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Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Cyclopentadienylosmium and (Pentamethylcyclopentadienyl)osmium Compounds. Synthesis and Reactions of $(\eta\text{-}C_5H_5)Os(CO)_2H$, $(\eta\text{-}C_5Me_5)Os(CO)_2H$, and Some of Their Derivatives

JAMES K. HOYANO, CHRISTOPHER J. MAY, and WILLIAM A. G. GRAHAM*

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Convenient preparations of $(\eta\text{-}C_5H_5)Os(CO)_2Br$, $(\eta\text{-}C_5Me_5)Os(CO)_2Br$, and $(\eta\text{-}C_5H_5)Os(CO)_2H$ (**3**) from $(OC)_4OsBr_2$ in yields of 30–60% are described. $(\eta\text{-}C_5Me_5)Os(CO)_2H$ (**4**) is prepared from $Os_3(CO)_{12}$ in 65% yield. Hydride abstraction from **3** and **4** by trityl cation in the presence of ligands affords $[(\eta\text{-}C_5H_5)Os(CO)_2(CH_3CN)][BF_4]$, $[(\eta\text{-}C_5Me_5)Os(CO)_2(THF)][PF_6]$, and $[(\eta\text{-}C_5R_5)Os(CO)_2(OH_2)][BF_4]$ (R = H, Me). The aquo cations react with CO under pressure to form $[(\eta\text{-}C_5R_5)Os(CO)_3][BF_4]$ (R = H, Me). Reaction of **3** and **4** with $[C_7H_7][BF_4]$ affords $[(\eta\text{-}C_5R_5)Os(CO)_2(1,2\text{-}\eta^2\text{-}C_7H_8)][BF_4]$, which can be deprotonated to provide $(\eta\text{-}C_5R_5)Os(CO)_2(7\text{-}\eta^1\text{-}C_7H_7)$ (R = H, Me). These are the first η^1-cycloheptatrienyl derivatives of osmium. The iodides $(\eta\text{-}C_5R_5)Os(CO)_2I$ (R = H, Me) are prepared from the hydrides. (Pentamethylcyclopentadienyl)osmium compounds have not been described previously.

Introduction

The $(\eta\text{-}C_5H_5)Fe(CO)_2$ group[1a] is ubiquitous in organometallic chemistry, and derivatives of the ruthenium analogue have received increasing attention in recent years. Yet little is known of the corresponding derivatives of osmium. This situation is no doubt due to the lack of efficient syntheses for starting materials in the osmium case, a factor that is especially critical in view of the high cost of osmium.

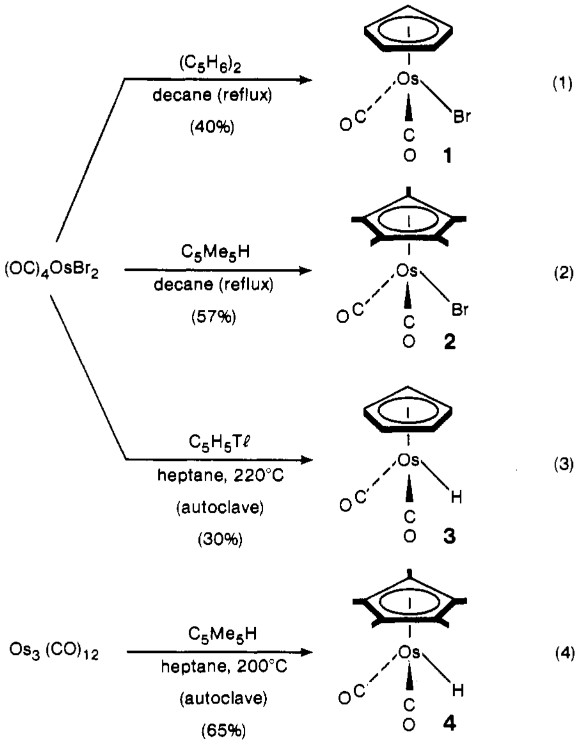
The synthesis of $[(\eta\text{-}C_5H_5)Os(CO)_2]_2$ was first reported in 1962 by Fischer and Bittler,[1b] although the yield was very low (1.8% from $Os(CO)_3Cl_2$); they concluded from the infrared spectrum that bridging carbonyls were absent, as was later confirmed by others.[2] Bromination of the dimer afforded $(\eta\text{-}C_5H_5)Os(CO)_2Br$.[1b] A low-yield preparation (ca. 11%) of $(\eta\text{-}C_5H_5)Os(CO)_2H$ from $H_2Os_3(CO)_{10}$ and C_5H_6 has been reported,[3] and the same hydride was prepared in 3.1% yield in liquid ammonia at 30 °C from $[(\eta\text{-}C_5H_5)Os(CO)_3][PF_6]$.[4a] The latter was prepared from $(\eta\text{-}C_5H_5)Os(CO)_2Cl$, which was in turn obtained from $[(\eta\text{-}C_5H_5)Os(CO)_2]_2$,[4b] although the yield of neither of these precursors was reported. By way of contrast, quite satisfactory routes to the phosphine complexes $(\eta\text{-}C_5H_5)Os(PPh_3)_2Br$[5,6] and $(\eta\text{-}C_5H_5)Os(CO)(PPh_3)Br$[5] are available, and reactions of the former have been investigated.[7]

There has been much interest in pentamethylcyclopentadienyl derivatives recently, and useful routes to $[(\eta\text{-}C_5Me_5)M(CO)_2]_2$ (M = Fe,[8] Ru[9]) are available; $[(\eta\text{-}C_5Me_4Et)Ru(CO)_2]_2$ has also been studied.[10] However, to our knowledge, no (pentamethylcyclopentadienyl)osmium compounds have been described.

