On the Reactivity of [(Mes)Os(CO)Cl_2] Toward Grignard Reagents. Unexpected Formation and X-ray Crystal Structure of [(Mes)Os(cyclohexene)(CO)]

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Reaction of [(Mes)Os(CO)Cl_2] (**3**) with PhLi in benzene gives the diphenylosmium compound [(Mes)OsPh_2(CO)] (**6**) whereas with PhMgBr [(Mes)OsPh(CO)Br] (**7**) is obtained. Treatment of **3** with TolMgBr in benzene or ether affords almost exclusively the monoaryl complex [(Mes)OsTol(CO)Br] (**8**). Compound **3** reacts with $C_6H_{11}MgCl$ to give both [(Mes)Os$(C_6H_{11})_2$(CO)] (**9**) and [(Mes)Os(C_6H_{10})(CO)] (**10**) in 60 and 30% yield, respectively. With $C_6H_{11}MgBr$, complex **10** is mainly obtained. Reaction of **7** and **8** with Na/Hg in THF/EtOH gives nearly quantitatively the arylhydridoosmium complexes [(Mes)OsC_6H_4R(CO)H] (**14**, **15**). The analogous hydrido methyl compound [(Mes)OsCH_3(CO)H] (**13**) reacts with CCl_4 to produce [(Mes)OsCH_3(CO)Cl] (**17**), which is not accessible from **3** and $LiCH_3$ or CH_3MgX. The X-ray structure analysis of **10** reveals that the cyclohexene is coordinated in the *endo* configuration.

Recently, we have described a new family of (arene)-osmium(0) and -osmium(II) complexes in which besides the six-membered ring one or two CO but no phosphane ligands are coordinated to the metal[1]. This particular work has been initiated by earlier studies performed in our laboratory on the chemistry of related (benzene)osmium complexes of the general type [(C_6H_6)Os(CO)(PR_3)] and [(C_6H_6)OsH_2(PR_3)][2,3], which surprisingly are photochemically inert and did not give the expected arylhydridometal derivatives upon irradiation in the presence of benzene or toluene. In contrast to [(C_6H_6)Os(CO)(PR_3)] and [(C_6H_6)OsH_2(PR_3)], the corresponding dicarbonyl and carbonyl dihydrido compounds [(mes)Os$(CO)_2$] (**1**) and [(mes)OsH_2(CO)] (**2**) are photoreactive and in CH_4 matrices form the carbonyl hydrido methyl complex [(mes)OsCH_3(CO)H][4]. Both compounds **1** and **2** also react photochemically in benzene and toluene solution to give the corresponding arylhydridometal compounds [(mes)OsC_6H_4R(CO)H][5]. This C – H activation reaction, however, is accompanied by the formation of byproducts, which are difficult to separate from the phenyl- and tolylhydridoosmium derivatives.

[(mes)Os$(CO)_2$] [(mes)OsH_2(CO)] mes = mesitylene
1 **2**

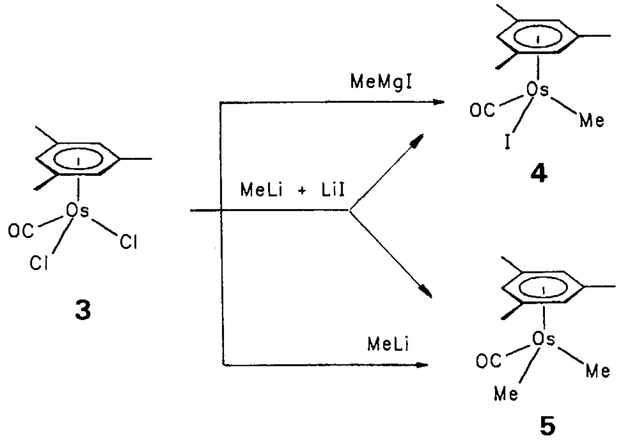
Taking these results into consideration, we have thought it necessary to prepare the arylhydridometal complexes by an independent route and to characterize them by analytical and spectroscopic methods. We note that in the well-known studies of Bergman[6], Graham[7], and Jones[8] the products obtained on photolysis of [(C_5Me_5)IrH_2(PMe_3)], [(C_5Me_5)-Ir$(CO)_2$], and [(C_5Me_5)RhH_2(PMe_3)] in the presence of hydrocarbons in most cases have not been isolated either but converted into more stable derivatives and for final identification usually synthesized by a separate method. During the preparation of the compounds [(mes)OsR(CO)H] via the intermediates [(mes)OsR(CO)X] we have found that the starting material [(mes)Os(CO)Cl_2] (**3**) reacts with Grignard reagents RMgX (X = Br, I) not only to give the expected products but for R = C_6H_{11} also to form an olefin complex that is not accessible by another route.

