Preparation, properties and reactions of metal-containing heterocycles
Part LXXXIX*. Metalla[n]- and metalla[m.n]orthocyclophanes as mediators for the synthesis of cyclic ketones

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Abstract

The reaction of the bis(triflates) 1,2-bis[2-(trifluoromethylsulfonyloxy)ethyl]benzene (1), 1,2-bis[3-(trifluoromethylsulfonyloxy)propyl]benzene (3) and 1,2-bis{2-[2-(trifluoromethylsulfonyloxy)ethyl]phenyl}ethane (6), respectively, with the carbonyl metalates $[M(CO)_4]^{2-}$ (M = Os (a), Ru (b), Fe (c)) results in the formation of the osmaorthocyclophanes 2a, 4a, 7a and 8a, the ruthenacylophane 2b and the ferracyclophanes 2c and 7c, respectively. Carbon monoxide insertion into the Fe–C σ bonds of the ferracycles 2c and 7c, respectively, affords the ketones 3-oxo[5]orthocyclophane (9) and 3-oxo[5.2]orthocyclophane (11). The structure of 2a was investigated by an X-ray structural analysis. 2a crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$.

Key words: Crystal structures; Iron complexes; Ruthenium complexes; Osmium complexes; Metallacyclophane complexes; Oxocyclophanes

Introduction

The formation of metal–carbon σ bonds is a crucial step in transition metal catalyzed or mediated organic synthesis [2–4]. As reactive intermediates metallacycloalkanes with at least two M–C σ bonds are of special interest in this field. In order to elucidate and understand such catalytic reactions it was necessary to prepare stable representatives of this class of heterocycles [3], which may serve as model compounds. An easy access to metallacycloalkanes has been opened by the bis(triflate) route [3, 5–10], which is a variant of cationic alkylation [7]. The excellent and inert leaving groups $CF_3SO_2O^-$ stabilize carbenium-like atoms at the ends of a hydrocarbon chain [11], thereby enabling an electrophilic attack of the terminal carbon atoms at a basic metal centre. For this reason the easily available bis(triflates) [12] are superior to bis(iodides), which were only successful in a few cases [13]. For instance metallacycloalkanes of iron and ruthenium with different ring size are only accessible by reaction of the cor-responding bivalent metalates $[M(CO)_4]^{2-}$ (M = Fe, Ru) with alkanediylbis(trifluoromethanesulfonates) [6, 8, 10]. In the case of $[Os(CO)_4]^{2-}$ tosylates have also been successfully employed [14].

Carbon monoxide insertion into transition metal–carbon σ bonds has become the subject of numerous experimental studies [15, 16], because it is the central step of several catalytic carbonylations used for the synthesis of both industrial and fine chemicals [15].

Cyclizations of functionalized hydrocarbon chains are still difficult in organic synthesis. In particular large rings are hardly available by classical methods. A promising tool for a more favourable access to such cyclic systems is the employment of the above-mentioned bis(triflate) method. In order to isolate cyclic ketones via the corresponding CO insertion intermediates we specifically investigated the thermolysis of metallacycles in the presence of carbon monoxide. Depending on the ring size and the number of metal atoms in the rings various ketones [1, 6] and diketones [10] were obtained.

In this article we describe the preparation of osma[n]-, ruthena[n]- and ferra[n]orthocyclophanes as well

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as the [m.n]orthocyclophanes of osmium and iron and the reaction of the ferracycles with carbon monoxide to the corresponding cycloalkanones.

Experimental

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. IR data were obtained with a Bruker IFS 48 instrument. Field desorption (FD) mass spectra were taken on a Finnigan MAT 711 A instrument (8 kV), modified by AMD; electron impact (EI) mass spectra were recorded on a Finnigan TSQ 70 instrument (200 °C). Elemental analyses were performed with a Carlo Erba 1106 analyzer. Osmium was determined with a Perkin-Elmer AAS model 4000. NMR spectra were obtained with a Bruker AC 80 spectrometer operating at 80.13 MHz for ^{1}H and 20.15 MHz for ^{13}C, or on a Bruker AC 250 instrument, operating at 250.13 MHz for ^{1}H and 62.90 MHz for ^{13}C. All ^{13}C spectra were proton decoupled. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to TMS.