We wished to extend our work on the $(\eta\text{-}C_5H_5)Re(NO)(CO)$ moiety[11] to the isoelectronic dicarbonylosmium system and also to examine the osmium analogues of (η^1-cycloheptatrienyl)ruthenium complexes recently prepared in this laboratory.[12] Accordingly, we have developed and now report reasonably satisfactory syntheses for the complexes $(\eta\text{-}C_5R_5)Os(CO)_2X$ (R = H, Me; X = H, halogen). These starting materials make organoosmium chemistry more accessible than heretofore, and we have used them for the preparation of a number of interesting mononuclear derivatives containing the $(\eta\text{-}C_5R_5)Os(CO)_2$ group.

Results and Discussion

Synthesis and Properties of Halides and Hydrides. Equations 1–4 summarize the preparative routes to the four key mononuclear osmium complexes. Dicyclopentadiene and pentamethylcyclopentadiene were used in excess, and yields stated are those of the pure isolated products.



Reactions 1 and 2 apparently proceed in a similar manner (the diene monomer is generated in situ in reaction 1); monitoring of the reactions by infrared shows that an intermediate

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[1] (a) In this paper the IUPAC rule to *omit* the superscript for *maximum* hapticity (η^5 for C_5H_5) is applied. (b) Fischer, E. O.; Bittler, K. *Z. Naturforsch., A* **1962**, *17A*, 274.
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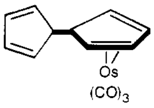
Table I. Spectroscopic Properties of the $(C_5R_5)Os(CO)_2$ Compounds

	infrared,[a] cm^{-1}		proton NMR,[b] δ	
compd	ν(CO)	other	C_5R_5	other
$(\eta\text{-}C_5H_5)Os(CO)_2Br$ (**1**)	2042 s, 1990 s		5.62 (s)	
$(\eta\text{-}C_5Me_5)Os(CO)_2Br$ (**2**)	2021 s, 1968 s		2.06 (s)	
$(\eta\text{-}C_5H_5)Os(CO)_2H$ (**3**)	2020 s, 1960 s	2089 w, br (ν(OsH))	5.42 (s)	−14.52 (s, 1 H)
$(\eta\text{-}C_5Me_5)Os(CO)_2H$ (**4**)	2001 s, 1941 s	2059 w, br (ν(OsH))	2.21 (s)	−14.00 (s, 1 H)
$(\eta\text{-}C_5H_5)Os(CO)_2I$ (**6**)	2039 s, 1988 s		5.68 (s)	
$(\eta\text{-}C_5Me_5)Os(CO)_2I$ (**7**)	2020 s, 1968 s		2.16 (s)	
$[(\eta\text{-}C_5H_5)Os(CO)_2(C_7H_8)]^+BF_4^-$ (**8**)	2071 s, 2024 s		6.10 (s)	2.10 (m, 1 H), 3.50 (m, 1 H), 4.46 (ddd, 1 H), 5.54 (dd, 1 H), 6.13 (m, 1 H), 6.50 (m, 2 H), 6.79 (dd, 1 H)
$[(\eta\text{-}C_5Me_5)Os(CO)_2(C_7H_8)]^+BF_4^-$ (**9**)	2058 s, 2008 s		2.18 (s)[c]	2.20 (m, 1 H), 3.50 (m, 1 H), 4.18 (dd, 1 H), 6.15 (m, 1 H), 6.48 (m, 2 H), 6.72 (dd, 1 H)
$(\eta\text{-}C_5H_5)Os(CO)_2C_7H_7$ (**10**)	2008 s, 1949 s		5.57 (s)[d]	3.99 (t, *J* = 7.5 Hz, 1 H), 5.05 (m, 2 H), 5.21 ("dd", 2 H), 5.63 (m, 2 H)
$(\eta\text{-}C_5Me_5)Os(CO)_2C_7H_7$ (**11**)	1992 s, 1934 s		2.02 (s)[d]	2.83 (t, *J* = 7.6 Hz, 1 H), 5.30 (m, 4 H), 6.04 (m, 2 H)
$[(\eta\text{-}C_5H_5)Os(CO)_2(CH_3CN)]^+BF_4^-$ (**12**)	2065 s, 2009 s		5.87 (s)	2.68 (s, 3 H)
$[(\eta\text{-}C_5Me_5)Os(CO)_2(THF)]^+PF_6^-$ (**13**)	2038 s, 1981 s		2.07 (s)	3.94 (m, 4 H), 2.03 (m, 4 H)
$[(\eta\text{-}C_5H_5)Os(CO)_2(H_2O)]^+BF_4^-$ (**14**)	2055 s, 1994 s		5.77 (s)	4.90 (coordinated H_2O)
$[(\eta\text{-}C_5Me_5)Os(CO)_2(H_2O)]^+BF_4^-$ (**15**)	2038 s, 1980 s		2.00 (s)	4.85 (coordinated H_2O)
$[(\eta\text{-}C_5H_5)Os(CO)_3]^+BF_4^-$ (**16**)	2129 s, 2062 vs[e]		6.54 (s)[g]	
$[(\eta\text{-}C_5Me_5)Os(CO)_3]^+BF_4^-$ (**17**)	2113 s, 2047 vs[e,f]		2.37 (s)[g]	

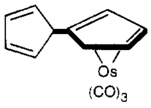
[a] In hexane for neutral compounds and CH_2Cl_2 for ionic compounds unless otherwise noted. [b] In CD_2Cl_2 solution unless otherwise noted. [c] One of the methylene protons of the C_7H_7 ring lies under the CH_3 resonance at 2.18. [d] In C_6D_{12} solution. [e] In CH_3CN solution. [f] In CH_2Cl_2 solution the IR bands are as follows: 2113 s, 2105 s, 2055 s, sh, 2041 vs cm^{-1}. See text. [g] In acetone-d_6 solution.