Results

Preparation of Diaryl- and Arylbromoosmium Complexes

In a preceding paper on (mesitylene)osmium compounds we have already described the synthesis of [(mes)Os-CH_3(CO)I] (**4**) and [(mes)Os$(CH_3)_2$(CO)] (**5**)[1]. Starting with **3**, the reaction with CH_3MgI leads to the formation of **4** whereas with $LiCH_3$ the dimethylosmium complex **5** is obtained. More recently, we have observed that if the meth-

Scheme 1



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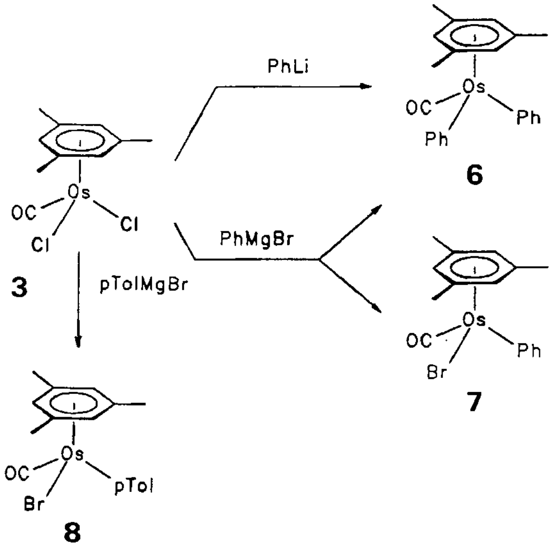
yllithium prepared from CH_3I and Li still contains lithium iodide besides **5** also the methyl iodo derivative **4** is formed (Scheme 1). From this it can be concluded that compound **4** reacts more slowly with $LiCH_3$ than the analogous chloroosmium complex [(mes)$OsCH_3$(CO)Cl], which is probably due to the stronger polarized and therefore more reactive Os–Cl bond.

The reactions of **3** with PhLi and PhMgBr also proceed differently. If equimolar amounts of the dichloroosmium complex and the respective phenylating reagent are used in benzene solution, with phenyllithium only the diphenylmetal compound [(mes)$OsPh_2$(CO)] (**6**) is obtained (Scheme 2). Some unreacted starting material is also isolated. In the reaction with phenylmagnesium bromide the main product is [(mes)OsPh(CO)Br] (**7**), which is separated from small quantities of **6** by column chromatography. Traces of [(mes)OsPh(CO)Cl] can also be detected (MS). Treatment of **3** with TolMgBr (Tol = 4-MeC_6H_4) in benzene or ether gives almost exclusively the monoaryl complex [(mes)Os-Tol(CO)Br] (**8**). Even on prolonged stirring of the reaction mixture only traces of [(mes)Os$(Tol)_2$(CO)] have been observed. Attempts to prepare [(mes)$OsCH_2Ph$(CO)Br] from **3** and $PhCH_2MgBr$ have been unsuccessful.

Scheme 2

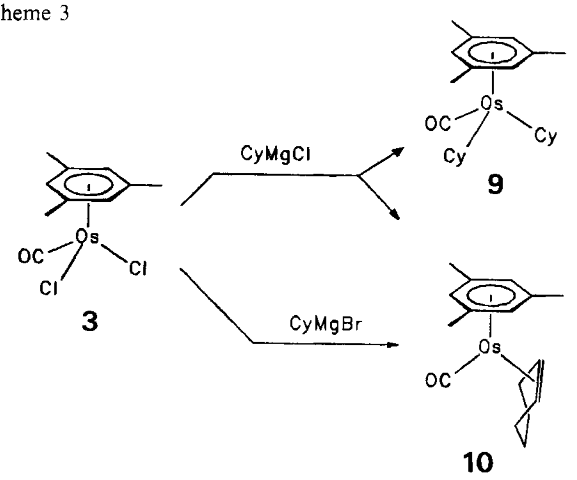


The IR spectra of the phenyl- and *p*-tolylosmium complexes **6**–**8**, which are yellow, only slightly air-sensitive solids, easily soluble in dichloromethane and benzene, show an intense CO stretching frequency at ca. 1910 (**6**) and 1940 cm^{-1} (**7** and **8**), which is shifted to significantly lower wave numbers compared with **3**. This result agrees with the supposed increase in electron density at the metal center when the chloro ligands are substituted by bromo or aryl groups.