Reagents

Na$_2$[Os(CO)$_4$] [17], Na$_2$[Ru(CO)$_4$] [18] and Na$_2$[Fe(CO)$_4$] [19] were synthesized according to literature methods. The bis(triflates) 1, 3 and 6 were prepared according to common routes [20, 21].

General route to the osmacyclophanes 2a, 4a, 7a

To an excess of Na$_2$[Os(CO)$_4$] in dimethyl ether at -50 °C the bis(triflates) 1, 3, 6 were added. By refluxing this mixture at -24 °C for 2 days a clear yellow solution was obtained in addition to a yellow–brown precipitate. After evaporation of the solvent under reduced pressure at -70 °C, the residue was extracted three times with 50 ml of n-pentane at room temperature within 30 min. The insoluble components were separated by filtration (G3), n-pentane was completely removed under vacuum leaving the crude product. 2a was separated by recrystallization from CHCl$_3$. 4a was precipitated from a CHCl$_3$ solution at -80 °C. Pure 7a was isolated by washing the crude product three times with 1 ml of n-pentane.

3,3,3,3-Tetracarbonyl-3-osma[5]orthocyclophane (2a)

236 mg (0.55 mmol) of 1 were reacted with 191 mg (0.55 mmol) of Na$_2$[Os(CO)$_4$] in 30 ml of dimethyl ether. 2a was obtained in 54% yield, m.p. 107 °C. FD-MS: m/z 435.8 [M^+]. Anal. Calc. for C$_{14}$H$_{12}$O$_4$Os (434.45): C, 38.71; H, 2.78; Os, 43.78. Found: C, 39.04; H, 2.96; Os, 43.17%. IR (n-pentane): ν(CO) 2124, 2046, 2037, 2013 cm^{-1}. ^{1}H NMR (80.13 MHz, CDCl$_3$, -10 °C): δ (ppm) 7.13–7.07 (m, CH$_{arom}$, 4H); 3.21–3.05 (m, OsCH$_2$CH_2, 4H); 1.85–1.69 (m, OsCH$_2$, 4H). ^{13}C{^{1}H} NMR (20.15 MHz, CDCl$_3$, -10 °C): δ (ppm) 178.20 (s, CO$_{ax}$); 169.43 (s, CO$_{eq}$); 143.77 (s, C$_{arom}$); 128.97, 126.04 (s, CH$_{arom}$); 34.26 (s, OsCH$_2$CH_2); -11.00 (s, OsCH$_2$).

4,4,4,4-Tetracarbonyl-4-osma[7]orthocyclophane (4a)

580 mg (1.27 mmol) of 3 were reacted with 550 mg (1.58 mmol) of Na$_2$[Os(CO)$_4$] in 30 ml of dimethyl ether. 4a was obtained in 27% yield, m.p. 97 °C. FD-MS: m/z 464.2 [M^+]. Anal. Calc. for C$_{16}$H$_{16}$O$_4$Os (462.50): C, 41.55; H, 3.49; Os, 41.12. Found: C, 41.21; H, 3.58; Os, 40.54%. IR (n-pentane): ν(CO) 2124, 2046, 2027, 2010 cm^{-1}. ^{1}H NMR (80.13 MHz, CDCl$_3$, 25 °C): δ (ppm) 7.16 (s, CH$_{arom}$, 4H); 2.71–2.52 (m, OsCH$_2$CH$_2$CH_2, 4H); 2.04–1.75 (m, OsCH$_2$CH_2); 1.22–0.99 (m, OsCH$_2$, 4H). ^{13}C{^{1}H} NMR (20.15 MHz, CDCl$_3$, 25 °C): δ (ppm) 178.72 (s, CO$_{ax}$); 170.24 (s, CO$_{eq}$); 140.74 (s, C$_{arom}$); 128.86, 125.45 (s, CH$_{arom}$); 34.95 (s, OsCH$_2$CH$_2$CH_2); 31.51 (s, OsCH$_2$CH_2); -4.11 (s, OsCH$_2$).