(likely $[Os(CO)_3Br_2]_2$, see Experimental Section) is first formed, which then reacts with the diene to form the product, with loss of CO and HBr.

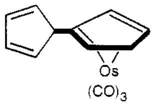
In reaction 3, small amounts of $[(\eta\text{-}C_5H_5)Os(CO)_2]_2$ were observed, but none of the corresponding dimer was noted in reaction 4. When reaction 3 was carried out at lower temperatures (~100 °C) and at atmospheric pressure, the major product (ca. 60% yield) regardless of reactant stoichiometry was a tricarbonyl species **5** of formula $C_{10}H_{10}Os(CO)_3$. In refluxing decane **5** was smoothly converted to the hydride **3**. On the basis of its very complex NMR spectrum, we propose that **5** is a mixture of isomers, of which some possibilities are shown as **5a–d**. The formation of **5** may resemble the reaction in which the tungsten complex $(\eta\text{-}C_5H_5)W(CO)_2C_{15}H_{15}$ arises;[13] that is, species such as $(OC)_4Os(\eta^1\text{-}C_5H_5)_2$ or $(OC)_3Os(\eta^1\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)$ may be formed initially, with conversion to **5** under reaction conditions. So far **5** has been obtained only as an oil, and attempts are continuing to recover a crystalline component suitable for X-ray investigation. The reported[3] diene complex $(\eta^4\text{-}C_5H_6)Os(CO)_3$ also forms **3** on heating and has carbonyl stretching bands at almost the same frequencies as **5**.



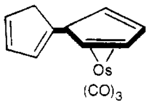
5a



5b



5c



5d

We initially carried out reactions 3 and 4 in refluxing mesitylene, a solvent from which recovery of the hydrides was difficult. Reaction mixtures were therefore treated with I_2 (eq 5), forming the less volatile iodides **6** and **7**, from which the mesitylene could be pumped off. After chromatography the iodides were converted to the hydrides (60–90% yield) with $NaBH_4$. Later the procedure was improved by use of heptane as solvent, in which reaction mixtures could be directly chromatographed and the hydrides separated.

$$\underset{\substack{\mathbf{3}\ (R = H)\\ \mathbf{4}\ (R = Me)}}{(\eta\text{-}C_5R_5)Os(CO)_2H} \xrightleftharpoons[NaBH_4,\ THF]{I_2,\ hexane} \underset{\substack{\mathbf{6}\ (R = H)\\ \mathbf{7}\ (R = Me)}}{(\eta\text{-}C_5R_5)Os(CO)_2I} \qquad (5)$$

When pure, the complexes **1–4**, **6** and **7** are all thermally stable and air stable, although the hydride **4** appears to discolor slowly in laboratory light. In contrast to the case for the iron and ruthenium analogues, the hydrides **3** and **4** are remarkably thermally stable as evidenced by their isolation from reactions carried out at temperatures in excess of 200 °C; as noted above, little formation of dimer was observed.

For the halides and hydrides, Table I gives the infrared and ^1H NMR data, while the mass spectral fragmentation data are given in the Experimental Section. As expected, in the infrared spectra two strong terminal ν(CO) stretching bands are observed and the pentamethyl complexes have ν(CO) bands 15–20 cm^{-1} lower than those of their $\eta\text{-}C_5H_5$ analogues. The Os–H stretches appear as weak, broad bands in the terminal M–H stretching region. Proton NMR spectra show sharp singlets for the $\eta\text{-}C_5Me_5$ or $\eta\text{-}C_5H_5$ protons in the appropriate chemical shift regions; the high-field hydride resonances are also sharp singlets. The mass spectra all exhibit molecular ion peaks and peaks corresponding to the stepwise loss of two carbonyl groups.

Reactions of Hydrides 3 and 4. Although the hydrides and halides are very stable, they undergo a number of interesting reactions. The iodide **6** is a convenient starting material for preparation of $(\eta\text{-}C_5H_5)Os(CO)_2R$ (R = Me, $SnMe_3$, $SnPh_3$) by reaction with RLi reagents, but the pentamethyl analogue **7** appears less reactive to nucleophilic substitution.[14] However, the main thrust of our initial investigations of reactivity has centered on the hydrides **3** and **4**, and these results will now be described.