Synthesis of [(mes)Os$(C_6H_{11})_2$(CO)] and [(mes)Os(C_6H_{10})(CO)]

The course of the reaction of **3** with cyclohexyl Grignard reagents depends on the type of the reagent used. With $C_6H_{11}MgCl$, the major product is the dicyclohexyl complex [(mes)Os$(C_6H_{11})_2$(CO)] (**9**), which is separated from the minor components by chromatographic techniques. One of the byproducts is the (cyclohexene)osmium compound [(mes)-Os(C_6H_{10})(CO)] (**10**), which is isolated in 65% yield if the starting material **3** is treated with an excess of $C_6H_{11}MgBr$ (Scheme 3). The bromo cyclohexyl derivative [(mes)-OsC_6H_{11}(CO)Br] (**11**) originally expected to be the preferred product cannot be detected. Nevertheless, we assume that **11** is formed as intermediate but reacts with a second molecule of the Grignard reagent by abstraction of a proton from the cyclohexyl group and generation of the olefin ligand. We note that most recently an analog of complex **9** of the composition [(C_6Me_6)Os$(C_6H_{11})_2$(CO)] has been prepared by Graham et al.[9] from [(C_6Me_6)Os(CO)Cl_2] and $C_6H_{11}MgCl$.

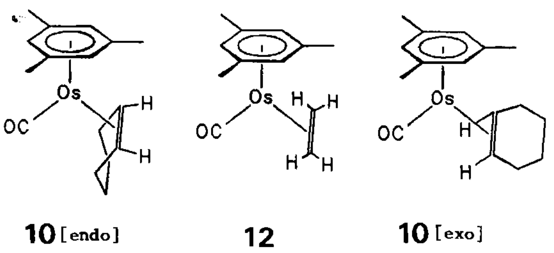
Scheme 3



[(mes)OsC_6H_{11}(CO)Br] **11**

The IR- and NMR-spectroscopic data of **10** are in full agreement with the structure shown in Scheme 3. In the ^{13}C-NMR spectrum, besides the resonances for the carbonyl and mesitylene carbon atoms three more signals are observed which correspond to the pairwise inequivalent ring carbon atoms of the cyclohexene unit. As the spectrum reveals only one set of ^{13}C-NMR signals both at 25°C and lower temperature, we conclude that only one of the two possible isomers of **10** is formed. These isomers are in principal derived by formal substitution of the "inner" or the "outer" hydrogen atoms of the ethylene ligand in [(mes)Os-(C_2H_4)(CO)] (**12**)[1] by the C_4H_8 fragment. Scheme 4 shows

Scheme 4



the relation between **12** and the *endo* and *exo* isomers of the cyclohexene complex.

Molecular Structure of 10

As it cannot be decided on the basis of the spectroscopic data which of the isomers of **10** has been formed, an X-ray structure determination has been undertaken. The results are summarized in Table 1. The ORTEP diagram (Figure 1) reveals that the cyclohexene is coordinated to the metal in the *endo* configuration. The C=C double bond distance of 143.2(8) pm is significantly longer than in (cyclohexene)-copper complexes [133(1) to 137(1) pm][10] and in the osmium cluster [$Os_4(CO)_{11}(C_6H_9)H_3$] [139.4(13) pm][11] where the olefinic unit is both π- and σ-bonded to the metal framework. The distances between the metal and the olefin carbons [215.5(5) and 213.9(6) pm] are about 10 pm shorter than the average bond length between osmium and the mesitylene ring carbon atoms (227.1 pm).

