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

Mono-, Di- and Trinuclear Metallacycloalkanes of the Iron-Triad☆

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The reaction of the bis(triflates) $[F_3CSO_3\text{-}(CH_2)_m\text{-}O_3SCF_3]$ [$m = 5-10, 12, 14, 16$ (**1a**–**i**)] with $Na_2[Os(CO)_4]$ in dimethyl ether affords the osmacycloalkanes **2a**, **2b** and **2f**–**i** ($m = 5, 6, 10, 12, 14, 16$), diosmacycloalkanes **3a**–**i** ($m = 5-10, 12, 14, 16$), and triosmacycloalkanes **4a**–**i** ($m = 5-10, 12, 14$ 16). The structure of **3f** was investigated by an X-ray structural analysis. This 22-membered diosmacycle crystallizes in the space group $P\bar{1}$ with $Z = 1$. If the unsaturated *cis*-4-octen-1,8-diyl bis(trifluoromethanesulfonate) (**5**) is treated with $Na_2[Os(CO)_4]$ the diosmacyclooctadeca-5,14-diene **6** is obtained. By treating the bis(triflates) **1a**, **d** with $Na_2[Fe(CO)_4]$ the corresponding ferracycloalkanes are formed only in situ. Insertion of carbon monoxide into the M–C σ bonds leads to the cyclic ketones **7a**, **d** and to the diketone **8d**.

Introduction

Heterocycles containing two or even more metal-carbon σ bonds are a topic of much interest in organometallic chemistry[1–3]. Metallacycloalkanes have often been mentioned in this context, in particular as reactive intermediates in numerous transition metal catalyzed syntheses, such as carbonyl olefination[4], olefin metathesis[5], or olefin di-[6] and oligomerization[7].

A facile access to metallacycles has been opened by the bis(triflate) route[1,8–15], which is a variant of cationic alkylation[8]. The excellent and inert leaving group $CF_3SO_2O^-$ stabilizes carbenium-like carbon atoms at the ends of a hydrocarbon chain[16], thereby enabling an electrophilic attack of the terminal carbon atoms at a basic metal center. For this reason the formation of metal-carbon σ bonds proceeds under very mild conditions. In this way, four- to six-membered metallacycloalkanes of iron, ruthenium and osmium could be obtained by the reaction of the corresponding bivalent metalates $[M(CO)_4]^{2-}$ (M = Fe, Ru, Os) with alkanediyl bis(trifluoromethanesulfonates)[8,9]. By employing the bis(triflate) method we were able to synthesize for the first time metallacyclophanes with one or two transition metal atoms in the ring frame[13–15]. The metal center has an impact on the geometrical properties[15] of the cavity which is formed by the metallacyclophanes. Additional interactions are possible between the metal fragment and guest molecules, which is of special interest with regard to molecular recognition[17].

In this paper we investigate the behaviour of α,ω-alkanebis(trifluoromethanesulfonates), with five to sixteen methylene groups, toward the dianionic metalates $[M(CO)_4]^{2-}$ (M = Fe, Os). It was anticipated that the ring-closure reactions would lead to small, medium or large metallacycles with one or more transition metal atoms in the ring. Because of the stability of the Os-C σ bond osmacycles may serve as model compounds for spectroscopic and structural analyses[9,18]. The properties of the obtained rings are compared with the corresponding organic cycles.

Cyclizations of hydrocarbon chains are still difficult in organic synthesis. In particular seven- to ten-membered rings are hardly accessible by classical organic methods[19]. A promising tool for a less problematic access to such cyclic systems is the employment of the aforementioned bis(triflate) method. In contrast to osmacycles, comparable ferracycles are capable of inserting carbon monoxide into the Fe-C σ bond, which is a crucial step in organometallic chemistry[20,21]. Reductive elimination of the organometallic fragment should then provide a facile access to cyclic ketones or diketones[12–14].

In the same fashion, an unsaturated metallacycle with two double bonds is accessible, which should be able to form host-guest complexes with π-electron interactions[22].

Results and Discussion

Osmacycloalkanes: The osma-, diosma- and triosmacycles **2a**[9], **2b**, **2f**–**i**, **3a**–**i**, and **4a**–**i** (Figure 1) were formed by adding the corresponding bis(triflates) **1a**–**i** to a suspension of the sodium salt of the organometallic Lewis base $[Os(CO)_4]^{2-}$ in dimethyl ether at −40 °C (Scheme 1). 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. Despite the lower nucleophilicity of the disodium tetracarbonyl osmate compared to $Na_2[Fe(CO)_4]$[23], no problems arose regarding the formation of Os-C σ bonds. This disadvantage is compensated by the remarkable electrophilic character of the terminal carbon atoms of the bis-

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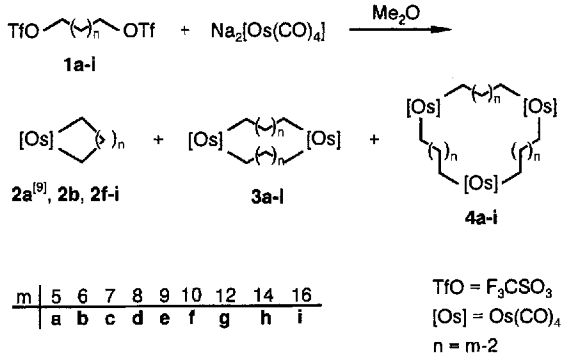
(triflates). Within the reaction time, a yellow solution containing the cycles **2a**[9], **2b**, **2f–i**, **3a–i**, and **4a–i** was obtained from the cream-colored $Na_2[Os(CO)_4]$ suspension, in addition to a yellow-brown precipitate. The residue, sparingly soluble in organic solvents, consisted of sodium triflate and metal-containing oligomers. The heterocycles **2a**[9], **2b**, **2f–i**, **3a–i**, and **4a–i** were fairly air-stable and could be handled at room temperature. The osmium-carbon σ bond is rather inert, which is in agreement with the stability of other 5d transition metal-carbon σ bonds[24].

Scheme 1



In the case of the bis(triflates) **1a** and **1g–i**, the mononuclear osmacycloalkanes **2a** and **2g–i** were formed concomitantly with the di- and trinuclear species **3a**, **3g–i**, and **4a**, **4g–i**. Their separation could be achieved by column chromatography (silica gel/*n*-pentane), whereupon the products were eluted in the order of mono-, followed by di-, and finally triosmacycloalkanes. For the attempted synthesis of the mononuclear seven- to eleven-membered osmacycloalkanes the "high dilution method" of Ziegler was employed[25]. Only in the case of the osmacycloheptane **2b** was the yield sufficient for characterization of the compound. The eight- to ten-membered rings were not accessible by this method. However, it was possible to detect the osmacycloundecane **2f** by its field desorption mass spectrum (FD-MS, 30 °C, *m/z*: 441.0 $[M^+]$) and in the $^{13}C\{^1H\}$ NMR spectrum [$CDCl_3$: $\delta = -6.0$ (s, α-CH_2Os)]. Because of the very poor yield of this metallacycle, no further spectroscopic or analytic data could be obtained.

In Figure 2 the yields of the osmacycloalkanes **2a**[9], **2b**, **2f–i**, **3a–i**, and **4a–i** are plotted against the number of methylene groups. The reaction of $Na_2[Os(CO)_4]$ with 1,4-butanediyl bis(trifluoromethanesulfonate) led exclusively to the remarkably thermally stable osmacyclopentane[9]. When the bis(triflate) **1a** was employed, the mononuclear species **2a**[9] was the major product and the higher nuclear compounds **3a** and **4a** were observed merely as by-products. Whereas the osmacycloheptane **2b** was only accessible by the aforementioned high dilution method, the eight- to ten-membered cycles were not formed under such conditions. The yields of the di- and trinuclear heterocycles **3c–f** and **4c–f** increase with increasing number of methylene groups.