The first η^1-cycloheptatrienyl derivative of a transition metal was recently prepared,[15] and subsequently other stable derivatives have been characterized.[11b,12] We anticipated that the $(\eta\text{-}C_5R_5)Os(CO)_2$ moiety would form a stable $\eta^1\text{-}C_7H_7$ complex, and as shown below this has been realized by a method similar to that used in the preparation of $(\eta\text{-}C_5H_5)$-

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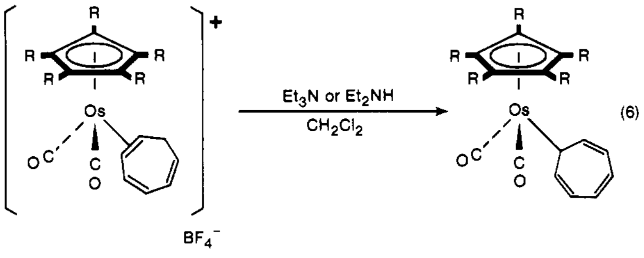
Re(NO)(CO)(η^1-C_7H_7).[11b] These are the first examples of η^1-cycloheptatrienyl complexes of osmium.

In the first step, hydrides **3** and **4** react with tropylium tetrafluoroborate forming the stable, isolable cations **8** and **9**, which have the 1,2-η^2 structure shown in eq 6. The formation of **8** requires 6 days to go to completion while **9** is formed quantitatively in only 5 h (both reactions in CH_2Cl_2 at 25 °C); this is probably an indication of the relative "hydridic" character of the two hydrides or perhaps of the relative electron-rich character of osmium in **3** and **4**. Complete deprotonation of **8** is effected with excess Et_3N (eq 6), while **9** requires the more basic Et_2NH for complete deprotonation. The relative acidity of the η^2-C_7H_8 cations accords with the view that the η-C_5Me_5 ligand is more electron releasing than η-C_5H_5. The cations are formed and deprotonated in high yield, and all four complexes **8**–**11** are air-stable crystalline solids.



(6)

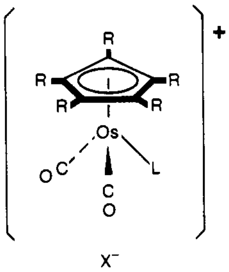
8 (R = H)
9 (R = Me)

10 (R = H)
11 (R = Me)

The 1,2-η^2-C_7H_8 structure for **8** and **9** follows from their ^1H NMR spectra, which are more complex than would be expected for the more symmetrical 3,4-η^2 coordination; they resemble spectra reported for (η-C_5H_5)Mn(CO)$_2$(1,2-η^2-C_7H_8)[16] and (η-C_5H_5)Re(CO)$_2$(1,2-η^2-C_7H_8).[17] This mode of coordination is also preferred over 3,4-η^2 in [(η-C_5H_5)Fe(CO)$_2$(1,2-η^2-C_7H_8)]$^+$ [18] and [(η-C_5H_5)Re(NO)(CO)(1,2-η^2-C_7H_8)]$^+$,[11b] which are the only other reported η^2-C_7H_8 complexes.

The ^1H NMR spectra of **10** and **11** resemble those of other 7-η^1-C_7H_7 complexes,[15] and it appears from coupling constant arguments (J_{H1-H7} = 7.5–7.6 Hz) that the osmium moiety is in the quasi-axial position of the boat conformation of the C_7H_7 ring. Both **10** and **11** are thermally quite stable, even in solution, and no fluxional behavior could be detected by the spin saturation transfer technique at ambient temperature.

Hydrides **3** and **4** react smoothly with trityl cation (as Ph_3CBF_4 or Ph_3CPF_6) in the presence of donor ligands L (L = CH_3CN, THF, H_2O) to form the stable 18-electron cations **12**–**15**. Abstraction of hydride from a transition metal is an interesting and synthetically important reaction discovered by Beck and Schloter;[19] it has been utilized in our laboratories[20] and by Legzdins and co-workers[21,22] for the synthesis of both mononuclear and dinuclear cations.



12 R = H, L = CH_3CN, X = BF_4
13 R = Me, L = THF, X = PF_6
14 R = H, L = H_2O, X = BF_4
15 R = Me, L = H_2O, X = BF_4
16 R = H, L = CO, X = BF_4
17 R = Me, L = CO, X = BF_4

The aquo cations **14** and **15** could not be isolated, but they were characterized spectroscopically in CH_2Cl_2 solution; thus ^1H NMR showed coordinated water as a broad singlet of correct integration that disappeared when D_2O was added. The chemical shift of the ring protons and the carbonyl stretching frequencies are both diagnostic of cationic species. The ^{11}B NMR spectrum of **15** consists of a broad singlet at −1.415 ppm (relative to $BF_3 \cdot Et_2O$) while a single broad peak at +10.64 ppm (relative to C_6F_6) is observed in the ^{19}F NMR. These observations suggest a nontetrahedral environment for the BF_4^- anion, which may be hydrogen bonded to the coordinated water as suggested for other aquo cations.[19] We note in passing that formation of the aquo cations in this work was initially surprising but was traced to a commercial sample of Ph_3CBF_4 that contained 1 mol of water. Reaction of the hydrides with anhydrous trityl reagents leads to intermediates of very different properties that are under investigation.