3,3,3,3-Tetracarbonyl-3-osma[5.2]orthocyclophane (7a)

275 mg (0.51 mmol) of 6 were reacted with 186 mg (0.53 mmol) of Na$_2$[Os(CO)$_4$] in 150 ml of dimethyl ether. 7a was obtained in 63% yield, m.p. > 150 °C dec. FD-MS: m/z 540.0 [M^+]. Anal. Calc. for C$_{22}$H$_{20}$O$_4$Os (538.6): C, 49.06; H, 3.74; Os, 35.32. Found: C, 48.57; H, 3.84; Os, 34.89%. IR (n-pentane): ν(CO) 2128, 2045, 2042, 2012 cm^{-1}. ^{1}H NMR (250.13 MHz, CDCl$_3$, 20 °C): δ (ppm) 7.40–7.00 (m, CH$_{arom}$, 8H); 3.20–3.13 (m, OsCH$_2$CH_2, 4H); 2.99 (s, CCH_2CH$_2$C, 4H) 1.53–1.46 (m, OsCH$_2$, 4H). ^{13}C{^{1}H} NMR (62.90 MHz, CDCl$_3$, 20 °C): δ (ppm) 177.10 (s, CO$_{ax}$); 170.39 (s, CO$_{eq}$); 145.85, 139.25, (s, C$_{arom}$); 130.11, 129.25, 126.39, 126.06 (s, CH$_{arom}$); 39.38 (s, OsCH$_2$CH_2); 35.38 (s, CCH_2CH$_2$C); -3.78 (s, OsCH$_2$).

3,3,3,3,22,22,22,22-Octacarbonyl-3,22-diosma[5.2.5.2]orthocyclophane (8a)

583.0 mg of Na$_2$[Os(CO)$_4$] (1.67 mmol) were suspended in 200 ml of dimethyl ether at -50 °C. 864 mg (1.62 mmol) of the bis(triflate) 6 were added and this mixture was refluxed at -24 °C for 2 days. A clear yellow solution was obtained with a yellow–brown precipitate. After evaporation of 100 ml of the dimethyl ether by warming up to room temperature, 50 ml of diethyl ether were added and the remaining dimethyl ether was allowed to evaporate completely. After filtering the diethyl ether solution (G3) and removing the solvent under reduced pressure the residue was extracted two times with 100 ml of n-pentane. Filtration

(G3) of this n-pentane solution, evaporation of the solvent under vacuum, and washing the crude product three times with 1 ml of diethyl ether leaves **8a** as a white powder in 29% yield, m.p. > 150 °C dec. FD-MS: m/z 1078.6 $[M^+]$. *Anal.* Calc. for $C_{44}H_{40}O_8Os_2$ (1077.2): C, 49.06; H, 3.74; Os, 35.32. Found: C, 49.58; H, 3.83; Os, 34.39%. IR (n-pentane): ν(CO) 2128, 2045, 2042, 2012 cm^{-1}. ^{1}H NMR (250.13 MHz, CDCl$_3$, 20 °C): δ (ppm) 7.25–6.85 (m, CH_{arom}, 16H); 2.85 (s, CCH_2CH_2C, 8H); 2.83–2.79 (m, $OsCH_2CH_2$, 8H); 1.13–1.06 (m, $OsCH_2$, 8H); $^{13}C\{^1H\}$ NMR (62.90 MHz, CDCl$_3$, 20 °C); δ (ppm) 178.53 (s, CO_{ax}); 170.61 (s, CO_{eq}); 145.58, 138.55 (s, C_{arom}); 129.21, 128.81, 126.23, 125.70 (s, CH_{arom}); 41.02 (s, $OsCH_2CH_2$); 33.42 (s, CCH_2CH_2C); -2.02 (s, $OsCH_2$).

General preparation of the ruthena- and ferracyclophanes 2b and 2c

An excess of Na$_2$[Ru(CO)$_4$] and Na$_2$[Fe(CO)$_4$], respectively, was suspended in dimethyl ether at -70 °C. The bis(triflate) **1** was added and the mixture was stirred until a clear solution appeared. The solvent was removed under reduced pressure and the residue was extracted three times with 30 ml of n-pentane. After filtration (G3) and removing the solvent under vacuum a crude product was obtained. **2b** and **2c** were precipitated as colourless products from a concentrated n-pentane solution at -80 °C.