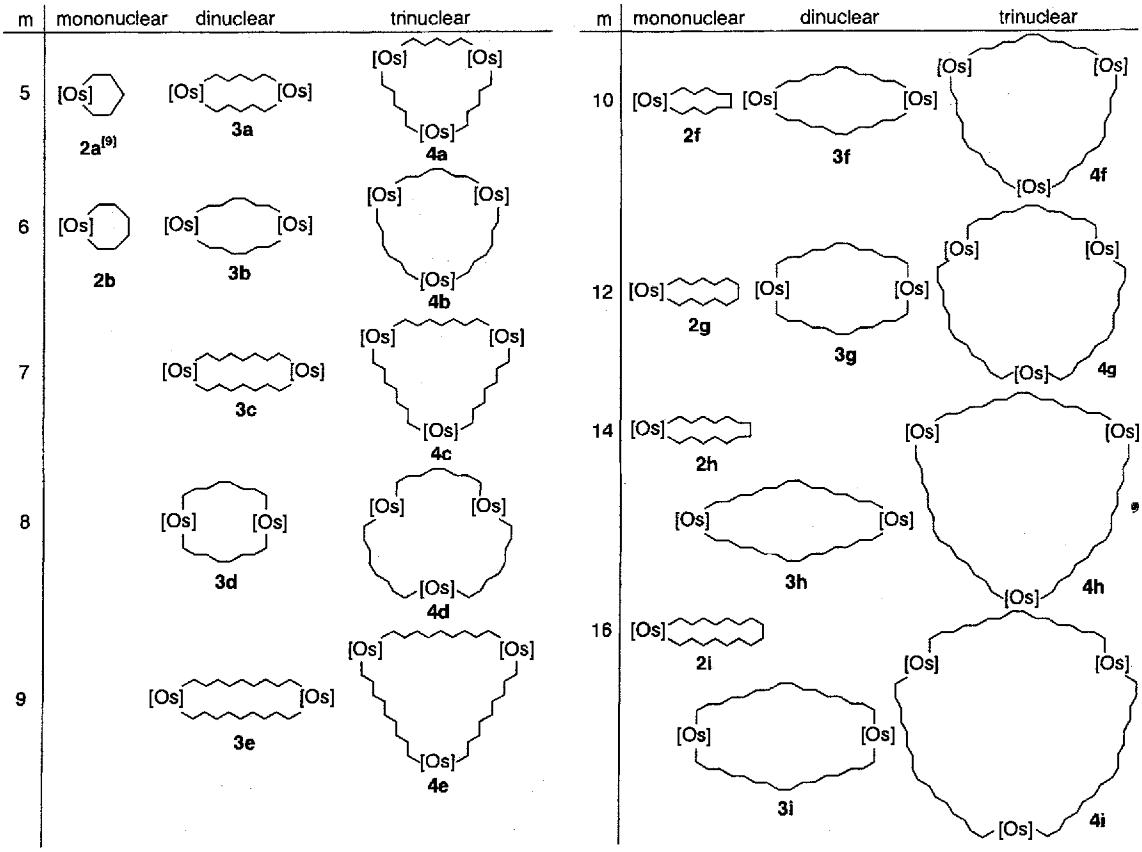


Figure 1. Osmacycloalkanes **2a**[9], **2b**, **2f–i**, **3a–i**, and **4a–i** from the reaction between the bis(triflates) **1a–i** and $Na_2[Os(CO)_4]$

However, when the ring size is increased beyond twelve methylene groups, the mononuclear species **2g**, **2h**, **2i** once more become the preferred products, with a concomitant decrease in the yields of the di- and trinuclear moieties **3g−i** and **4g−i**. Compared to the cyclization of dinitriles according to the Thorpe-Ziegler reaction[26], the present results obtained with the mononuclear osmium rings show a similar behavior. Between ring sizes of nine to twelve and eight to eleven, respectively, the yields tend to zero. Obviously these rings suffer from strong H/H repulsion between CH_2 groups across the ring[19]. These transannular interactions could account for the fact that the ring-closure reactions to give the medium-sized osmacycles were not successful. For cycloalkanes larger than cycloundecane the strain energies are small[19], which is in agreement with the formation of the mononuclear osmacycloalkanes **2g−i**. Nevertheless, with the exception of **2a**, the yields of the osmacycloalkanes **2b** and **2g−i** are rather low compared to the yields offered by the Thorpe-Ziegler reaction. This observation is attributed to the fact that higher nuclear species can be formed during the reaction of the bis(triflates) **1a−i** and $Na_2[Os(CO)_4]$. Even tetranuclear compounds could be detected in the FD mass spectra in the case of **b−d**, **f**, and **g** {FD-MS, 30 °C, *m/z*: 1547.5 [M^+] (**b**), 1603.9 [M^+] (**c**), 1659.5 [M^+] (**d**), 1771.8 [M^+] (**f**), 1881.1 [M^+] (**g**)}. Finally, the insoluble residue of the reaction mixture contains polymeric materials containing residual *cis*-$Os(CO)_4$ groups [IR (KBr): $\tilde{\nu}$ = 2124 cm^{-1}, 2043, 2030, 2003 (CO)] and $Os_3(CO)_{12}$ as a decomposition product [IR (KBr): $\tilde{\nu}$ = 2070 cm^{-1}, 2037, 2016, 2000 (CO)[27]]. A special minimum for the ring strain was found for cyclohexane[19]. In accordance with this finding the osmacyclohexane **2a** was obtained in excellent yields from the bis(triflate) **1a** and $Na_2[Os(CO)_4]$[9]. The synthesis and structure of this heterocycle, which has a chair conformation, was published a couple of years ago by our group[9].

The molecular composition of the osmacycloalkanes **2f−i**, **3a−i**, and **4a−i** was corroborated by FD mass spectra displaying in each case the molecular peak. The isotopic distribution of the observed molecular peaks was in agreement with the calculated isotopic pattern. Only the osmacyclohexane **2a**[9] and -heptane **2b** were characterized by their EI mass spectra revealing the corresponding M^+ peak and peaks which could be assigned to the successive abstraction of CO ligands. While the di- and trinuclear heterocycles **3a−i**, **4a**, and **4b** are colorless solids, **2b**, **2g−i**, and **4c−i** were obtained as colorless to pale-yellow oils. All osmacycles are easily soluble in chlorinated hydrocarbons. In *n*-pentane the solubility increases with the number of methylene groups. In the region between 2130 and 2000 cm^{-1} the IR spectra (*n*-pentane) of the mononuclear compounds **2b**, **2f−i** exhibit four sharp CO absorptions, which are consistent with a *cis*-$Os(CO)_4$ unit. However, in the IR spectra of the di- and trinuclear species **3a−i** and **4a−i** only three bands are observed, because the central absorptions are not resolved even in *n*-pentane solution.

Owing to the hindered rotation of the C_α-C_β σ bonds, the ^1H NMR spectra of the osmacycloalkanes **2b**, **2g−i**, **3a−i**, and **4a−i** exhibit two complex multiplet structures, namely an AA'MM' spin system for the α-CH_2 and an AA'MM'XX' pattern for the β-CH_2 groups. Between these two absorptions a third signal appears, the shape of which changes from a symmetrical via an unsymmetrical multiplet to a broad signal in the cases of compounds **2b**, **3a**, **3b**, **4a**, **4b**, and **3c**, **4c**, and **2g−i**, **3d−i**, **4d−i**, respectively. According to the integration of all ^1H peaks this third signal is ascribed to the methylene protons other than α- and β-CH_2.