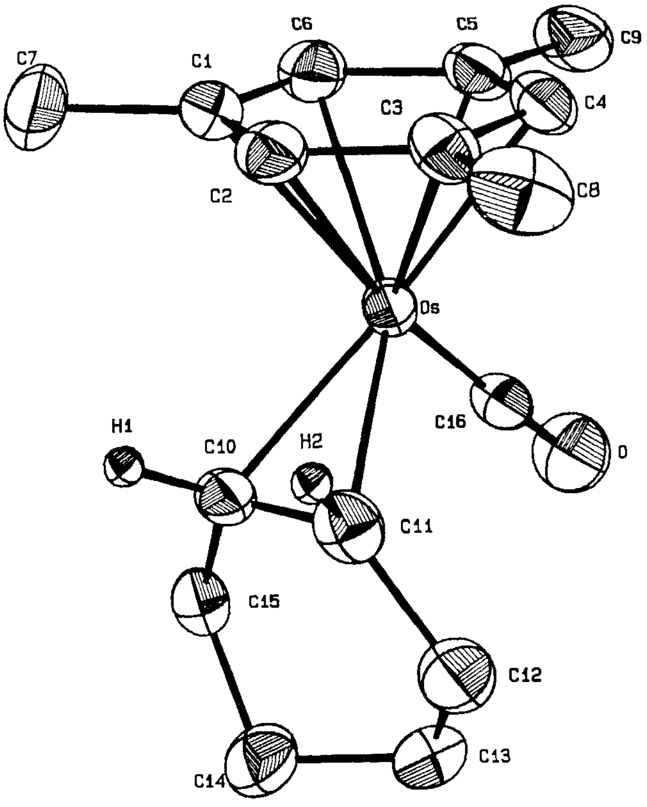


Figure 1. ORTEP diagram of complex **10**

With regard to the *endo* configuration of the molecule it should be mentioned that as far as we know the structure of half-sandwich-type complexes containing cyclohexene as ligand has not been determined. In related compounds such as [$(C_5H_5)Ru(\eta^3\text{-}C_6H_9)(CO)$] and [$(C_5H_5)Ru(\eta^4\text{-}C_6H_8)(CO)$]$^+$ the six-membered ring as in **10** also points to the carbonyl and not to the cyclopentadienyl group[12]. In contrast, in the η^2-arene complexes [$(C_5H_5)Rh(\eta^2\text{-}C_6F_6)(PMe_3)$][13] and [$(C_5Me_5)Rh(\eta^2$-phenanthrene)$(PMe_3)$][14] the configuration is the reverse, which could be due to the bulkiness of the phosphane ligand compared with CO.

Table 1. Intramolecular bond distances [pm] and bond angles [°] of **10**

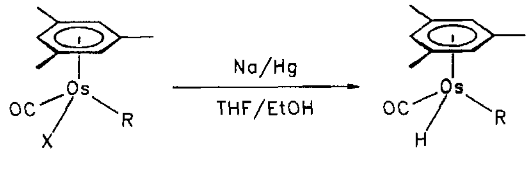
Os-C1	228.4(5)	C1-C2	139.8(8)	C16-O	116.9(7)
Os-C2	224.2(5)	C1-C6	139.4(8)	C10-C11	143.2(8)
Os-C3	228.0(5)	C2-C3	142.6(8)	C10-C15	152.5(8)
Os-C4	228.1(5)	C3-C4	141.0(8)	C11-C12	154.1(8)
Os-C5	224.7(5)	C4-C5	140.2(8)	C12-C13	152.0(8)
Os-C6	229.3(5)	C5-C6	145.3(8)	C13-C14	152.3(8)
Os-C10	215.5(5)	C1-C7	151.8(8)	C14-C15	150.7(8)
Os-C11	213.9(6)	C3-C8	149.9(8)	C10-H1	98.8(8)
Os-C16	183.6(6)	C5-C9	148.5(8)	C11-H2	98.4(8)

C10-Os-C11	39.0(2)	C4-C5-C6	120.0(5)
C10-Os-C16	93.1(2)	C1-C6-C5	118.8(5)
C11-Os-C16	92.8(2)	C2-C1-C6	120.1(5)
Os-C10-C11	69.9(3)	C11-C10-C15	121.5(5)
C11-C10-H1	111.6(6)	C10-C11-C12	120.1(5)
C10-C11-H2	106.8(6)	C11-C12-C13	114.6(5)
Os-C16-O	177.2(5)	C12-C13-C14	111.6(5)
C1-C2-C3	122.2(5)	C13-C14-C15	110.8(5)
C2-C3-C4	117.6(5)	C10-C15-C14	111.6(5)
C3-C4-C5	121.1(5)		