3,3,3,3-Tetracarbonyl-3-ruthena[5]orthocylophane (2b)

315 mg (0.91 mmol) of **1** were reacted with 333 mg (1.29 mmol) of Na$_2$[Ru(CO)$_4$] in 50 ml of dimethyl ether. **2b** was obtained in 19% yield, m.p. -30 °C (dec.). IR (n-pentane): ν(CO) 2118, 2052, 2039, 2027 cm^{-1}. ^{1}H NMR (80.13 MHz, CDCl$_3$, -40 °C): δ (ppm) 7.16 (s, CH_{arom}, 4H); 3.12–2.96 (m, $RuCH_2CH_2$, 4H); 1.73–1.57 (m, $RuCH_2$, 4H). $^{13}C\{^1H\}$ NMR (20.15 MHz, CDCl$_3$, -40 °C): δ (ppm) 196.03 (s, CO_{ax}); 187.99 (s, CO_{eq}); 143.64 (s, C_{arom}); 128.96, 128.11 (s, CH_{arom}); 34.98 (s, $RuCH_2CH_2$); 2.51 (s, $RuCH_2$).

3,3,3,3-Tetracarbonyl-3-ferra[5]orthocyclophane (2c)

473 mg (1.09 mmol) of **1** were reacted with 218 mg (1.02 mmol) of Na$_2$[Fe(CO)$_4$] in 50 ml of dimethyl ether. **2c** was obtained in 22% yield, m.p. -30 °C (dec.). IR (n-pentane): ν(CO) 2094, 2032, 2016, 2014 cm^{-1}. ^{1}H NMR (80.13 MHz, CDCl$_3$, -40 °C): δ (ppm) 7.17 (m, CH_{arom}, 4H); 3.11–2.95 (m, $FeCH_2CH_2$, 4H); 1.93–1.78 (m, $FeCH_2$, 4H). $^{13}C\{^1H\}$ NMR (20.15 MHz, CDCl$_3$, -40 °C): δ (ppm) 210.28 (s, CO_{ax}); 204.71 (s, CO_{eq}); 142.14 (s, C_{arom}); 129.07, 126.62 (s, CH_{arom}); 34.76 (s, $FeCH_2CH_2$); 14.54 (s, $FeCH_2$).

General route to the cycloalkanones 9 and 11

To an excess of Na$_2$[Fe(CO)$_4$] in dimethyl ether at -50 °C the bis(triflates) **1** and **6**, respectively, were added. After a clear red–brown solution appeared, dichloromethane was added and the mixture was warmed up to room temperature in which the dimethyl ether was allowed to evaporate. During that time carbon monoxide was bubbled through the solution. The product was purified by column chromatography using activated silica gel (column 3 × 20 cm). First the different iron carbonyl compounds were separated with CH$_2$Cl$_2$, before the ketones **9** and **11**, respectively, were eluated with acetone. The solvent of the latter fraction was removed under vacuum. **9** and **11** were recrystallized from dichloromethane and dichloromethane/n-hexane 1/1, respectively.

3-Oxo[5]orthocyclophane (9)

374 mg (0.87 mmol) of **1** were reacted with 277 mg (1.06 mmol) of Na$_2$[Fe(CO)$_4$] in 50 ml of dimethyl ether. **9** was obtained in 29% yield from CH$_2$Cl$_2$, m.p. 41 °C (lit. [22] 41–42 °C). EI-MS: m/z 160.2 $[M^+]$. *Anal.* Calc. for $C_{11}H_{12}O$ (160.2): C, 82.46; H, 7.55. Found: C, 82.64; H, 7.38%. IR (CH$_2$Cl$_2$): ν($>$C=O) 1699 cm^{-1}. ^{1}H NMR (80.13 MHz, CDCl$_3$, 25 °C): δ (ppm) 7.19 (s, CH_{arom}, 4H); 2.98–2.83 (m, $OCCH_2CH_2$, 4H); 2.64–2.49 (m, $OCCH_2$, 4H); $^{13}C\{^1H\}$ NMR (20.15 MHz, CDCl$_3$, 25 °C): δ (ppm) 210.97 (s, $>$C=O); 140.51 (s, C_{arom}); 129.09, 127.12 (s, CH_{arom}); 44.56 (s, $OCCH_2$); 30.50 (s, $OCCH_2CH_2$).