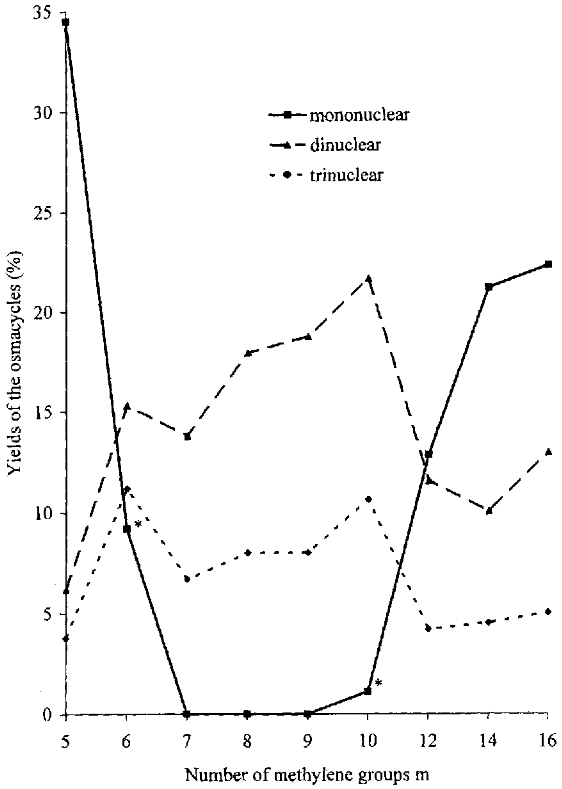
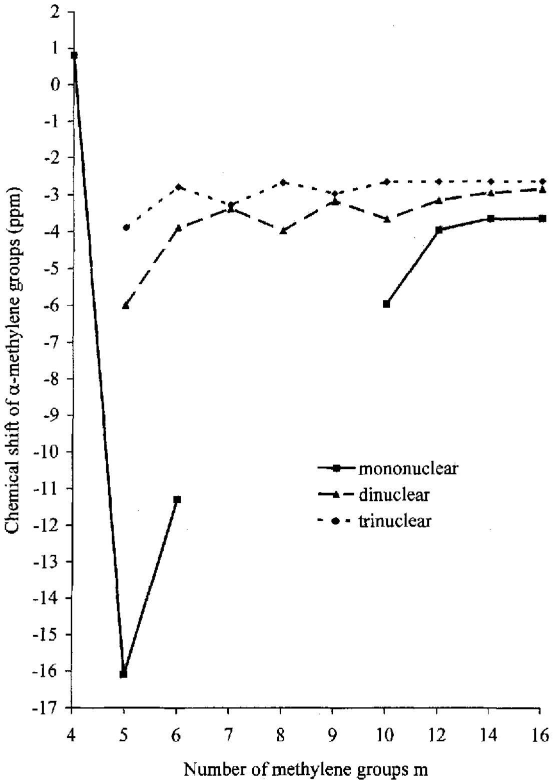


Figure 2. Dependence of the yields of the mono-, di- and trinuclear osmacycles **2a**[9], **2b**, **2f−i**, **3a−i**, and **4a−i** on the number of methylene groups (* high dilution method)

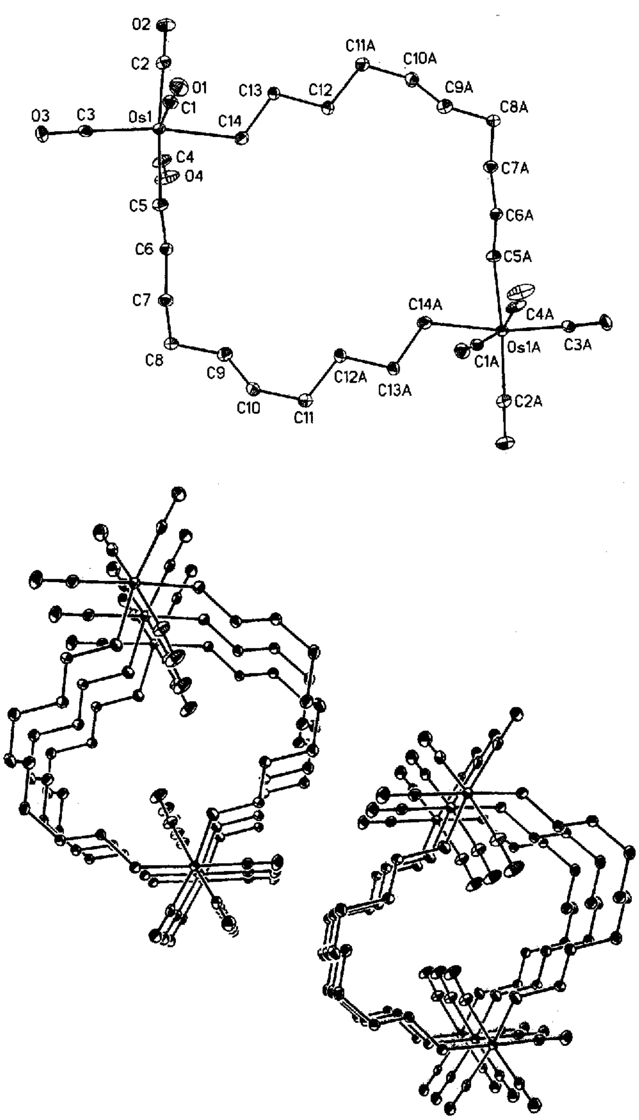
Compared to the bis(triflates) **1a−i**, in the $^{13}C\{^1H\}$ NMR spectra of the heterocycles **2a**[9], **2b**, **2f−i**, **3a−i**, and **4a−i** the α-ring carbon atoms are distinguished by their remarkable high field position with a maximum for the osmacyclohexane[9]. The appearance of *m*/2 signals for an even and (*m* + 1)/2 (Scheme 1) for an odd number of methylene groups in the alkane region of the spectra is indicative of a cyclic, and furthermore, of a symmetric structure of the compounds **2b**, **2f−i**, **3a−i**, and **4a−i** in solution at room temperature. A crystal structure analysis of **4b** was of poor quality but nevertheless the trinuclear structure could be confirmed. In Figure 3 the chemical shifts of the α-CH_2 carbon atoms are represented as a function of the number of methylene groups. The big differences between the chemical shifts of the small mononuclear osmacycles, Δδ = 16.9 for the five- to six-membered and Δδ = 4.8 for the six- to seven-membered species, are conspicuous. An approximate sequence for the difference of the δ(^{13}C) values was also established for the di- and trinuclear osmacycles **3a−f** and **4a−f**, which become smaller with an increasing number of CH_2 groups. In the case of the mononuclear rings, the chemical shift values increase as the ring size is increased beyond ten CH_2 groups. Recently, similar results for phospha-[28] and diphosphametallacycloalkanes[29] were reported.

Figure 3. Dependence of the chemical shift of the α-CH_2 groups of the osmacycloalkanes **2a**[9], **2b**, **2f–i**, **3a–i**, and **4a–i** on the ring size



Structure of **3f**: In order to examine the structure of the diosmacyclodocosane **3f** and to compare it with the corresponding diosmacyclophane[14] an X-ray crystal structural analysis was carried out (Figure 4). To the best of our knowledge this is the first crystal structure of a dinuclear osmacycle with only methylene groups in the ring skeleton. Compound **3f** crystallizes with a center of inversion, the backbone of which can be described as an approximate rectangle. Two edges are occupied by the nearly octahedrally coordinated osmium atoms. Proceeding from these $Os(CO)_4$ fragments are two "zigzag" carbon atom chains defined by the least-squares planes Os1, C5, C6, C7, C8 and Os1, C14, C13, C12, C11A, which are nearly perpendicular to one another (80°). The other two edges are not so well-defined, which is shown by the torsion angles C6–C7–C8–C9 (81.9°), C7–C8–C9–C10 (82.6°), C8–C9–C10–C11 (−179.3°), and C9–C10–C11–C12A (70.6°). For further investigations of host-guest complexes with the established metallacyclophanes[13–15] the size and shape of the cavities of these heterocycles play an important role. The expansion of the interior of **3f** is defined by the distances of the atoms C12–C12A (6.73 Å) and by the parallel planes determined by the atoms Os1, C5, C6, C7, C8 and Os1A, C5A, C6A, C7A, C8A (9.04 Å). The other significant distances are given by the length of the diagonals Os1–Os1A (10.92 Å) and C9–C9A (9.01 Å) of the "rectangle". To demonstrate the influence of the organic building blocks between the metal fragments on the cavity, it is appropriate to compare compound **3f** with the twenty-two-membered diosma[7.7]-paracyclophane[14]. This metallacyclophane crystallizes in a "bowl" conformation, whereby the osmium atoms and the phenyl rings occupy the positions of a distorted tetrahedron with the distances 10.07 Å (Os–Os) and 5.64 Å (phenyl rings). Hence the "cavity" of **3f** is better described as a "two-dimensional hole" with a larger extent in contrast to the diosma[7.7]paracyclophane, which has a smaller, but three-dimensional interior. In the solid state structure of compound **3f** the molecules are arranged in such a manner that the holes form continuous channels (Figure 4, bottom). Similar structures have been found for other metal-contain-

Figure 4. Top: ORTEP plot of the molecular structure of compound **3f**[a]; bottom: two channels of molecules of compound **3f** viewed along the *b* axis



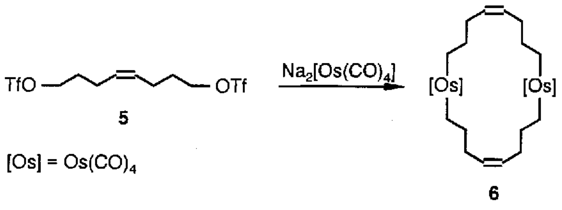
[a] Selected bond lengths [Å] and angles [°]: Os1–C2 1.957(5), Os1–C3 1.947(6), Os1–C5 2.204(5), C5–C6 1.528(6), C1–Os1–C4 167.3(2), C2–Os1–C3 96.6(2), C5–Os1–C14 83.6(2), Os1–C5–C6 118.5(3), C5–C6–C7 112.1(4).

ing macrocycles[17] that are capable of molecular recognition.