Preparation of Arylhydridoosmium Complexes

The hydrido methyl compound [(mes)$OsCH_3(CO)H$] (**16**), which is the photoproduct generated both from **1** and **2** in CH_4 matrices, has recently been prepared by treatment of **4** with Na/Hg in THF/EtOH[1]. This method of substituting a halide by a hydride ligand can also be applied to the synthesis of the aryl hydrido complexes [(mes)$OsC_6H_4R(CO)H$] (**13**, **14**) (Scheme 5). They are isolated as pale yellow solids, which are only slightly more air-sensitive than the halide derivatives. The most characteristic feature of the ^1H-NMR spectra of **13** and **14** is the high-field signal at $\delta \approx -10.2$ for the metal-bound hydrogen, the chemical shift of which is almost equal to that of **16**.

Scheme 5



7	X = Br, R = Ph	**13**
8	X = Br, R = pTol	**14**

An alternative route for the preparation of compounds **13** and **14** failed. Although it has been shown by others[15,16] that rhodium and iridium complexes of the general type [$(C_5Me_5)MR(PMe_3)H$] (R = alkyl or cycloalkyl) thermally react with arenes to give [$(C_5Me_5)M(aryl)(PMe_3)H$], the hydrido methyl derivative **16** on warming in benzene or toluene proved to be inert. There is also no exchange of CH_4 for C_6H_6 if **16** is chromatographed on Al_2O_3 by using benzene as eluant. Bennett et al. have most recently reported that alkanes are quantitatively eliminated, and the complexes $[(mes)OsC_6H_4R(PMe_3)H]$ are formed if benzene or toluene solutions of $[(mes)OsCH_2R(PMe_3)H]$ (R = H, CMe_3) are treated at room temperature with traces of Al_2O_3 or SiO_2[17].

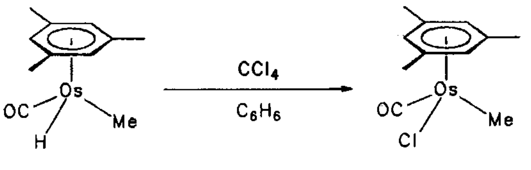
The remarkably high stability of **16** compared with the analogous compounds $[(mes)OsCH_2R(PMe_3)H]$[17] and $[(C_6H_6)OsCH_3(PiPr_3)H]$ (**15**)[18] is also supported by electrochemical data. Whereas the cyclovoltamogram of **15** shows an irreversible oxidation wave with a peak potential of +0.33 V, the corresponding value (also measured in acetonitrile with a sweep rate of 50 mV/s) for **16** is +0.92 V and for **14** +0.85 V. This significant difference is in good agreement with the experimental finding that **15** is much more sensitive to oxygen than the carbonyl complexes **13**, **14**, and **16**.

$[(C_6H_6)OsCH_3(PiPr_3)H]$ **15**

Studies on the Reactivity of 16

The stabilizing influence of the CO ligand in **16** compared with the phosphane ligand in $[(mes)OsCH_3(PMe_3)H]$ is also illustrated by the rather inert behavior of the carbonyl complex towards electrophiles and unsaturated substrates. The only reaction which proceeds cleanly is that with CCl_4 to give $[(mes)OsCH_3(CO)Cl]$ (**17**) in more than 80% yield. As **17** is not accessible from **3** and $LiCH_3$ or CH_3MgX and a possible halide exchange starting with **4** and LiCl does not take place, the synthesis outlined in Scheme 6 seems to be the preferred one to obtain the chloro methyl derivative.

Scheme 6



16 **17**

In contrast to the five-coordinate carbonylhydridoosmium compounds $[OsHCl(CO)(PR_3)_2]$ (PR_3 = $PiPr_3$, $PtBu_2Me$)[19], complex **16** does not react at room temperature with 1-alkynes such as $HC{\equiv}CMe$ and $HC{\equiv}CCO_2Me$ to give the corresponding vinyl derivatives. At 25°C and 1 atm of carbon monoxide, also no CO insertion into the $Os-CH_3$ bond occurs. On stirring a benzene solution of **16** at a CO pressure of 80 atm for three days, the ring-to-metal bond is split, and by reductive elimination of methane mainly $Os(CO)_5$ is formed. In the presence of CS_2 and PPh_3, compound **16** is completely inert and remains unchanged even after the addition of oxidizing reagents such as $[(C_5H_5)_2Fe]^+$ or $[CPh_3]^+$. At present, the synthesis of related alkyl and arylhydrido(isocyanide)osmium complexes is being studied. According to recently published results by Jones and his group[20] these complexes might be more suitable candidates for insertion reactions.