3-Oxo[5.2]orthocyclophane (11)

1.14 g (2.13 mmol) of **6** were reacted with 474 mg (2.21 mmol) of Na$_2$[Fe(CO)$_4$] in 100 ml of dimethyl ether. After recrystallization from CH$_2$Cl$_2$/n-hexane **11** was obtained in 23% yield, m.p. 145 °C. FD-MS: m/z 264.3 $[M^+]$. *Anal.* Calc. for $C_{19}H_{20}O$ (264.4): C, 86.32; H, 7.63. Found: C, 86.80; H, 7.91%. IR (KBr): ν($>$C=O) 1700 cm^{-1}. ^{1}H NMR (250.13 MHz, CDCl$_3$, 20 °C): δ (ppm) 7.30–7.05 (m, CH_{arom}, 8H); 2.96 (m, $OCCH_2$, 4H); 2.72 (m, $OCCH_2CH_2$, 4H); 2.68 (s, CCH_2CH_2C, 8H). $^{13}C\{^1H\}$ NMR (62.90 MHz, CDCl$_3$, 20 °C): δ (ppm) 208.74 (s, $>$C=O); 139.78, 139.32 (s, C_{arom}); 130.21, 129.53, 126.62, 126.27 (s, CH_{arom}); 44.16 (s, $OCCH_2$); 34.20 (s, CCH_2CH_2C); 27.35 (s, $OCCH_2CH_2$).

X-ray structure determination of the 3,3,3,3-tetracarbonyl-3-osma[5]orthocyclophane (2a)*

Single crystals of **2a** were obtained from CHCl$_3$. A crystal with the approximate dimensions 0.1 × 0.5 × 0.5 mm was mounted on a glass fibre and transferred to a P4 Siemens diffractometer, using graphite-monochromatized Mo Kα radiation. Two check reflections

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*See 'Supplementary material'.

were monitored every 58 intensity measurements, they showed no systematic decrease in the intensity. The structure was solved by Patterson methods [23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (riding model). The fine cell parameters and specific data

TABLE 1. Summary of crystallographic data and parameters for data collection and refinement of **2a**

Formula	$C_{14}H_{12}O_4Os$
Formula weight	434.4
Crystal system	monoclinic
Space group	$P2_1/n$
a (pm)	642.6(1)
b (pm)	3550.8(7)
c (pm)	642.6(1)
β (°)	110.03(3)
V (pm$^3 \times 10^6$)	1377.7(4)
Z	4
μ (Mo Kα) (mm^{-1})	9.261
D_{calc} (g cm^{-3})	2.094
Temperature (K)	173
$F(000)$	816
2θ Scan limits (°)	4–45
Scan type	ω
Scan speed (° min^{-1})	var. 10–30
Scan range (°)	1.2
Data collected, h, k, l	$-6 \to 6$, $-38 \to 38$, $-6 \to 6$
Absorption correction	Ψ-scan
Reflections collected	5793
Unique reflections $F \geqslant 4\sigma(F)$	1406
Parameters refined	172
GOF	1.39
R	0.031
R_w	0.032

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (pm$^2 \times 10^{-1}$) of **2a**

| Atom	x	y	z	U_{eq}
Os(1)	3730(1)	774(1)	1628(1)	26(1)
C(1)	5976(18)	451(3)	1129(13)	34(4)
O(1)	7285(13)	272(2)	835(11)	53(3)
C(2)	3552(16)	443(3)	3813(14)	36(4)
O(2)	2932(14)	245(2)	5081(12)	59(3)
C(3)	1235(17)	594(3)	−885(14)	37(4)
O(3)	−285(12)	532(2)	−2397(10)	49(3)
C(4)	5845(16)	1101(3)	3787(14)	31(3)
O(4)	7035(11)	1303(2)	4973(10)	44(3)
C(5)	4392(16)	1129(3)	−926(12)	34(3)
C(6)	3224(16)	1506(3)	−1645(12)	34(3)
C(7)	3626(16)	1790(3)	194(12)	32(3)
C(8)	5322(17)	2041(3)	649(15)	46(4)
C(9)	5740(19)	2299(3)	2409(17)	58(4)
C(10)	4470(20)	2294(3)	3695(15)	56(5)
C(11)	2711(18)	2048(3)	3250(14)	40(4)
C(12)	2259(15)	1785(3)	1528(12)	30(3)
C(13)	405(15)	1508(3)	1130(13)	35(3)
C(14)	1138(15)	1130(3)	2297(12)	30(3)

collection parameters are summarized in Table 1. The final atomic positional data are listed in Table 2.