Osmacycloalkenes: Di- and trinuclear metallacycles of the iron triad with an unsaturated backbone containing only carbon atoms between the $M(CO)_4$ fragments are hitherto unreported in the literature. Such heterocycles should have a large potential for further reactions and be particularly amenable to host-guest chemistry. In contrast to the osmacycloalkanes described above, with only methylene groups in the organic ring skeleton, these unsaturated species should be capable of forming complexes with π-electron interactions in- or outside the "cavity"[22]. Moreover, the C=C double bonds offer the possibility of introducing functional groups by addition reactions, thus providing a route to molecules with well-defined properties.

For the synthesis of unsaturated metallacycles with one or more metal atoms in the ring, the bis(triflate) route was again the method of choice. Because of the thermolability of the bis(triflate) **5** this compound was added to a suspension of $Na_2[Os(CO)_4]$ in dimethyl ether at −60 °C (Scheme 2). After work-up of the reaction mixture the diosmacyclooctadeca-5,14-diene **6** was obtained as the major product. Whereas the expected osmacyclononene was not accessible via this route, the trinuclear osmacycle was detected in the FD mass spectrum {FD-MS, 34 °C, *m/z*: 1238.9 $[M^+]$}. To account for the preferred formation of the dinuclear heterocycle **6** and the tri- and oligonuclear species, the same arguments hold true that were discussed for the saturated osmium-containing cycles above. Compound **6** is remarkably stable and can be handled at room temperature without any decomposition. Even in atmospheric oxygen the colorless solid or an *n*-pentane solution is stable for a few days. However, in chlorinated hydrocarbons, in which **6** is readily soluble, decomposition occurs within several days under argon.

Scheme 2



The dinuclear character of compound **6** was confirmed by the FD mass spectrum and the observed and calculated isotopic patterns were in agreement. In the IR spectrum of **6** only three CO absorptions appear in the 5 μm region since the central bands are not resolved. Nevertheless, the spectrum is consistent with a *cis*-$Os(CO)_4$ fragment.

In the ^1H-NMR spectrum of **6** a total of four multiplets are characteristic for the heterocycle. Two of them exhibit AA′MM′ and AA′MM′XX′ patterns, and are ascribed to the protons of the α- and β-methylene groups, respectively. These multiplets originate from the hindered rotation along the $C_\alpha-C_\beta$ axis. The mirror plane perpendicular to the double bonds gives rise to pairwise chemical equivalence of CH and CH_2 groups. Due to the different coupling distances these groups become magnetically non-equivalent and are responsible for the remaining two complex multiplets at distinct chemical shifts. Three signals in the high field region ($\delta = -4$ to 40) of the $^{13}C\{^1H\}$ NMR spectrum of **6** and another one at very low field ($\delta = 130.2$) are consistent with the cyclic structure of the diosmacyclooctadecadiene and are attributed to the aliphatic carbon atoms and the C=C double bond, respectively.

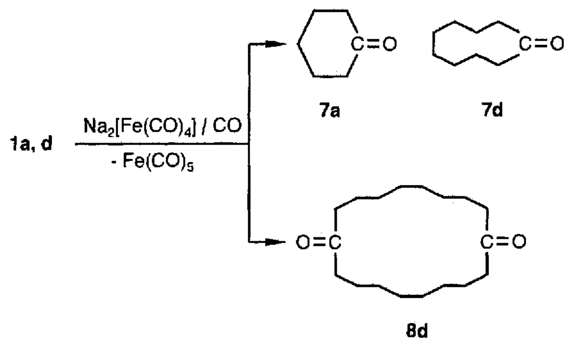
Further investigations into the synthesis of osmacycles with carbon-carbon triple bonds utilizing the bis(triflate) method have not yet been successful. A nucleophilic attack of the $[Os(CO)_4]^{2-}$ anion at the C≡C triple bond can take place. Alternatively, the same dianion is able to abstract a proton from a methylene group adjacent to the C≡C function. Hence several side reactions are possible and indeed the $^{13}C\{^1H\}$ NMR spectra of such reaction mixtures exhibit signals at shifts characteristic of alkenes.

Reactions of $Na_2[Fe(CO)_4]$ with the Bis(triflates) **1a–g** *in the Presence of Carbon Monoxide:* Carbon monoxide insertions into transition metal-carbon σ bonds are an important aspect of organometallic chemistry and have become the subject of numerous experimental[20,21] and theoretical studies[30]. In particular, such insertions are a central step in several catalytic carbonylations employed for the synthesis of industrial and fine chemicals[31].

In the field of organic chemistry, ring-closure reactions of functionalized hydrocarbons are very well-investigated. However, the formation of medium- and large-sized rings is still difficult[32]. The involved synthesis of several odoriferous substances like exaltone[33] is an example of this. To overcome such difficulties, a possible approach might be a variant of olefin carbonylation, proceeding via unstable metallacycloalkanones[21c]. Reductive elimination of the metal fragment would then lead to the expected cyclic ketones. Investigations into the thermally induced decomposition of metallacycles of the iron triad in the presence of carbon monoxide have indicated an enhanced stability of these species on going from iron to osmium[9]. Hence osmium-containing heterocycles would seem to be most useful as model compounds for structural studies[9,18]. On the other hand, it has already been demonstrated that the generally thermally unstable ferracycles, accessible via the bis(triflate) route, are suitable precursors for the synthesis of cyclic ketones[12–14].

By analogy with our synthesis of the mono-, di- and trinuclear osmacycles (Scheme 1), it was anticipated that the reaction of the bis(triflates) **1a–g** with $Na_2[Fe(CO)_4]$ in dimethyl ether at −80 °C would have lead, at least in situ, to the corresponding ferracycles, which in the presence of carbon monoxide would have afforded cyclic ketones, diketones, or eventually triketones. However, after work-up of the reaction mixtures, only the cycloalkanones **7a** and **7d**, and the cycloalkanedione **8d** could be isolated (Scheme 3). They were characterized by their IR and mass spectra and in the case of **7a** also by NMR spectra (see Experimental Section). Sharp $\nu(>C=O)$ absorptions between 1700 and 1720 cm^{-1} in the IR spectra (dichloromethane) indicated that additional ketones or diketones were also present, albeit only in trace amounts. An attempt to form an unsaturated cyclic ketone with the bis(triflate) **5** under the aforementioned conditions was not successful.

Scheme 3



These largely unsatisfactory results are attributed to the critical in situ formation of the required ferracycloalkanes. Because of the higher reactivity of $Na_2[Fe(CO)_4]$ with bis(triflates) compared to $Na_2[Os(CO)_4]$ and the smaller size of iron, the formation of oligomeric species is preferred. Moreover, ferracycloalkanes with a ring size above six are extremely unstable and undergo a fast decomposition even at −80°C.