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Experimental

All operations were carried out under argon with Schlenk-tube technique. The starting materials **3** and **16** were prepared by published procedures[1]. – Melting points: measured by DTA. – Cyclovoltametry: Potentioscan Wenking POS 73 of Bank Electronics, platinum electrodes, $Hg/HgCl_2$ as a reference electrode; supporting electrolyte $[NBu_4]PF_6$.

Preparation of $[(mes)OsPh_2(CO)]$ (**6**): A suspension of 120 mg (0.29 mmol) of **3** in 7 ml of benzene was treated dropwise at room temp. with 0.7 ml of a 0.4 M solution of PhLi in ether (0.28 mmol). After the reaction mixture has been stirred for 15 min, the solvent was removed, and the residue was dissolved in 2 ml of benzene. The solution was chromatographed on Al_2O_3 (neutral, activity grade III), and the yellow fraction was concentrated to ca. 1 ml in vacuo. The addition of 10 ml of hexane led to the formation of a yellow precipitate which was filtered off, washed with hexane, and dried in vacuo. Yield 57 mg (40% relative to **3**; 83% relative to PhLi). – IR (hexane): ν(CO) = 1912 cm^{-1}. – ^1H NMR (C_6D_6, 90 MHz): δ = 7.75 (m) and 7.06 (m) (C_6H_5); 4.42 (s) ($C_6H_3Me_3$); 1.52 (s) ($C_6H_3Me_3$). – MS (70 eV): *m/z* (%) = 494 (49) [M$^+$]; 340 (100) [M$^+$ – 2 Ph]; 312 (23) [(mes)Os$^+$].

$C_{22}H_{22}OOs$ (492.6) Calcd. C 53.64 H 4.50
Found C 53.33 H 4.21

Preparation of the Complexes $[(mes)OsC_6H_4R(CO)Br]$ (**7**, **8**): A suspension of 99 mg (0.24 mmol) of **3** in 7 ml of benzene or ether was treated at room temp. with 0.5 ml of a 0.5 M solution of PhMgBr or TolMgBr in ether. After the reaction mixture has been stirred for 20 min, the solvent was removed in vacuo. The further workup was carried out as described for **6**. Yield 66 mg (55%) of **7** and 71 mg (58%) of **8**.

7: IR (hexane): ν(CO) = 1940 cm^{-1}. – ^1H NMR (C_6D_6, 90 MHz): δ = 7.72 (m) and 7.07 (m) (C_6H_5); 4.28 (s) ($C_6H_3Me_3$); 1.57 (s) ($C_6H_3Me_3$). – MS (70 eV): *m/z* (%) = 496 (34) [M$^+$]; 468 (41) [M$^+$ – CO].

$C_{16}H_{17}BrOOs$ (495.4) Calcd. C 38.79 H 3.46
Found C 38.96 H 3.23

8: IR (hexane): ν(CO) = 1939 cm^{-1}. – ^1H NMR (C_6D_6, 200 MHz): δ = 7.66 ("d") and 6.99 ("d"), both *J*(HH) = 7.8 Hz (C_6H_4Me); 4.30 (s) ($C_6H_3Me_3$); 2.32 (s) (C_6H_4Me); 1.59 (s) ($C_6H_3Me_3$). – MS (70 eV): *m/z* (%) = 510 (46) [M$^+$]; 482 (56) [M$^+$ – CO].

$C_{17}H_{19}BrOOs$ (509.4) Calcd. C 40.08 H 3.76
Found C 40.45 H 3.74

Preparation of the Complexes $[(mes)Os(C_6H_{11})_2(CO)]$ (**9**) *and $[(mes)Os(C_6H_{10})(CO)]$* (**10**): A suspension of 200 mg (0.49 mmol) of **3** in 10 ml of ether was treated with 1 ml of a 1.0 M solution of $C_6H_{11}MgCl$ in ether. The reaction mixture was worked up in the same manner as described for **6**. Column chromatography gave two fractions from which, after removal of the solvent, yellow crystals were obtained. Yield 145 mg (59%) of **9** and 62 mg (30%) of **10**.