Results and discussion

Synthesis and general characterization

The seven-membered osma-, ruthena- and ferracycles **2a–c** are formed by treating the bis(triflate) **1** [20] with a suspension of the metal Lewis bases $[Os(CO)_4]^{2-}$ and $[M(CO)_4]^{2-}$ (M = Ru, Fe) in dimethyl ether at −24 and −70 °C, respectively (Scheme 1). Because of the lower basicity the reaction of $[Os(CO)_4]^{2-}$ with **1** proceeds only in refluxing dimethyl ether. To prevent decomposition of the very unstable benzometallacycle **2c** the isolation of the compound has to be carried out within a short time. Whereas **2a** can be handled at room temperature, the iron and ruthenium containing metallacycles decompose completely above −20 °C.

By employment of the bis(triflate) **3** only the reaction with $[Os(CO)_4]^{2-}$ in dimethyl ether resulted in the formation of the rather stable monomeric benzoosmacyclononane (**4a**) and the dimeric diosma[7.7]-orthocyclophane (**5a**) (Scheme 1). The X-ray crystal structure of the latter has recently been determined [10]. No metallacyclic products resulted from the reaction between $[Ru(CO)_4]^{2-}$ and the bis(triflate) **3**. A highly decomposable compound has been isolated from the system $[Fe(CO)_4]^{2-}/3$ in dimethyl ether. The IR spectrum (n-pentane) of this product shows four CO absorptions which are characteristic for a *cis*-Fe(CO)$_4$ fragment. In the field desorption mass spectrum only the diketone **10** was detected (FD-MS: m/z 376.1 [M^+],
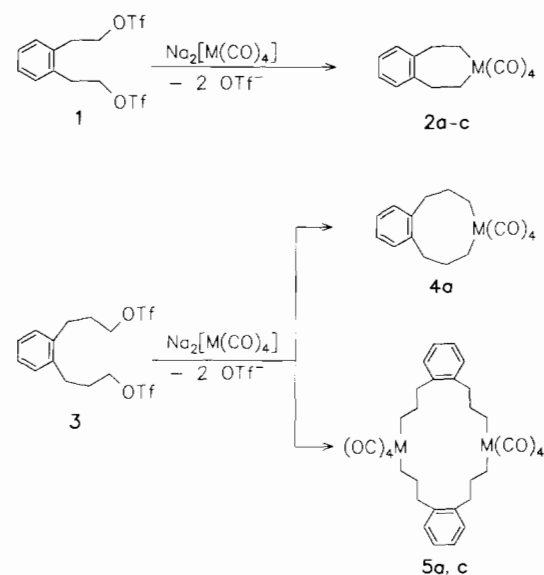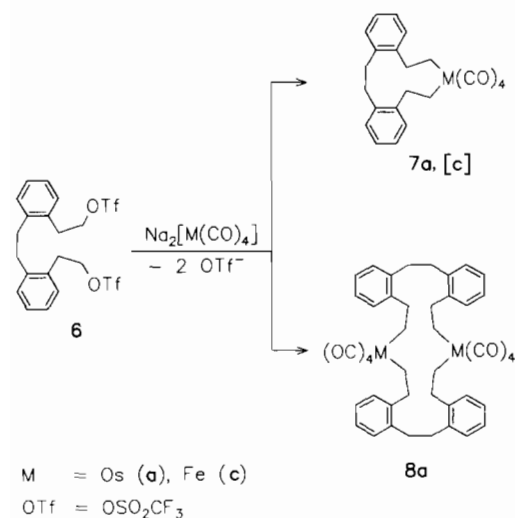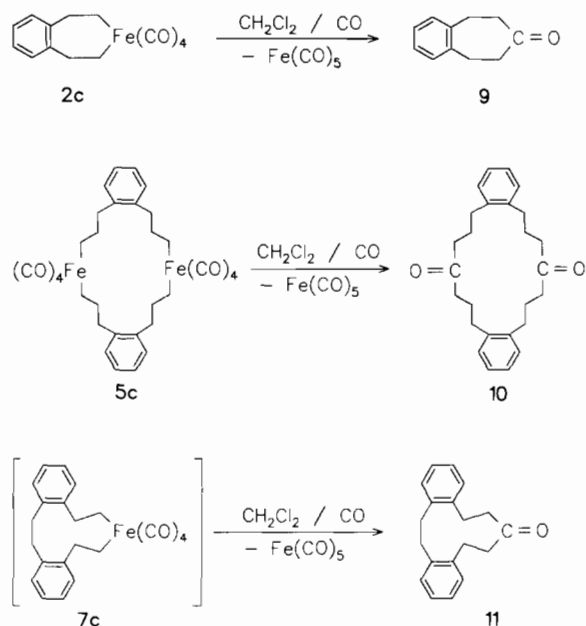