Conclusion

Metallacycloalkanes of the iron triad with a ring size larger than six are scarcely described in the literature[34]. The bis(triflate) method offers an easy access not only for the formation of small rings but also for macrocycles with one or more $Os(CO)_4$ units. In this article the reaction of the bis(triflates) **1a−i** with $Na_2[Os(CO)_4]$ is described, which results in the formation of the mono-, di- and trinuclear osmacycles **2a**, **2b**, **2f−i**, **3a−i**, and **4a−i** with six to fifty-one atoms in the ring skeleton. However, the eight- to ten-membered osmacycles could not be obtained by this method. This is attributed to the ring strain energies of medium-sized rings, which is in agreement with results obtained for corresponding rings with an alkane framework[19]. The X-ray structure of the 22-membered diosmacycloalkane **3f** shows that the molecule almost forms a rectangle with a "two-dimensional" hole, similar to structures obtained for cycloalkanes[35]. On the contrary, osmacyclophanes prefer three-dimensional cavities in the solid state[14,15]. Because of the rigid backbone of the unsaturated *cis*-octendiyl bis(triflate) **5** the reaction with the $[Os(CO)_4]^{2-}$ dianion leads preferentially to the diosmacyclooctadeca-5,14-diene **6**. Analogous results are obtained for osmacyclophanes with two aromatic rings in the skeleton[15]. Ferracycles undergo easy carbon monoxide insertions and thus should be suitable precursors for the synthesis of cycloalkanones with one or more keto groups. Therefore, the system bis(triflates) (**1a−g**)/$Na_2[Fe(CO)_4]$ was investigated in the presence of carbon monoxide. However, the expected ferracycloalkanes with a ring-size larger than six could not be detected. Nevertheless, in the case of the bis(triflates) **1a**, **d**, the cyclic ketones **7a**, **d** and the diketone **8d** were obtained.

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Experimental Section

All reactions and manipulations were carried out under an atmosphere of argon by using standard Schlenk techniques. Solvents were dried with appropriate reagents and stored under argon. Column chromatography: Activated silica gel, 0.032−0.064 mm (Merck), diameter of the columns 4 cm; the lengths of the columns are reported in the specific sections describing the synthesis of the compounds. − Elemental analyses: Carlo Erba 1106. − AAS: Perkin-Elmer model 4000. − FD-MS: Finnigan MAT 711A (8 kV) modified by AMD. − EI-MS Finnigan TSQ 70 (200°C). − IR: Bruker IFS 48 FT-IR. − ^{1}H NMR: Bruker DRX 250 (250.13 MHz, 25°C). − $^{13}C\{^{1}H\}$ NMR: Bruker DRX 250 (62.90 MHz, 25°C). − Chemical shifts were recorded relative to tetramethylsilane. − $Na_2[Os(CO)_4]$[18a], $Na_2[Fe(CO)_4]$[27] and the bis(triflates) **1a−i**[36] were synthesized according to literature methods.

General Procedure for the Preparation of the Osmacycloalkanes **2a**, **2g−i**, **3a−i**, and **4a−i**: To a suspension of excess $Na_2[Os(CO)_4]$ in 300 ml of dimethyl ether, the bis(triflates) **1a−i** were added at −60°C. By stirring this mixture at −40°C for 3 d, a clear yellow solution and a yellow-brown precipitate were obtained. The solvent was then allowed to bubble off through a mercury valve. The residue was extracted with two 300 ml portions of *n*-pentane for 2 h. The insoluble components were separated by filtration (D4) and the solvent was removed under reduced pressure (500 mbar, 25°C) leaving the crude osmacycles. The mono-, di- and trinuclear compounds were separated by means of column chromatography (*n*-pentane/silica gel). The monoosmacycles were eluted first, followed by the di- and triosmacycles. *n*-Pentane was evaporated under reduced pressure leaving the products.

1,1,1,1-Tetracarbonyl-1-osmacyclohexane (**2a**): Starting materials: 689 mg (1.98 mmol) of $Na_2[Os(CO)_4]$ and 720 mg (1.96 mmol) of **1a**. Column length 20 cm. Yield 251 mg (34.5%) of **2a**, colorless solid, m.p. 39°C, [ref.[9]: 36°C]. − IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2043, 2036, 2009 (CO), [ref.[9]: 2124, 2043, 2035, 2008]. − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −16.1 (s, CH_2Os), 29.8 (s, CH_2CH_2Os), 32.9 [s, $CH_2(CH_2)_2Os$], 170.0 (s, equatorial CO), 178.7 (s, axial CO), [ref.[9]: −16.5, 30.1, 33.1, 170.4, 179.0]. − MS (EI, 70 eV, 50°C), *m/z*: 372.9 [M^+].

1,1,1,1,7,7,7,7-Octacarbonyl-1,7-diosmacyclododecane (**3a**): Starting materials and column length; see **2a**. Yield 45 mg (6.2%) of **3a**, colorless solid, m.p. >115°C (dec.). − IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2042, 2008 (CO). − ^{1}H NMR ($CDCl_3$): δ = 0.94−1.01 (m, 8H, CH_2Os), 1.27−1.36 [m, 4H, $CH_2(CH_2)_2Os$], 1.87−1.94 (m, 8H, CH_2CH_2Os). − $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −6.0 (s, CH_2Os), 32.2 (s, CH_2CH_2Os), 38.7 [s, $CH_2(CH_2)_2Os$], 171.2 (s, equatorial CO), 177.7 (s, axial CO). − MS (FD, 30°C), *m/z*: 746.1 [M^+]. − $C_{18}H_{20}O_8Os_2$ (744.8): calcd. C 29.03, H 2.71, Os 51.08; found C 28.64, H 2.86, Os 50.69.

1,1,1,1,7,7,7,7,13,13,13,13-Dodecacarbonyl-1,7,13-triosmacyclooctadecane (**4a**): Starting materials and column length; see **2a**. Yield 28 mg (3.8%) of **4a**, colorless solid, m.p. 67°C. − IR (*n*-

pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2042, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.96–1.03 (m, 12H, CH_2Os), 1.23–1.31 [m, 6H, $CH_2(CH_2)_2Os$], 1.76–1.82 (m, 12H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.9 (s, CH_2Os), 36.1 (s, CH_2CH_2Os), 41.6 [s, $CH_2(CH_2)_2Os$], 171.1 (s, equatorial CO), 179.1 (s, axial CO). – MS (FD, 30°C), *m/z*: 1117.8 [M^+]. – $C_{27}H_{30}O_{12}Os_3$ (1117.1): calcd. C 29.03, H 2.71, Os 51.08; found C 29.29, H 2.74, Os 50.83.

1,1,1,1,8,8,8,8-Octacarbonyl-1,8-diosmacyclotetradecane (**3b**): Starting materials: 470 mg (1.35 mmol) of $Na_2[Os(CO)_4]$ and 504 mg (1.32 mmol) of **1b**. Column length 20 cm. Yield 78 mg (15.3%) of **3b**, colorless solid, m.p. >97°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2043, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.97–1.04 (m, 8H, CH_2Os), 1.34–1.39 [m, 8H, $CH_2(CH_2)_2Os$], 1.74–1.81 (m, 8H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.9 (s, CH_2Os), 33.5, 35.0 [s, $(CH_2)_2CH_2Os$], 171.1 (s, equatorial CO), 178.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 774.2 [M^+]. – $C_{20}H_{24}O_8Os_2$ (772.8): calcd. C 31.08, H 3.13, Os 49.22; found C 30.78, H 3.44, Os 48.92.

1,1,1,1,8,8,8,8,15,15,15,15-Dodecacarbonyl-1,8,15-triosmacycloheneicosane (**4b**): Starting materials and column length; see **3b**. Yield 57 mg (11.2%) of **4b**, colorless solid, m.p. >64°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2041, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.94–1.01 (m, 12H, CH_2Os), 1.27–1.32 [m, 12H, $CH_2(CH_2)_2Os$], 1.68–1.74 (m, 12H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −2.8 (s, CH_2Os), 34.9, 37.5 [s, $(CH_2)_2CH_2Os$], 171.1 (s, equatorial CO), 179.3 (s, axial CO). – MS (FD, 30°C), *m/z*: 1160.6 [M^+]. – $C_{30}H_{36}O_{12}Os_3$ (1159.2): calcd. C 31.08, H 3.13, Os 49.22; found C 31.14, H 3.46, Os 49.60.

1,1,1,1,9,9,9,9-Octacarbonyl-1,9-diosmacyclohexadecane (**3c**): Starting materials: 590 mg (1.69 mmol) of $Na_2[Os(CO)_4]$ and 648 mg (1.64 mmol) of **1c**. Column length 20 cm. Yield 91 mg (13.8%) of **3c**, colorless solid, m.p. >107°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2041, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.96–1.04 (m, 8H, CH_2Os), 1.25–1.41 [m, 12H, $(CH_2)_2(CH_2)_2Os$], 1.70–1.78 (m, 8H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.4 (s, CH_2Os), 25.9 [s, $CH_2(CH_2)_3Os$], 34.6, 36.6 [s, $(CH_2)_2CH_2Os$], 171.2 (s, equatorial CO), 178.8 (s, axial CO). – MS (FD, 30°C), *m/z*: 801.1 [M^+]. – $C_{22}H_{28}O_8Os_2$ (800.9): calcd. C 32.99, H 3.52, Os 47.50; found C 33.19, H 3.22, Os 47.87.