9: IR (hexane): ν(CO) = 1892 cm^{-1}. – ^1H NMR (C_6D_6, 200 MHz): δ = 4.42 (s) ($C_6H_3Me_3$); 2.3–1.3 (m) (C_6H_{11}); 1.84 (s) ($C_6H_3Me_3$). – MS (70 eV): *m/z* (%) = 506 (0.3) [M$^+$]; 423 (0.3) [M$^+$ – C_6H_{11}]; 340 (0.6) [M$^+$ – 2 C_6H_{11}].

$C_{22}H_{34}OOs$ (504.7) Calcd. C 52.36 H 6.78
Found C 52.79 H 6.67

10: IR (hexane): ν(CO) = 1899 cm^{-1}. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 4.49 (s) ($C_6H_3Me_3$); 2.92, 2.72, 2.43, 1.85, 1.55 (each m) (C_6H_{11}); 1.91 (s) ($C_6H_3Me_3$). – ^{13}C NMR (C_6D_6, 22.5 MHz): δ = 184.6 (CO); 97.7 (CCH_3); 84.2 (CH of mes); 32.6 and 31.3 (CH_2 of C_6H_{10}); 24.1 (CH of C_6H_{10}); 19.3 (CCH_3). – MS (70 eV): *m/z* (%) = 422 (35) [M$^+$]; 340 (100) [M$^+$ – C_6H_{10}].

$C_{16}H_{22}OOs$ (420.55) Calcd. C 45.70 H 5.27
Found C 45.66 H 5.31

The analogous reaction with $C_6H_{11}MgBr$ instead of $C_6H_{11}MgCl$ gave mainly **10**. Yield 140 mg (65%).

Preparation of the Complexes [(mes)OsC$_6$H$_4$R(CO)H] (**13**, **14**): A solution of 0.12 mmol (60 and 63 mg, respectively) of **7** or **8** in 10 ml of THF/EtOH (100:1) was stirred after the addition of an excess of Na/Hg at room temp. for 30 min. The reaction mixture was worked up as described for **16**[1]. Yellow microcrystalline solids were obtained. Yield 40 mg (79%) of **13** and 45 mg (84%) of **14**.

13: IR (hexane): ν(OsH) = 2070; ν(CO) = 1960 cm^{-1}. – ^{1}H NMR (C_6D_6, 90 MHz): δ = 7.81 (m) and 7.08 (m) (C_6H_5); 4.56 (s) ($C_6H_3Me_3$); 1.77 (s) ($C_6H_3Me_3$); –10.19 (s) (OsH).

$C_{16}H_{18}OOs$ (416.5) Calcd. C 46.14 H 4.36
Found C 46.28 H 4.14

14: IR (hexane): ν(OsH) = 2070; ν(CO) = 1959 cm^{-1}. – ^{1}H NMR (C_6D_6, 200 MHz): δ = 7.72 ("d") and 6.94 ("d"), both *J*(HH) = 7.9 Hz (C_6H_4Me); 4.56 (s) ($C_6H_3Me_3$); 2.30 (s) (C_6H_4Me); 1.78 (s) ($C_6H_3Me_3$); –10.17 (s) (OsH). – MS (70 eV): *m/z* (%) = 432 (47) [M$^+$]; 340 (100) [M$^+$ – C_7H_8]; 312 (44) [(mes)Os$^+$].

$C_{17}H_{20}OOs$ (430.55) Calcd. C 47.43 H 4.68
Found C 47.27 H 4.50

Preparation of [(mes)OsCH$_3$(CO)Cl] (**17**): A solution of 40 mg (0.11 mmol) of **16** in 4 ml of benzene was treated with 0.2 ml of CCl_4 and stirred at room temp. for 5 min. After removal of the solvent, the residue was dissolved in 2 ml of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity grade III) with C_6H_6/CH_2Cl_2 (1:1). The yellow fraction was brought to dryness in vacuo and the microcrystalline solid dried for some hours. Yield 36 mg (81%). – IR (KBr): ν(CO) = 1951 cm^{-1}. – ^{1}H NMR (C_6D_6, 90 MHz): δ = 4.31 (s) ($C_6H_3Me_3$); 1.75 (s) ($C_6H_3Me_3$); 1.45 (s) ($OsCH_3$). – MS (70 eV): *m/z* (%) = 390 (3) [M$^+$]; 375 (2) [M$^+$ – CH_3]; 347 (11) [M$^+$ – CO – CH_3].