The aquo cations proved useful precursors in the high-yield synthesis of the tricarbonyl cations **16** and **17** (eq 7). Similar

$$\underset{\substack{\mathbf{14}\ (R = H)\\ \mathbf{15}\ (R = Me)}}{[(\eta\text{-}C_5R_5)Os(CO)_2(OH_2)]BF_4} \xrightarrow[CH_2Cl_2,\ 40\ °C]{CO\ (210\ atm)} \underset{\substack{\mathbf{16}\ (R = H)\\ \mathbf{17}\ (R = Me)}}{[(\eta\text{-}C_5R_5)Os(CO)_3]BF_4} \qquad (7)$$

reactions of CO with the CH_3CN or THF cations **12** or **13** gave only low yields of the carbonyl cations. The aquoiron cation [(η-C_5H_5)Fe(CO)$_2$(OH$_2$)]$^+$ has long been known, in which water is readily displaced by a variety of neutral or anionic ligands.[23]

The spectroscopic features of cations **12**–**17** (Table I) are consistent with the assigned structures. An interesting feature of the IR spectrum of [(η-C_5Me_5)Os(CO)$_3$]BF$_4$ (**17**) in CH_2Cl_2 is the appearance of four ν(CO) bands, while in CH_3CN only the two expected symmetrical bands occur; we attribute this to ion-pairing effects in CH_2Cl_2.

Concluding Remarks. Methods have been developed for convenient syntheses on a gram scale of the hydrides and halides of the (η-C_5H_5)Os(CO)$_2$ and (η-C_5Me_5)Os(CO)$_2$ moieties, thus opening the way to a systematic investigation of their chemistry. One facet of this chemistry is hydride abstraction of triphenylcarbenium (trityl) cation, which has been utilized here to prepare mononuclear cations. A variation of this reaction leads to the dimers [(η-C_5R_5)Os(CO)$_2$]$_2$ and their derivatives and forms the basis of a separate study.[24] An outgrowth of the present work is an investigation[24] of the stepwise reduction of carbon monoxide in the tricarbonyl cations **16** and **17**, which is related to our work with [(η-C_5R_5)Re(NO)(CO)$_2$]$^+$ (R = H,[11a,25] Me[25]).

Experimental Section

General Considerations. All syntheses were carried out under an inert atmosphere (Ar or purified nitrogen) with degassed solvents. Solvents were dried by standard procedures and distilled and degassed prior to use. Commercial samples of OsO_4 (Engelhardt), Ph_3CBF_4,

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Ph_3CPF_6, $C_7H_7BF_4$ (Aldrich), and C_5Me_5H (Strem) were used without further purification. $Os_3(CO)_{12}$ and $(CO)_4OsBr_2$ were prepared by literature methods.[26,27]

Proton NMR spectra were recorded on a Varian HA-100/Digilab FT system and on Bruker WH200 and WH400 FT spectrometers. Infrared spectra were recorded on a Nicolet MX-1 FT instrument, and mass spectra were obtained on an MS-12 instrument. Elemental analyses were carried out in the microanalytical laboratory of this department.

Preparation of $(\eta\text{-}C_5H_5)Os(CO)_2Br$ (1). A mixture of $(CO)_4OsBr_2$ (1.00 g, 2.16 mmol) and dicyclopentadiene (3.0 mL) in 100 mL of decane was heated at 180 °C for 18 h. The infrared spectrum taken at intervals during the reaction showed development of bands at 2126 (s) and 2053 (vs) cm^{-1}, which disappeared as heating continued; they are attributed to $[Os(CO)_3Br_2]_2$.[28] The reaction mixture was poured onto a 50-g column of silicic acid; after elution with 400 mL of hexane for the removal of the decane and organic byproducts of the reaction, the product was eluted with dichloromethane as a pale yellow band. Crystallization from hexane–CH_2Cl_2 afforded pale yellow crystals of the product (0.35 g, 41%): mp 120–122 °C; mass spectrum (75 °C, 16 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$. Anal. Calcd for $C_7H_5BrO_2Os$: C, 21.49; H, 1.29. Found: C, 21.65; H, 1.36.

Preparation of $(\eta\text{-}C_5Me_5)Os(CO)_2Br$ (2). A mixture of $(CO)_4OsBr_2$ (1.00 g, 2.16 mmol) and pentamethylcyclopentadiene (2.0 mL) in 100 mL of decane was gently refluxed (oil bath temperature 185 °C) for 30 h. The reaction mixture was chromatographed as above with the product emerging as a pale yellow band with use of 2:1 dichloromethane–hexane. Evaporation of solvent afforded pale yellow crystals of the product (0.51 g, 57%): mp 185–187 °C; mass spectrum (130 °C, 16 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$. Anal. Calcd for $C_{12}H_{15}BrO_2Os$: C, 31.24; H, 3.28. Found: C, 30.99; H, 3.31.

Preparation of $(\eta\text{-}C_5H_5)Os(CO)_2H$ (3). Samples of $(CO)_4OsBr_2$ (1.66 g, 3.59 mmol) and TlC_5H_5 (3.90 g, 14.5 mmol) were combined with 100 mL of heptane in a 500-mL stainless steel rocking autoclave. After it was sealed, the autoclave was heated to 220 °C for 20 h. Following cooling and depressurization, the contents of the autoclave were removed and filtered through a coarse sintered-glass funnel and the solid residue was washed with 25 mL of heptane. The combined filtrate was placed on a column of silicic acid (50 g, packed with pentane) and eluted with pentane. The first 400 mL of eluant contained cyclopentadiene but no carbonyl-containing species. Further elution with 500 mL of pentane removed the $(\eta\text{-}C_5H_5)Os(CO)_2H$ complex, which was isolated on removal of solvent as a colorless oil (350 mg, 31%): mp ~15 °C; mass spectrum (40 °C, 70 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$ (loss of H superimposed on these 3 fragments increasing in the lower mass fragments). Anal. Calcd for $C_7H_6O_2Os$: C, 26.92; H, 1.94. Found: C, 27.17; H, 1.96.