1,1,1,1,9,9,9,9,17,17,17,17-Dodecacarbonyl-1,9,17-triosmacyclotetracosane (**4c**): Starting materials and column length; see **3c**. Yield 44 mg (6.7%) of **4c**, colorless oil, m.p. 13°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2040, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.95–1.02 (m, 12H, CH_2Os), 1.24–1.31 [m, 18H, $(CH_2)_2(CH_2)_2Os$], 1.69–1.75 (m, 12H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.3 (s, CH_2Os), 27.6 [s, $CH_2(CH_2)_3Os$], 36.1, 37.7 [s, $(CH_2)_2CH_2Os$], 171.1 (s, equatorial CO), 179.3 (s, axial CO). – MS (FD, 30°C), *m/z*: 1201.2 [M^+]. – $C_{33}H_{42}O_{12}Os_3$ (1201.3): calcd. C 32.99, H 3.52, Os 47.50; found C 32.86, H 3.58, Os 47.93.

1,1,1,1,10,10,10,10-Octacarbonyl-1,10-diosmacyclooctadecane (**3d**): Starting materials: 545 mg (1.57 mmol) of $Na_2[Os(CO)_4]$ and 614 mg (1.50 mmol) of **1d**. Column length 25 cm. Yield 111 mg (17.9%) of **3d**, colorless solid, m.p. >114°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2040, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.96–1.03 (m, 8H, CH_2Os), 1.32 [br, 16H, $(CH_2)_2(CH_2)_2Os$], 1.72–1.79 (m, 8H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −4.0 (s, CH_2Os), 28.0, 35.5, 36.7 [s, $(CH_2)_3CH_2Os$], 171.1 (s, equatorial CO), 179.0 (s, axial CO). – MS (FD, 30°C), *m/z*: 830.1 [M^+]. – $C_{24}H_{32}O_8Os_2$ (828.9): calcd. C 34.78, H 3.89, Os 45.89; found C 35.27, H 4.25, Os 46.12.

1,1,1,1,10,10,10,10,19,19,19,19-Dodecacarbonyl-1,10,19-triosmacycloheptacosane (**4d**): Starting materials and column length; see **3d**. Yield 49.9 mg (8.0%) of **4d**, colorless oil, m.p. 6°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2040, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.92–0.99 (m, 12H, CH_2Os), 1.28 [br, 24H, $(CH_2)_2(CH_2)_2Os$], 1.66–1.72 (m, 12H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −2.7 (s, CH_2Os), 28.7, 36.3, 38.1 [s, $(CH_2)_3CH_2Os$], 171.1 (s, equatorial CO), 179.3 (s, axial CO). – MS (FD, 30°C), *m/z*: 1244.3 [M^+]. – $C_{36}H_{48}O_{12}Os_3$ (1243.4): calcd. C 34.78, H 3.89, Os 45.89; found C 34.95, H 3.94, Os 46.26.

1,1,1,1,11,11,11,11-Octacarbonyl-1,11-diosmacycloeicosane (**3e**): Starting materials: 511 mg (1.47 mmol) of $Na_2[Os(CO)_4]$ and 604 mg (1.42 mmol) of **1e**. Column length 25 cm. Yield 114 mg (18.7%) of **3e**, colorless solid, m.p. >138°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2039, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.94–1.01 (m, 8H, CH_2Os), 1.29 [br, 20H, $(CH_2)_3(CH_2)_2Os$], 1.69–1.77 (m, 8H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.2 (s, CH_2Os), 28.5 [s, $CH_2(CH_2)_4Os$], 27.8, 35.5, 37.1 [s, $(CH_2)_3CH_2Os$], 171.1 (s, equatorial CO), 179.0 (s, axial CO). – MS (FD, 30°C), *m/z*: 858.0 [M^+]. – $C_{26}H_{36}O_8Os_2$ (857.0): calcd. C 36.44, H 4.23, Os 44.39; found C 36.31, H 4.45, Os 44.11.

1,1,1,1,11,11,11,11,21,21,21,21-Dodecacarbonyl-1,11,21-triosmacyclotriacontane (**4e**): Starting materials and column length; see **3e**. Yield 49 mg (8.0%) of **4e**, colorless oil, m.p. −7°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.92–0.99 (m, 12H, CH_2Os), 1.27 [br, 30H, $(CH_2)_3(CH_2)_2Os$], 1.67–1.73 (m, 12H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.0 (s, CH_2Os), 29.7 [s, $CH_2(CH_2)_4Os$], 28.7, 36.3, 38.3 [s, $(CH_2)_3CH_2Os$], 171.1 (s, equatorial CO), 179.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 1286.0 [M^+]. – $C_{39}H_{54}O_{12}Os_3$ (1285.5): calcd. C 36.44, H 4.23, Os 44.39; found C 35.97, H 4.40, Os 44.77.

1,1,1,1,12,12,12,12-Octacarbonyl-1,12-diosmacyclodocosane (**3f**): Starting materials: 408 mg (1.17 mmol) of $Na_2[Os(CO)_4]$ and 476 mg (1.09 mmol) of **1f**. Column length 25 cm. Yield 104 mg (21.6%) of **3f**, colorless solid, m.p. >126°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2039, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.94–1.01 (m, 8H, CH_2Os), 1.29 [br, 24H, $(CH_2)_3(CH_2)_2Os$], 1.69–1.76 (m, 8H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −3.7 (s, CH_2Os), 27.9, 29.0, 35.8, 37.4 [s, $(CH_2)_4CH_2Os$], 171.1 (s, equatorial CO), 179.2 (s, axial CO). – MS (FD, 30°C), *m/z*: 886.1 [M^+]. – $C_{28}H_{40}O_8Os_2$ (885.0): calcd. C 38.00, H 4.56, Os 42.98; found C 38.14, H 4.63, Os 43.06.

1,1,1,1,12,12,12,12,23,23,23,23-Dodecacarbonyl-1,12,23-triosmacyclotritriacosane (**4f**): Starting materials and column length; see **3f**. Yield 51 mg (10.6%) of **4f**, colorless oil, m.p. 3°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.92–0.98 (m, 12H, CH_2Os), 1.26 [br, 36H, $(CH_2)_3(CH_2)_2Os$], 1.65–1.70 (m, 12H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −2.7 (s, CH_2Os), 28.8, 29.5, 36.4, 38.2 [s, $(CH_2)_4CH_2Os$], 171.1 (s, equatorial CO), 179.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 1328.8 [M^+]. – $C_{42}H_{60}O_{12}Os_3$ (1327.5): calcd. C 38.00, H 4.56, Os 42.98; found C 38.21, H 4.62, Os 43.27.

1,1,1,1-Tetracarbonyl-1-osmacyclotridecane (**2g**): Starting materials: 620 mg (1.78 mmol) of $Na_2[Os(CO)_4]$ and 744 mg (1.59 mmol) of **1g**. Column length 30 cm. Yield 96 mg (12.8%) of **2g**, colorless oil, m.p. 12°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2125 cm^{-1}, 2043, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.95–1.02 (m, 4H, CH_2Os), 1.32 [br, 16H, $(CH_2)_4(CH_2)_2Os$], 1.74–1.81 (m, 4H, CH_2CH_2Os). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = −4.0 (s, CH_2Os), 24.0, 24.6, 25.7, 33.5, 33.6 [s, $(CH_2)_5CH_2Os$], 171.0 (s, equatorial CO), 178.1 (s, axial CO). – MS (FD, 30°C), *m/z*: 472.2 [M^+]. –

$C_{16}H_{24}O_4Os$ (470.6): calcd. C 40.84, H 5.14, Os 40.42; found C 41.15, H 5.21, Os 40.74.

