanes **2a–g**. Once an Fe–C σ bond between dianionic $[Fe(CO)_4]^{2-}$ and a bis(triflate) molecule (e.g., **1c, e, g**) with a stretched arrangement of the molecular framework has been formed, intermolecular attack of the carbon atom of a second bis(triflate) molecule carrying a triflate group is preferred. Thus, the products of that reaction are either dimeric or oligomeric species. In addition, the extreme instability of ferracyclophanes can lead to uncontrollable decomposition, even at low temperatures. Although the method described represents an easy synthesis for cyclic ketones[4,27], it is not applicable for access to the ketones **5a–c, e, g** and **6a–c, e, g** on a preparative scale.

Conclusion

Cyclophane chemistry is very important in the field of host-guest interactions[17]. The bis(triflate) route offers easy access to metallacyclophanes[4,5]. With regard to the possibility to form host-guest complexes, new metallacyclophanes were prepared. In this paper we described the behavior of bis(triflates), in which both $CH_2CH_2OSO_2CF_3$ groups are linked by two bridged aromatic rings, toward the dianion $[Os(CO)_4]^{2-}$. The resulting products are the diosma[5.*n*.5.*n*]cyclophanes **2a–e, g** containing an 18-membered ring skeleton in the case of **2a** and a 30-membered ring frame in the case of **2g**. The solid-state structure of the diosmacyclophane **2e** shows a cavity with a size and shape comparable to that of cyclophanes that form stable complexes with guest molecules. Ferracycles reveal a high ability for the insertion of carbon monoxide into the Fe–C σ bonds. Hence, the reactivity of the metal center in the cyclophanes was investigated in the presence of carbon monoxide. Ferracyclophanes were formed only in situ by treatment of **1a–c, e, g** with $Na_2[Fe(CO)_4]$ in dimethyl ether. They immediately undergo a reductive elimination of $Fe(CO)_5$ to give diketones, as shown in the case of **6a, b**.

Scheme 3



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Experimental

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques. Solvents were dried with appropriate reagents and stored under an inert atmosphere. – Column chromatography: Activated silica gel, 0.063–0.200 mm (Merck), diameter/length of the column 4/25 cm. – Elemental analyses: Carlo Erba 1106. – AAS: Perkin-Elmer model 4000. – FD-MS: Finnigan MAT 711A (8 kV) modified by AMD. – IR: Bruker IFS 48 FT-IR. – ^1H NMR: Bruker DRX 250 (250.13 MHz, 25 °C); $^{13}C\{^1H\}$ NMR: Bruker DRX 250 (62.90 MHz, 25 °C). Chemical shifts were recorded relative to tetramethylsilane. – $Na_2[Os(CO)_4]$[15] and $Na_2[Fe(CO)_4]$[29] were synthesized according to literature methods. The bis(triflates) **1a–f** were prepared as described in the Ph. D. Thesis of M. W. P.[14].

General Procedure for the Preparation of the Osmacyclophanes **2a–e, g**: Solutions of the bis(triflates) **1a–e, g** in diethyl ether were added to an excess of $Na_2[Os(CO)_4]$ in dimethyl ether at –50 °C. Stirring this mixture at –30 °C for 3 d gave a clear yellow solution and a yellow-brown precipitate. The solvent was removed at room temp., the dimethyl ether being replaced stepwise by a mixture of 150 ml of *n*-pentane and of 50 ml of diethyl ether. The suspension was stirred for 1 d and, after the insoluble components were separated by filtration (D4), the solvent was removed in vacuo leaving the crude product.