Preparation of $(\eta\text{-}C_5Me_5)Os(CO)_2H$ (4). Samples of $Os_3(CO)_{12}$ (5.00 g, 5.52 mmol) and pentamethylcyclopentadiene (100 mL) were combined with 150 mL of heptane in the aforementioned autoclave, and the mixture was heated at 200 °C for 25 h and then cooled and depressurized.[32] The autoclave was heated again at 200 °C for 24 h followed by cooling, depressurization, and removal of the yellow solution for chromatography. Additional heptane (100 mL) and C_5Me_5H (5 mL) were added to the residue in the autoclave, which was closed and heated at 200 °C for a further 24 h. Chromatography of the combined heptane solutions (50-g silicic acid column, hexane elution) afforded first C_5Me_5H and carbonyl-containing impurities and then 4, which was isolated, after removal of hexane and vacuum sublimation, as a colorless solid (4.60 g, 65%): mp 60.5–61.0 °C; mass spectrum (40 °C, 16 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$ (no detectable H loss from these ions). Anal. Calcd for $C_{12}H_{16}O_2Os$: C, 37.69; H, 4.22. Found: C, 37.84; H, 4.39.

Preparation of $(C_{10}H_{10})Os(CO)_3$ (5). A mixture of $(CO)_4OsBr_2$ (0.300 g, 0.65 mmol) and TlC_5H_5 (0.40 g, 1.49 mmol) was refluxed in 50 mL of heptane for 6 h; the infrared spectrum at this point indicated the formation of the tricarbonyl product in good yield along with a small amount of $(\eta\text{-}C_5H_5)Os(CO)_2H$. After cooling to room temperature, the mixture was filtered and the filtrate was chromatographed on a 50-g silicic acid column packed with heptane. Infrared monitoring of the fractions showed a good separation of the tricarbonyl. Evaporation of solvent and sublimation afforded the product as a colorless oil (0.160 g, 60%): IR (heptane) 2061 (s), 1987 (s), 1979 (s) cm^{-1}; mass spectrum (60°C, 16 eV) $(C_{10}H_{10})Os(CO)_n^+$ (n = 0–3), $(C_5H_5)Os(CO)_n^+$ (n = 0–3); proton NMR ($CDCl_3$) δ 2.6–3.2 (m, ~4 H), 3.8–4.3 (m, ~1 H), 5.3–6.3 (m, ~5 H). Anal. Calcd for $C_{13}H_{10}O_3Os$: C, 38.61; H, 2.49. Found: C, 39.12; H, 2.53.

Preparation of $(\eta\text{-}C_5H_5)Os(CO)_2I$ (6). A mixture of $(CO)_4OsBr_2$ (1.98 g, 4.29 mmol) and TlC_5H_5 (4.5 g, 16.7 mmol) was refluxed in 65 mL of mesitylene for 50 h (infrared indicated the formation of $C_5H_5Os(CO)_2H$ and some $[(C_5H_5)Os(CO)_2]_2$). This reaction mixture was treated with I_2 (1.00 g, 3.94 mmol), stirred for 10 h, and then filtered to remove most of the thallium residues. The filtrate was evaporated to dryness, and the residue was chromatographed on a 50-g silicic acid column. The product eluted with 3:1 dichloromethane–heptane as a yellow band, and evaporation of solvent afforded yellow crystals of the product (0.950 g, 51%): mp 141–142 °C; mass spectrum (65 °C, 70 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$. Anal. Calcd for $C_7H_5IO_2Os$: C, 19.19; H, 1.15. Found: C, 19.24; H, 1.20.

Preparation of $(\eta\text{-}C_5Me_5)Os(CO)_2I$ (7). A solution of $Os_3(CO)_{12}$ (1.60 g, 1.76 mmol) and C_5Me_5H (3.0 mL) in 50 mL of mesitylene was refluxed for 6 days (at this point infrared indicated that a good yield of $(\eta\text{-}C_5Me_5)Os(CO)_2H$ had formed). This solution was treated with I_2 (1.00 g, 3.94 mmol) and stirred for 2 h, followed by filtration and washing with dichloromethane (2 × 25 mL). The combined filtrate was evaporated on the vacuum line to remove most of the mesitylene, and then the residue was chromatographed on a 50-g silicic acid column. The product eluted as a yellow band with 1:1 dichloromethane–heptane. Crystallization from dichloromethane–heptane gave yellow crystals of the product (1.00 g, 38%): mp 198–200 °C; mass spectrum (80 °C, 70 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$. Anal. Calcd for $C_{12}H_{15}IO_2Os$: C, 28.35; H, 2.97. Found: C, 28.27; H, 2.88.

Preparation of $[(\eta\text{-}C_5H_5)Os(CO)_2C_7H_8]BF_4$ (8). A solution of $(\eta\text{-}C_5H_5)Os(CO)_2H$ (0.100 g, 0.32 mmol) and $C_7H_7BF_4$ (0.050 g, 0.28 mmol) in 30 mL of acetonitrile was stirred for 6 days at room temperature. The solvent was evaporated, and then the residue was dissolved in 20 mL of CH_2Cl_2, the mixture was filtered, and hexane (20 mL) was added to precipitate white crystals of the product (0.110 g, 80%). Anal. Calcd for $C_{14}H_{13}BF_4O_2Os$: C, 34.30; H, 2.67. Found: C, 34.36; H, 2.70.