$C_{11}H_{15}ClOOs$ (388.9) Calcd. C 33.97 H 3.89
Found C 34.56 H 4.05

X-ray Structure Analysis of **10**: Single crystals were obtained from hexane at room temperature. A crystal (0.15 × 0.2 × 0.2 mm) was mounted on an Enraf Nonius CAD4 diffractometer. Mo-K_α radiation (λ = 0.70930 Å, graphite monochromator) was used for all measurements. Centering and refinement of 23 reflections (10.0° < Θ < 15.0°) gave the unit-cell parameters: a = 11.628(3), b = 9.644(1), c = 13.210(4) Å, β = 104.29(1)°, V = 1435.5 Å^3, Z = 4, d(calcd.) = 1.95 gcm^{-3}, μ = 88.9 cm^{-1}, space group $P2_1/n$. Intensities were measured in an ω/Θ-scan mode; 2Θ(max) = 50°; T = 223 K. Reflections measured: 2740, unique reflections: 2464, reflections with $F_o > 3\sigma(F_o)$: 1740. The reflection-to-parameter ratio was 10.4. Intensity data were corrected for Lorentz and polarization effects; an empirical absorption correction was applied. The structure was solved by direct methods (SHELXS-86); the positions of the two olefinic hydrogen atoms of the cyclohexene ligand were taken from a difference Fourier map and refined with fixed thermal parameters. The positions of the other hydrogen atoms were calculated according to ideal geometry; for the final refinement the riding model was used. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. Final R = 0.026 and R_w = 0.029. Residual electron density +1.30/–0.80 eÅ^{-3}. The atomic parameters of **10** are listed in Table 2. Further details of the crystal structure investigations including tables with the final positional parameters are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, 7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54950, the names of the authors, and the journal citation.

Table 2. Atomic parameters of **10**

Atom	x/a	y/b	z/c	B_{eq}
Os	0.24818(3)	0.07922(3)	0.57283(2)	1.968(5)
O	0.1003(6)	0.3383(7)	0.5332(5)	4.0(2)
C1	0.2379(8)	-0.1574(8)	0.5750(7)	2.4(2)
C2	0.3511(8)	-0.1142(9)	0.6291(6)	2.7(2)
C3	0.3694(7)	-0.022(1)	0.7160(6)	2.6(2)
C4	0.2683(8)	0.029(1)	0.7450(6)	2.8(2)
C5	0.1536(8)	-0.0074(9)	0.6882(6)	2.7(2)
C6	0.1377(8)	-0.1064(9)	0.6029(6)	2.9(2)
C7	0.2230(9)	-0.263(1)	0.4871(7)	4.0(2)
C8	0.4921(8)	0.018(1)	0.7756(8)	4.0(2)
C9	0.0473(8)	0.052(1)	0.7156(7)	3.7(2)
C10	0.3036(7)	0.0944(9)	0.4291(6)	2.7(2)
C11	0.3866(7)	0.165(1)	0.5113(7)	2.7(2)
C12	0.4100(9)	0.321(1)	0.5021(7)	3.6(2)
C13	0.3253(9)	0.393(1)	0.4113(7)	3.9(2)
C14	0.2969(9)	0.302(1)	0.3138(7)	3.6(2)
C15	0.2343(9)	0.172(1)	0.3325(7)	3.2(2)
C16	0.1591(7)	0.238(1)	0.5466(6)	2.6(2)
H1	0.164(9)	0.51(1)	0.089(8)	3.4
H2	0.949(9)	0.40(1)	0.042(8)	3.6

CAS-Registry-Numbers

3: 126724-10-5 / **6**: 130831-06-0 / **7**: 130858-23-0 / **8**: 130831-07-1 / **9**: 130831-08-2 / **10**: 130831-09-3 / **13**: 130831-10-6 / **14**: 130831-11-7 / **16**: 123725-75-7 / **17**: 130831-12-8 / CyMgCl: 931-51-1 / CyMgBr: 931-50-0

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