3,3,3,3,20,20,20,20-Octacarbonyl-3,20-diosma[5.0.5.0]orthocyclophane (**2a**): Starting materials were 452 mg (1.298 mmol) of $Na_2[Os(CO)_4]$ in 200 ml of Me_2O and 550 mg (1.086 mmol) of **1a** in 5 ml of Et_2O. The purification involved washing the crude product three times with 2 ml of *n*-pentane at –65 °C. Yield 57 mg (5.1%) of **2a**, colorless solid, m.p. >160 °C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2127 cm^{-1}, 2044, 2040, 2011 (CO). – ^1H NMR ($CDCl_3$): δ = 0.75–0.98 (m, 8H, CH_2Os), 2.50–2.78 (m, 8H, CH_2CH_2Os), 6.86–7.24 (m, 16H, aromatic H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –1.90 (s, CH_2Os), 41.3 (s, CH_2CH_2Os), 124.8, 127.1, 128.7, 130.1 (s, aromatic CH), 139.4, 145.9 (s, aromatic C), 170.5 (s, equatorial CO), 176.9, 179.5 (s, axial CO). – MS (FD, 32 °C), *m/z*: 1023.6 [M^+]. – $C_{40}H_{32}O_8Os_2$ (1021.1): calcd. C 47.05, H 3.16, Os 37.25; found C 47.32, H 3.56, Os 36.93.

3,3,3,3,20,20,20,20-Octacarbonyl-3,20-diosma[5.0.5.0]metacyclophane (**2b**): Starting materials were 1.160 g (3.331 mmol) of $Na_2[Os(CO)_4]$ in 150 ml of Me_2O and 1.680 g (3.317 mmol) of **1b** in 10 ml of Et_2O. The crude product was purified by column chromatography (Et_2O). The product obtained was subsequently washed five times with 4 ml of Et_2O/*n*-pentane (1:1) at –65 °C. Yield 283 mg (8.3%) of **2b**, colorless solid, m.p. >140 °C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2125 cm^{-1}, 2044, 2040, 2012 (CO). – ^1H NMR ($CDCl_3$): δ = 1.23–1.30 (m, 8H, CH_2Os), 2.93–3.00 (m, 8H, CH_2CH_2Os), 7.05–7.32 (m, 16H, aromatic H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –0.66 (s, CH_2Os), 44.3 (s, CH_2CH_2Os), 124.8, 126.7, 126.8, 128.6 (s, aromatic CH), 142.1, 148.3 (s, aromatic C), 170.8 (s, equatorial CO), 178.5 (s, axial CO). – MS (FD, 32 °C), *m/z*: 1022.9 [M^+]. – $C_{40}H_{32}O_8Os_2$ (1021.1): calcd. C 47.05, H 3.16, Os 37.25; found C 47.01, H 3.28, Os 37.06.

3,3,3,3,20,20,20,20-Octacarbonyl-3,20-diosma[5.0.5.0]paracyclophane (**2c**): Starting materials were 1.100 g (3.159 mmol) of $Na_2[Os(CO)_4]$ in 150 ml of Me_2O and 1.606 g (3.171 mmol) of **1c** in 10 ml of Et_2O. The purification involved washing the crude product successively with 2 ml of Et_2O and three times with 5 ml of *n*-pentane at –65 °C. Yield 193 mg (5.9%) of **2c**, colorless solid, m.p. >125 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2125 cm^{-1}, 2043, 2033, 1999 (CO). – ^1H NMR ($CDCl_3$): δ = 1.15–1.47 (m, 8H, CH_2Os), 2.82–2.89 (m, 8H, CH_2CH_2Os), 7.01 (A part of an AB pattern, $^3J_{AB}$ = 8.3 Hz, 8H, aromatic H), 7.50 (B part of an AB pattern, $^3J_{AB}$ = 8.3 Hz, 8H, aromatic H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.50 (s, CH_2Os), 44.0 (s, CH_2CH_2Os), 127.0, 127.9 (s, aromatic CH), 138.5, 147.1 (s, aromatic C), 170.8 (s, equatorial CO), 178.7 (s, axial CO). – MS (FD, 30 °C), *m/z*: 718.4 [$M^+ - Os(CO)_4$]. – $C_{40}H_{32}O_8Os_2$ (1021.1): calcd. C 47.05, H 3.16, Os 37.25; found C 47.20, H 3.07, Os 37.22.