Preparation of $[(\eta\text{-}C_5Me_5)Os(CO)_2C_7H_8]BF_4$ (9). A solution of $(\eta\text{-}C_5Me_5)Os(CO)_2H$ (0.100 g, 0.26 mmol) in 20 mL of dichloromethane was stirred with $C_7H_7BF_4$ (0.045 g, 0.25 mmol) for 10 h to produce a clear solution. This solution was evaporated to dryness and then extracted with pentane to remove any unreacted $(\eta\text{-}C_5Me_5)Os(CO)_2H$. The white solid residue was crystallized from dichloromethane–heptane to yield crystals of the product (0.120 g, 83%). Anal. Calcd for $C_{19}H_{23}BF_4O_2Os$: C, 40.72; H, 4.14. Found: C, 40.74; H, 4.13.

Preparation of $(\eta\text{-}C_5H_5)Os(CO)_2(\eta^1\text{-}C_7H_7)$ (10). A solution of $[(\eta\text{-}C_5H_5)Os(CO)_2C_7H_8]BF_4$ (0.100 g, 0.20 mmol) in 20 mL of dichloromethane was treated with 0.20 mL of Et_3N for 30 min. Then the solvent was removed at reduced pressure, and the residue was extracted with 30 mL of pentane and filtered. The filtrate was evaporated, and the remaining solid was sublimed at 50 °C in vacuo to provide yellow crystals of the product (0.040 g, 50%): mp 108–110 °C; mass spectrum (35 °C, 16 eV) M^+, $(M - CO)^+$, $(M - 2CO)^+$, $C_7H_7^+$ (base peak). Anal. Calcd for $C_{14}H_{12}O_2Os$: C, 41.78; H, 3.01. Found: C, 41.84; H, 2.99.

Preparation of $(\eta\text{-}C_5Me_5)Os(CO)_2(\eta^1\text{-}C_7H_7)$ (11). A sample of $[(\eta\text{-}C_5Me_5)Os(CO)_2C_7H_8]BF_4$ (0.100 g, 0.18 mmol) was treated for 2 h with Et_2NH (0.5 mL) in 30 mL of dichloromethane. The solution was evaporated, and the residue was extracted with hexane (30 mL).

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(28) Although an osmium carbonyl bromide of this composition has been prepared,[29] an infrared spectrum has not been reported. However, the bands observed here are reasonable given the bands reported[30] for $[Os(CO)_3Cl_2]_2$ in CCl_4 (2134 (m) and 2059 (s) cm^{-1}) and the Cl to Br frequency shift in the analogous ruthenium compounds.[31] There is clearly an accidental degeneracy of the two $\nu(CO)$ bands at lower frequency in the case of osmium. Carbonyl stretching bands at 2125 and 2052 cm^{-1} for $[Os(CO)_3Br_2]_2$ in CH_2Cl_2 have very recently been reported: Choi, H. W.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 2664.

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(32) When the reaction was worked up at this stage (after a single heating cycle), the yield of **4** was only 35%. Clearly an equilibrium involving the displaced CO is limiting conversion to product.

Filtration and cooling the filtrate at −30 °C for 3 days yielded yellow crystals of the product (0.065 g, 75%): mp 144–146 °C; mass spectrum (65 °C, 16 eV) M^+ (base peak), $(M - CO)^+$, $(M - 2CO)^+$, $(M - C_7H_7)^+$, $C_7H_7^+$. Anal. Calcd for $C_{19}H_{22}O_2Os$: C, 48.29; H, 4.69. Found: C, 48.41; H, 4.81.

Preparation of $[(\eta\text{-}C_5H_5)Os(CO)_2(CH_3CN)]BF_4$ (12). The hydride $(\eta\text{-}C_5H_5)Os(CO)_2H$ (0.058 g, 0.19 mmol) was dissolved in 20 mL of CH_3CN, and then Ph_3CPF_6 (0.061 g, 0.16 mmol) was added. After the solution was stirred for 30 min, the solvent was evaporated and the residue recrystallized from acetone–ether, giving $[(\eta\text{-}C_5H_5)Os(CO)_2CH_3CN]BF_4$ as an off-white solid (0.065 g, 80%), dec pt 125–126 °C. Anal. Calcd for $C_9H_8BF_4NO_2Os$: C, 24.61; H, 1.84. Found: C, 24.71; H, 1.89.

Preparation of $[(\eta\text{-}C_5Me_5)Os(CO)_2(THF)]PF_6$ (13). The hydride (4) (0.071 g, 0.19 mmol) dissolved in a mixture[33] of 15 mL of CH_2Cl_2 and 0.20 mL of THF was treated with Ph_3CPF_6 (0.074 g, 0.19 mmol), and the resulting solution was stirred for 30 min. The volume of the mixture was reduced to 2 mL by evaporation, and then 15 mL of Et_2O was slowly added. The resulting pale yellow precipitate was collected, washed with 10 mL of Et_2O, and dried under vacuum. Recrystallization from CH_2Cl_2–Et_2O gave $[(\eta\text{-}C_5Me_5)Os(CO)_2THF]PF_6$ as an off-white solid (0.070 g, 63%), dec pt 101–103 °C. Anal. Calcd for $C_{16}H_{23}F_6O_3OsP$: C, 32.11; H, 3.87. Found: C, 32.46; H, 3.65.