Scheme 1.

IR (CH_2Cl_2): ν(CO) 1711 cm^{-1}, see Scheme 3). The corresponding diketone with a *meta*-cyclophane framework has been described recently [10]. In the light of these results the reaction product from [Fe(CO)$_4$]$^{2-}$ and **3** can only be the diferracyclophane **5c** (Scheme 1). From the *meta*- and *para*-isomers of the bis(triflate) **3** and [Os(CO)$_4$]$^{2-}$ the homologous 20- and 22-membered dimetallacyclophanes have been exclusively obtained [10]. Entropic effects support the formation of these dimeric species [24]. The lower homologous diferra[7.7]metacyclophane undergoes CO insertion with formation of the corresponding diketone which is a *meta*-isomer of **10**.

The reaction of the bis(triflate) **6** with [Os(CO)$_4$]$^{2-}$ in dimethyl ether affords a mixture of the monomeric osmacyclophane **7a** and the dimeric diosma[5.2.5.2]orthocyclophane **8a** (Scheme 2). However, **7a** could be separated from **8a** by extraction with diethyl ether.

In dimethyl ether at -70 °C Na$_2$[Fe(CO)$_4$] and the bis(triflate) **6** do not form monomeric or dimeric ferracyclophanes **7c** or **8c**. In contrast to **2c** the IR spectrum indicates only CO absorptions which can be traced back to the formation of Fe(CO)$_5$, Fe$_3$(CO)$_{12}$ and the cyclic ketone **11**. The occurrence of this organic moiety is an indirect proof for **7c** as a reactive intermediate. Compared to **7c** the ferracycle **2c** is more stable and could be characterized by its IR, ^{1}H and ^{13}C{^{1}H} NMR spectra. However, under an atmosphere of carbon monoxide both iron compounds **2c** and **7c** insert CO, immediately followed by a reductive elimination of Fe(CO)$_5$ with formation of **9** and **11** as the main organic products. In order to obtain these ketones in a preparative scale it is not necessary to isolate the ferracycles **2c** and **7c**. The best way to the ketones **9** and **11** is the treatment of a mixture of Na$_2$[Fe(CO)$_4$] in dichloromethane and the bis(triflate) **1** and **6**, respectively, in dimethyl ether

Scheme 3.

with carbon monoxide (Scheme 3). Together with the FD mass spectra, the characteristic ^{13}C{^{1}H} NMR resonances and the IR absorptions of the $>$C=O groups confirm the successful syntheses of the ketones **9** and **11**. Thermolysis of the comparable ruthena- and osmacycles **2b** and **2a** results only in the formation of the clusters M$_3$(CO)$_{12}$ and unidentified products.