3,3,3,3,21,21,21,21-Octacarbonyl-3,21-diosma[5.1.5.1]metacyclophane (**2d**): Starting materials were 862 mg (2.475 mmol) of $Na_2[Os(CO)_4]$ in 150 ml of Me_2O and 1.160 g (2.229 mmol) of **1d** in 10 ml of Et_2O. The crude product was purified by column chromatography (*n*-pentane/Et_2O, 15:1). The product obtained was subsequently washed five times with 4 ml of *n*-pentane at –50 °C. Yield 134 mg (5.7%) of **2d**, pale yellow solid, m.p. >128 °C (dec.). – IR (*n*-hexane): $\tilde{\nu}$ = 2125 cm^{-1}, 2042, 2040, 2011 (CO). – ^1H NMR ($CDCl_3$): δ = 1.11–1.19 (m, 8H, CH_2Os), 2.82–2.91 (m, 8H, CH_2CH_2Os), 3.86 (s, 4H, CCH_2C), 6.92–7.18 (m, 16H, aromatic H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = –1.23 (s, CH_2Os), 42.0 (s, CCH_2C), 44.0 (s, CH_2CH_2Os), 125.6, 126.4, 128.3, 128.3 (s, aromatic CH), 141.3, 147.8 (s, aromatic C), 170.6 (s, equatorial CO), 178.4 (s, axial CO). – MS (FD, 30 °C), *m/z*: 1049.9 [M^+]. – $C_{42}H_{36}O_8Os_2$ (1049.1): calcd. C 48.08, H 3.46, Os 36.26; found C 48.37, H 3.75, Os 36.39.

3,3,3,3,21,21,21,21-Octacarbonyl-3,21-diosma[5.1.5.1]paracyclophane (**2e**): Starting materials were 554 mg (1.591 mmol) of $Na_2[Os(CO)_4]$ in 150 ml of Me_2O and 776 mg (1.491 mmol) of **1e** in 10 ml of Et_2O. The crude product was purified by column chromatography (*n*-pentane/Et_2O, 10:1). The product obtained was subsequently washed three times with 3 ml of *n*-pentane at –65 °C. Yield 238 mg (15.2%) of **2e**, colorless solid, m.p. >140 °C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2042, 2040, 2011 (CO). – ^1H NMR ($CDCl_3$): δ = 1.00–1.08 (m, 8H, CH_2Os), 2.73–2.81 (m, 8H, CH_2CH_2Os), 3.77 (s, 4H, CCH_2C), 7.00–7.04 (m, 16H, aromatic H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.31 (s, CH_2Os), 41.2 (s, CCH_2C), 44.2 (s, CH_2CH_2Os), 127.5, 128.8 (s, aromatic CH), 138.7, 145.9 (s, aromatic C), 170.8 (s, equatorial CO), 178.9 (s, axial CO). – MS (FD, 35 °C), *m/z*: 1050.9 [M^+]. – $C_{42}H_{36}O_8Os_2$ (1049.1): calcd. C 48.08, H 3.46, Os 36.26; found C 48.88, H 3.70, Os 36.63.

3,3,3,3,22,22,22,22-Octacarbonyl-3,22-diosma[5.2.5.2]paracyclophane (**2g**): Starting materials were 998 mg (2.866 mmol) of $Na_2[Os(CO)_4]$ in 150 ml of Me_2O and 1.512 g (2.828 mmol) of **1g** in 10 ml of Et_2O. The crude product was purified by column chromatography (*n*-pentane/Et_2O, 15:1). The product obtained was subsequently washed five times with 2 ml of Et_2O at –65 °C. Yield 126 mg (4.1%) of **2g**, pale yellow solid, m.p. >120 °C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2125 cm^{-1}, 2042, 2040, 2011 (CO). – ^1H NMR ($CDCl_3$): δ = 1.13–1.21 (m, 8H, CH_2Os), 2.77 (s, 8H, CCH_2CH_2C), 2.81–2.89 (m, 8H, CH_2CH_2Os), 7.04–7.06 (m, 16H, aromatic H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.04 (s, CH_2Os), 37.8 (s, CCH_2CH_2C), 43.8 (s, CH_2CH_2Os), 127.6, 128.3 (s, aromatic CH), 139.3, 145.8 (s, aromatic C), 170.8 (s, equatorial CO), 178.6 (s, axial CO). – MS (FD, 30 °C), *m/z*: 1077.6 [M^+]. – $C_{44}H_{40}O_8Os_2$ (1077.2): calcd. C 49.06, H 3.74, Os 35.31; found C 48.97, H 3.75, Os 35.57.