1,1,1,1,14,14,14,14-Octacarbonyl-1,14-diosmacyclohexacosane (**3g**): Starting materials and column length; see **2g**. Yield 87 mg (11.5%) of **3g**, colorless solid, m.p. 70°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.93–1.00 (m, 8H, CH_2Os), 1.27 [br, 32H, $(C\mathit{H}_2)_4(CH_2)_2Os$], 1.68–1.74 (m, 8H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –3.2 (s, CH_2Os), 28.4, 29.2, 29.5, 36.3, 38.0 [s, $(\mathit{C}H_2)_5CH_2Os$], 171.1 (s, equatorial CO), 179.3 (s, axial CO). – MS (FD, 30°C), *m/z*: 942.1 [M^+]. – $C_{32}H_{48}O_8Os_2$ (941.1): calcd. C 40.84, H 5.14, Os 40.42; found C 41.21, H 4.75, Os 40.57.

1,1,1,1,14,14,14,14,27,27,27,27-Dodecacarbonyl-1,14,27-triosmacyclononatriacontane (**4g**): Starting materials and column length; see **2g**. Yield 32 mg (4.2%) of **4g**, pale-yellow oil, m.p. –11°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.91–0.98 (m, 12H, CH_2Os), 1.25 [br, 48H, $(C\mathit{H}_2)_4(CH_2)_2Os$], 1.64–1.69 (m, 12H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –2.7 (s, CH_2Os), 28.9, 29.5, 29.7, 36.6, 38.6 [s, $(\mathit{C}H_2)_5CH_2Os$], 171.1 (s, equatorial CO), 179.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 1412.1 [M^+]. – $C_{48}H_{72}O_{12}Os_3$ (1411.7): calcd. C 40.84, H 5.14, Os 40.42; found C 41.09, H 5.37, Os 40.87.

1,1,1,1-Tetracarbonyl-1-osmacyclopentadecane (**2h**): Starting materials: 470 mg (1.35 mmol) of $Na_2[Os(CO)_4]$ and 615 mg (1.24 mmol) of **1h**. Column length 30 cm. Yield 131 mg (21.1%) of **2h**, colorless oil, m.p. –3°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2125 cm^{-1}, 2043, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.96–1.03 (m, 4H, CH_2Os), 1.32 [br, 20H, $(C\mathit{H}_2)_5(CH_2)_2Os$], 1.72–1.79 (m, 4H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –3.7 (s, CH_2Os), 26.4, 26.5, 26.7, 27.0, 33.9, 35.2 [s, $(\mathit{C}H_2)_6CH_2Os$], 171.1 (s, equatorial CO), 178.6 (s, axial CO). – MS (FD, 30°C), *m/z*: 500.1 [M^+]. – $C_{18}H_{28}O_4Os$ (498.6): calcd. C 43.36, H 5.66, Os 38.15; found C 43.60, H 5.75, Os 38.51.

1,1,1,1,16,16,16,16-Octacarbonyl-1,16-diosmacyclotriacontane (**3h**): Starting materials and column length; see **2h**. Yield 62 mg (10.0%) of **3h**, colorless solid, m.p. >69°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.92–0.99 (m, 8H, CH_2Os), 1.26 [br, 40H, $(C\mathit{H}_2)_5(CH_2)_2Os$], 1.67–1.73 (m, 8H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –3.0 (s, CH_2Os), 28.7, 29.3, 29.6, 29.7, 36.3, 38.2 [s, $(\mathit{C}H_2)_6CH_2Os$], 171.1 (s, equatorial CO), 179.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 998.5 [M^+]. – $C_{36}H_{56}O_8Os_2$ (997.2): calcd. C 43.36, H 5.66, Os 38.15; found C 43.60, H 5.37, Os 37.83.

1,1,1,1,16,16,16,16,31,31,31,31-Dodecacarbonyl-1,16,31-triosmacyclopentatetracontane (**4h**): Starting materials and column length; see **2h**. Yield 28 mg (4.5%) of **4h**, pale-yellow oil, m.p. –19°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.91–0.97 (m, 12H, CH_2Os), 1.25 [br, 60H, $(C\mathit{H}_2)_5(CH_2)_2Os$], 1.65–1.70 (m, 12H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –2.7 (s, CH_2Os), 28.9, 29.5, 29.6, 36.4, 38.3 [s, $(\mathit{C}H_2)_6CH_2Os$], 171.0 (s, equatorial CO), 179.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 1496.8 [M^+]. – $C_{54}H_{84}O_{12}Os_3$ (1495.9): calcd. C 43.36, H 5.66, Os 38.15; found C 43.40, H 5.37, Os 37.95.

1,1,1,1-Tetracarbonyl-1-osmacycloheptadecane (**2i**): Starting materials: 403 mg (1.16 mmol) of $Na_2[Os(CO)_4]$ and 533 mg (1.02 mmol) of **1i**. Column length 30 cm. Yield 120 mg (22.2%) of **2i**, pale-yellow oil, m.p. 0°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2042, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.95–1.02 (m, 4H, CH_2Os), 1.30 [br, 24H, $(C\mathit{H}_2)_6(CH_2)_2Os$], 1.72–1.79 (m, 4H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –3.7 (s, CH_2Os), 26.2, 26.6, 27.1, 27.6, 27.8, 34.7, 36.6 [s, $(\mathit{C}H_2)_7CH_2Os$], 171.1 (s, equatorial CO), 178.9 (s, axial CO). – MS (FD, 30°C), *m/z*: 528.1 [M^+]. – $C_{20}H_{32}O_4Os$ (526.7): calcd. C 45.61, H 6.12, Os 36.11; found C 45.35, H 5.77, Os 35.71.

1,1,1,1,18,18,18,18-Octacarbonyl-1,18-diosmacyclotetratriacontane (**3i**): Starting materials and column length; see **2i**. Yield 70 mg (12.9%) of **3i**, colorless solid, m.p. >77°C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2042, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.91–0.98 (m, 8H, CH_2Os), 1.25 [br, 48H, $(C\mathit{H}_2)_6(CH_2)_2Os$], 1.66–1.73 (m, 8H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –2.9 (s, CH_2Os), 28.7, 29.4, 29.5, 29.7, 36.3, 38.2 [s, $(\mathit{C}H_2)_7CH_2Os$], 171.1 (s, equatorial CO), 179.4 (s, axial CO). – MS (FD, 30°C), *m/z*: 1054.8 [M^+]. – $C_{40}H_{64}O_8Os_2$ (1053.3): calcd. C 45.61, H 6.12, Os 36.11; found C 46.07, H 6.06, Os 35.84.

1,1,1,1,18,18,18,18,35,35,35,35-Dodecacarbonyl-1,18,35-triosmacyclohenpentacontane (**4i**): Starting materials and column length; see **2i**. Yield 27 mg (5.0%) of **4i**, pale-yellow oil, m.p. –15°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2042, 2038, 2008 (CO). – ^{1}H NMR ($CDCl_3$): δ = 0.90–0.97 (m, 12H, CH_2Os), 1.24 [br, 72H, $(C\mathit{H}_2)_6(CH_2)_2Os$], 1.64–1.69 (m, 12H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –2.7 (s, CH_2Os), 29.0, 29.2, 29.6, 29.7, 36.5, 38.4 [s, $(\mathit{C}H_2)_7CH_2Os$], 171.1 (s, equatorial CO), 179.5 (s, axial CO). – MS (FD, 30°C), *m/z*: 1580.9 [M^+]. – $C_{60}H_{96}O_{12}Os_3$ (1580.0): calcd. C 45.61, H 6.12, Os 36.11; found C 45.72, H 6.01, Os 35.80.

General Procedure for the Preparation of the Monoosmacycles **2b** *and* **2f**: To a suspension of $Na_2[Os(CO)_4]$ in 1.7 l of dimethyl ether, a solution of the bis(triflates) **1b** and **1f** in 250 ml of dimethyl ether was added dropwise (over 1 d) at –30°C. After stirring this mixture for 2 d, a clear yellow solution and a yellow-brown precipitate were obtained. The solvent was then allowed to bubble off through a mercury valve. The residue was extracted with two 300 ml portions of *n*-pentane. The insoluble components were separated by filtration (D4). The solvent was removed under reduced pressure (500 mbar, 25°C) leaving the crude osmacycles, which were purified by column chromatography (silica gel/*n*-pentane, column length 20 cm). The mononuclear species were eluted first, followed by the di- and triosmacycles.