The IR spectra of the colourless, in common organic solvents well soluble, heterocycles **2a–c**, **4a**, **7a** and **8a** exhibit four characteristic CO absorptions in the 5 μm region. In the ^{1}H NMR spectra of **2a–c**, **4a**, **7a** and **8a** the methylene protons 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. Compared to the bis(triflates) **1**, **3** and **6** in the ^{13}C{^{1}H} NMR spectra of the rather airstable osmacycles **2a**, **4a**, **7a** and **8a** the α-ring carbon atoms show a remarkable high field shift which is increased with a smaller ring size. According to the heavy metal atom effect [25] this shift moves upward in the sequence **2c** > **2b** > **2a**. In the heterocycles **2a–c** and **4a** the aromatic ring is symmetrically substituted. Therefore only three resonances occur in the ^{13}C{^{1}H} NMR spectra for the aromatic ring carbon atoms. Because of the different substituents in the *ortho*-position of the aromatic cores, however, in the spectra of **7a** and **8a** six signals are observed for the aromatic carbon atoms.

Structure of 2a

In order to examine the structure of the osma[5]orthocyclophane (**2a**) an X-ray crystal structural analysis was carried out (Fig. 1, Table 3). The basic cyclophane skeleton consists of two best planes, which
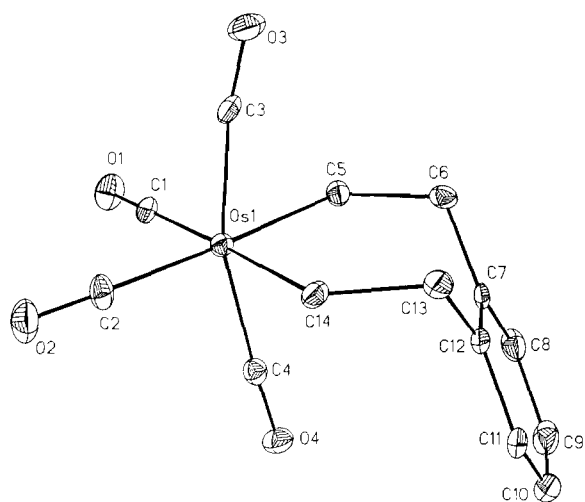

M = Os (a), Fe (c)
OTf = OSO$_2$CF$_3$

Scheme 2.

Fig. 1. ORTEP plot and atom labelling scheme of **2a**.

TABLE 3. Selected bond distances and angles for **2a**

Bond distances (pm)

Os(1)–C(5)	222.2(9)	C(7)–C(12)	142.2(15)
Os(1)–C(14)	224.7(10)	C(12)–C(13)	149.7(13)
C(5)–C(6)	152.8(13)	C(13)–C(14)	153.1(13)
C(6)–C(7)	150.5(12)		

Bond angles (°)

C(1)–Os(1)–C(2)	94.1(4)	C(3)–Os(1)–C(5)	83.5(4)
C(1)–Os(1)–C(3)	96.6(4)	Os(1)–C(5)–C(6)	121.4(7)
C(1)–Os(1)–C(4)	95.3(4)	Os(1)–C(14)–C(13)	121.5(7)
C(1)–Os(1)–C(5)	82.7(4)	C(5)–Os(1)–C(14)	99.5(4)
C(1)–Os(1)–C(14)	177.8(4)	C(5)–C(6)–C(7)	114.5(4)
C(2)–Os(1)–C(5)	176.7(4)	C(6)–C(7)–C(12)	119.3(8)
C(3)–Os(1)–C(4)	162.8(4)	C(8)–C(7)–C(12)	119.6(8)

are determined by the atoms Os1, C5, C6, C13, C14 and C6, C7, C8, C9, C10, C11, C12, C13. These planes form a torsion angle of 110.9° at their common edge, which is defined by C6 and C13. The equatorial carbonyl ligands C1–O1 and C2–O2 are nearly in a straight line with the opposite methylene groups C14 and C5 (C1–Os1–C14 177.8(4)°, C2–Os1–C5 176.7(4)°). The axial CO molecules C3–O3 and C4–O4 are bent toward the plane which is formed by the atoms C6, C5, Os1, C14 and C13 (C3–Os1–C4 162.8(4)°). Recently this well-known phenomenon of the distorted *cis*-M(CO)₄ fragments in metallacycles has been theoretically investigated [26]. The angles at the methylene carbon atoms C5 and C14 are remarkably expanded (121.4(7) and 121.5(7)°, respectively). The corresponding bond lengths are in the range of C–C single bonds (C5–C6 152.8(13), C13–C14 153.1(13) pm).

Supplementary material

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum

Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-57924, the names of the authors and the journal citation.

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