General Procedure for the Preparation of the Cycloalkanones **6a, b**: The bis(triflates) **1a** and **1b** were added to an excess of $Na_2[Fe(CO)_4]$ in dimethyl ether at –60 °C. After a clear-red-brown solution appeared, 20 ml of dichloromethane was added and the mixture allowed to warm to room temp. and the dimethyl ether allowed to evaporate. During that time carbon monoxide was bubbled into the solution. The ketones **6a** and **6b** were detectable from the CH_2Cl_2 solution.

3,20-Dioxo[5.0.5.0]orthocyclophane (**6a**): 607 mg (1.198 mmol) of **1a** was treated with 272 mg (1.272 mmol) of $Na_2[Fe(CO)_4]$ in 100 ml of dimethyl ether. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1713 cm^{-1} (CO). – MS (FD, 35 °C), *m/z*: 472.2 [M^+].

3,20-Dioxo[5.0.5.0]metacyclophane (**6b**): 1.057 g (2.087 mmol) of **1b** was allowed to react with 556 mg (2.600 mmol) of $Na_2[Fe(CO)_4]$ in 100 ml of dimethyl ether. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1713 cm^{-1} (CO).

X-Ray Structural Analysis of **2e**: Single crystals were obtained from a CH_2Cl_2 solution. $C_{42}H_{36}O_9Os_2$, M = 1065.11 g mol^{-1}, triclinic space group $P\bar{1}$ (no. 2), a = 12.731(2), b = 12.948(2), c = 14.671(2) Å, α = 101.09(2), β = 97.10(1), γ = 114.49(2)°, V = 2103.0(5) Å^3, $\rho_{calcd.}$ = 1.682 g cm^{-3}, Z = 2, $F(000)$ = 1024, measurement at 173 K, $\mu(\text{Mo-}K_\alpha)$ = 6.086 mm^{-1}, scan mode = ω, h, k, l range = ±16, ±16, ±19, 2θ limits = 4–50, measured reflexions = 20027, observed reflexions = 9659, observed reflexions ($F_0 \geqslant 4\sigma F_0$) = 7262, refined parameters = 479, S = 1.677, $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ = 0.056, $wR2 = [\Sigma[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ = 0.142. A crystal with the dimensions 0.31 × 0.38 × 0.49 mm was mounted on a glass fiber and transferred to a P4 Simens diffractometer by taking rotation photographs and performing a photo search to find a suitable reduced cell (graphite-monochromator, Mo-K_α radiation). The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The structure was solved by the Patterson method[30] and refined by the least-squares method (based on F^2) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). An absorption correction Ψ scan was applied. Max. and min. transmission were 1.00 and 0.142, respectively. Maximum and minimum peaks in the final difference synthesis were 4.68 and −3.55 eÅ^{-3}. A water molecule was found in the asymmetric unit. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404709, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Erwin Weiss* on the occasion of his 70th birthday.

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[20] X-Ray Structural Analysis of **2a**: $C_{40}H_{32}O_8Os_2$, M = 1021.09 g mol^{-1}, monoclinic space group $P2_1/c$ (no. 14), a = 11.887(4), b = 14.229(5), c = 42.87(3) Å, β = 94.04(4)°, V = 7233(6) Å^3, Z = 8; in the asymmetric unit there is one whole molecule and two halves of a molecule, measured reflexions = 24640, observed reflexions 12706, observed reflexions ($F_o \geqslant 4\sigma F_o$) = 6163, refined parameters = 422, S = 0.845, $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ = 0.061, $wR2 = [\Sigma[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ = 0.143.
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