1,1,1,1-Tetracarbonyl-1-osmacycloheptane (**2b**): Starting materials: 448 mg (1.29 mmol) of $Na_2[Os(CO)_4]$ and 421 mg (1.10 mmol) of **1b**. The product obtained by column chromatography was subsequently washed with 2 ml of *n*-pentane at –80°C. Yield 39 mg (9.2%) of **2b**, colorless oil, m.p. 18°C. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2043, 2035, 2009 (CO). – ^{1}H NMR ($CDCl_3$): δ = 1.36–1.41 (m, 4H, CH_2Os), 1.45–1.50 [m, 4H, $C\mathit{H}_2(CH_2)_2Os$], 2.13–2.19 (m, 4H, $C\mathit{H}_2CH_2Os$). – $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –11.3 (s, CH_2Os), 29.4, 32.4 [s, $(\mathit{C}H_2)_2CH_2Os$], 170.3 (s, equatorial CO), 179.7 (s, axial CO). – MS (EI, 70 eV, 50°C), *m/z* (%): 386.4 (13) [M^+], 356.0 (53) [M^+ – CO], 328.0 (67) [M^+ – 2 CO]; 300.3 (100) [M^+ – 3 CO], 270.2 (67) [M^+ – 4 CO]. – $C_{10}H_{12}O_4Os$ (386.40): calcd. C 31.08, H 3.13, Os 49.22; found C 31.27, H 3.43, Os 49.34.

1,1,1,1,8,8,8,8-Octacarbonyl-1,8-diosmacyclotetradecane (**3b**): Starting materials: see **2b**. Yield 58 mg (13.6%) of **3b**.

1,1,1,1,8,8,8,8,15,15,15,15-Dodecacarbonyl-1,8,15-triosmacycloheneicosane (**4b**): Starting materials: see **2b**. Yield 45 mg (10.6%) of **4b**.

1,1,1,1-Tetracarbonyl-1-osmacycloundecane (**2f**): Starting materials: 523 mg (1.50 mmol) of $Na_2[Os(CO)_4]$ and 651 mg (1.49 mmol) of **1f**. Estimated yield 7 mg (1.1%) of **2f**. – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2041, 2037, 2008 (CO). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = –6.0 (s, CH_2Os), 22.1, 24.2, 30.5, 33.1 [s, $(\mathit{C}H_2)_4CH_2Os$], 171.1

(s, equatorial CO), 179.5 (s, axial CO). – MS (FD, 30 °C), *m/z*: 441.0 [M^+]. – $C_{14}H_{20}O_4Os$ (442.5). Because of the poor yield no further characterization was possible.

1,1,1,1,12,12,12,12-Octacarbonyl-1,12-diosmacyclodocosane (**3f**): Starting materials: see **2f**. Yield 112 mg (16.9%) of **3f**.

1,1,1,1,12,12,12,12,23,23,23,23-Dodecacarbonyl-1,12,23-triosmacyclotritriacosane (**4f**): Starting materials: see **2f**. Yield 63 mg (9.5%) of **4f**.

1,1,1,1,10,10,10,10-Octacarbonyl-1,10-diosmacyclooctadeca-5,14-diene (**6**): To a suspension of 319 mg (0.92 mmol) of $Na_2[Os(CO)_4]$ in 300 ml of dimethyl ether, 350 mg (0.86 mmol) of the bis(triflate) **5** was added at −60 °C. Upon stirring the mixture at this temperature for 5 d, a clear yellow solution and a yellow-brown precipitate were obtained. Subsequently, the dimethyl ether was allowed to bubble off through a mercury valve. The residue was extracted for 4 h at room temperature with three 300 ml portions of *n*-pentane. The insoluble components were separated by filtration (D4). The solvent was removed under reduced pressure leaving the crude product. Purification was achieved by column chromatography (silica gel/*n*-pentane; column 10 × 2.5 cm) and recrystallization from 5 ml of *n*-pentane at −60 °C. Yield 65 mg (18.6%) of **6**, colorless solid, m.p. >67 °C (dec.). – IR (*n*-pentane): $\tilde{\nu}$ = 2124 cm^{-1}, 2040, 2009 (CO). – ^1H NMR ($CDCl_3$): δ = 0.94–0.99 (m, 8H, CH_2Os), 1.72–1.84 (m, 8H, CH_2CH_2Os), 2.00–2.08 [m, 8H, $CH_2(CH_2)_2Os$], 5.33 [AA' part of an $AA'X_2X'_2$ spin system N = 9.4 Hz, 4H, $CH(CH_2)_3Os$]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −3.2 (s, CH_2Os), 34.1, 38.4 [s, $(CH_2)_2CH_2Os$], 130.2 [s, $CH(CH_2)_3Os$], 170.9 (s, equatorial CO), 179.1 (s, axial CO). – MS (FD, 35 °C), *m/z*: 826.8 [M^+]. – $C_{24}H_{28}O_8Os_2$ (824.9): calcd. C 34.95, H 3.42, Os 46.12; found C 34.83, H 3.60, Os 46.19.

General Procedure for the Preparation of the Cycloalkanones **7a**, **7d**, *and* **8d**: The bis(triflates) **1a** and **1d** were added to a suspension of $Na_2[Fe(CO)_4]$ in 1.5 l of dimethyl ether at −80 °C. After 3 h a clear, dark-red solution was obtained. Subsequently, 300 ml of dichloromethane (−80 °C) was added and carbon monoxide was immediately bubbled into the solution. The mixture was allowed to warm to room temperature and the dimethyl ether was evaporated. The ketones were purified by column chromatography using activated silica gel/CH_2Cl_2 (column 6 × 20 cm). The first fraction contained the various iron carbonyls, while the second fraction contained the ketones **7a**, **7d**, and **8d**. The solvent of the latter fraction was removed under reduced pressure leaving **7a**. The cycloalkanones **7d** and **8d** were detectable in a concentrated dichloromethane fraction.

Cyclohexanone (**7a**): Starting materials: 2.531 g (11.83 mmol) of $Na_2[Fe(CO)_4]$ and 4.114 g (11.17 mmol) of **1a**. Yield 211 mg (19.3%) of **7a**, colorless oil. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1706 cm^{-1} (CO), [ref.[37]: 1710]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.8 [s, $CH_2(CH_2)_2CO$], 26.9 (s, CH_2CH_2CO), 41.8 (s, CH_2CO), 212.0 (s, CO), [ref.[37]: 23.8, 26.5, 40.4, 208.5]. – MS (EI, 70 eV, 35 °C), *m/z*: 98.2 [M^+].

Cyclononanone (**7d**): Starting materials: 2.245 g (10.50 mmol) of $Na_2[Fe(CO)_4]$ and 4.263 g (10.39 mmol) of **1d**. IR (CH_2Cl_2): $\tilde{\nu}$ = 1710 cm^{-1} (CO). – MS (EI, 70 eV, 50 °C), *m/z*: 140.1 [M^+].

Cyclooctadecadione-1,10 (**8d**): Starting materials: see **7d**. IR (CH_2Cl_2): $\tilde{\nu}$ = 1710 cm^{-1} (CO). MS (EI, 70 eV, 50 °C), *m/z*: 280.4 [M^+].

X-Ray Structural Analysis of **3f**: Single crystals were obtained from an *n*-pentane solution. $C_{28}H_{40}O_8Os_2$, M = 885.00 g mol^{-1}, triclinic space group $P\bar{1}$ (no. 2), a = 6.021(3), b = 11.625(5), c = 11.793(6) Å, α = 73.10(4), β = 76.63(4), γ = 86.50(4)°, V = 768.4(6) $Å^3$, $\rho_{calcd.}$ = 1.913 g cm^{-3}, Z = 1, F_{000} = 424, measurement at 173 K, μ(Mo-K_α) = 8.304 mm^{-1}, scan mode = Wyckoff, h, k, l range = ±7, ±13, ±14, 2Θ limits = 4–50°, measured reflections = 5384, observed reflections = 2691, observed reflections ($F_o \geqslant 4\sigma F_o$) = 2516, refined parameters = 173, S = 1.827, $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ = 0.028, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.065. A crystal with the dimensions 0.30 × 0.15 × 0.10 mm was mounted on a glass fibre and transferred to a *P*4 Siemens 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[38] and refined by the least-squares method (based on F^2) with anistropic 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 0.9960 and 0.3465, respectively. Maximum and minimum peaks in the final difference synthesis were 1.107 and −2.216 e$Å^{-3}$. 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-405907, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 65th birthday.

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