Preparation of $[(\eta\text{-}C_5H_5)Os(CO)_3]BF_4$ (16). Anomalies in the reactions of one commercial sample of Ph_3CBF_4 were cleared up when it was shown by ^1H NMR to contain 1 mol of H_2O (to the limits of accuracy of the integration). Only a trace of the expected Ph_3COH hydrolysis product was observed. A solution of $(\eta\text{-}C_5H_5)Os(CO)_2H$ (0.225 g, 0.72 mmol) in 25 mL of CH_2Cl_2 was added over 45 min to a sample of $Ph_3CBF_4{\cdot}H_2O$ (0.255 g, 0.73 mmol) in 5 mL of CH_2Cl_2. The resulting yellow solution on the basis of spectroscopic results (Table I and text) contained $[(\eta\text{-}C_5H_5)Os(CO)_2(OH_2)]BF_4$ (15), but attempted isolation led only to pale yellow oils or tars. The solution was placed in the 500-mL stainless steel autoclave, pressurized to 210 atm with CO, and heated at 40 °C for 20 h. After cooling and depressurization, the contents of the bomb were removed, evaporated to dryness, and washed with 50 mL of Et_2O. The solid was recrystallized from acetone–Et_2O to afford $[(\eta\text{-}C_5H_5)Os(CO)_3]BF_4$ as colorless crystals (0.150 g, 60%), dec pt >315 °C. Anal. Calcd for $C_8H_5BF_4O_3Os$: C, 22.55; H, 1.18. Found: C, 22.48; H, 1.29.

The aquo cation is a necessary intermediate in this synthesis. No **16** was formed when **3** was treated with water-free Ph_3CPF_6 in the presence of CO at 1 atm. Furthermore, when a CH_2Cl_2 solution of Ph_3CPF_6 and **4** in equimolar properties was subjected to high-pressure CO, only a small amount of **17** was formed.

Preparation of $[(\eta\text{-}C_5Me_5)Os(CO)_3]BF_4$ (17). The preparation was similar to that for **16**, except for the final recrystallization of the product, which was performed from a minimum volume of CH_2Cl_2: yield 90%, dec pt >310 °C. Anal. Calcd for $C_{13}H_{15}BF_4O_3Os$: C, 31.46; H, 3.05. Found: C, 31.86, H, 3.04.

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Registry No. **1**, 81554-88-3; **2**, 81554-89-4; **3**, 42442-16-0; **4**, 81554-96-3; **5**, 81571-96-2; **6**, 81554-97-4; **7**, 81554-98-5; **8**, 81571-98-4; **9**, 81555-00-2; **10**, 81555-01-3; **11**, 81555-02-4; **12**, 81555-04-6; **13**, 81554-80-5; **14**, 81554-82-7; **15**, 81554-84-9; **16**, 81554-85-0; **17**, 81554-87-2; $(CO)_4OsBr_2$, 14878-21-8; $Os_3(CO)_{12}$, 15696-40-9; $(C_5H_6)_2$, 21423-86-9.

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[33] Pure THF was unsatisfactory as the solvent because of a reaction with Ph_3CPF_6 that led to darkening. Use of a dilute CH_2Cl_2 solution avoids this problem.

Contribution from the Laboratoire des Organométalliques, Equipe de recherche associée au CNRS No. 554,
Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cedex, France

Reactivity of μ-Silanediyl Iron Carbonyl Complexes with Alkynes. Molecular Structure of $(CO)_4FeSiPh_2CEt{=}CEtSiPh_2$ and of $(CO)_3FeCMe{=}CMeSiPh_2CMe{=}CMeFe(CO)_3$

FRANCIS H. CARRÉ* and JOËL J. E. MOREAU*

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The diiron complex $[Fe_2(CO)_8(SiPh_2)_2]$ containing two bridging diphenylsilyl ligands has been prepared photochemically by reaction of iron pentacarbonyl and diphenylsilane. A related compound $[Fe_2(CO)_7(SiMePh)_2]$ with one bridging carbonyl ligand has been obtained from methylphenylsilane. $[Fe_2(CO)_8(SiPh_2)_2]$ readily reacts with alkynes, yielding new mono- and diiron carbonyl complexes $(CO)_4FeSiPh_2CR{=}CRSiPh_2$ (R = Ph, Et, Me) and $(CO)_3FeCMe{=}CMeSiPh_2CMe{=}CMeFe(CO)_3$. The crystal structures of two of these new compounds have been determined by X-ray diffraction studies. The complex $(CO)_4FeSiPh_2CEt{=}CEtSiPh_2$ crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The unit cell parameters are $a = 11.748$ (2) Å, $b = 17.246$ (3) Å, $c = 8.602$ (3) Å, $\alpha = 86.70$ (2)°, $\beta = 110.94$ (2)°, $\gamma = 107.68$ (2)°, $V = 1548$ Å^3, $d_{calcd} = 1.324$ g cm^{-3}, and $d_{obsd} = 1.32$ (1) g cm^{-3}. The molecule has no rigorous element of symmetry. Some of the principal bond lengths are Fe–Si 2.405 (3) and 2.418 (2) Å and Fe–C average 1.782 Å; the angle Si–Fe–Si′ is 81.92 (2)°. The compound $(CO)_3FeCMe{=}CMeSiPh_2CMe{=}CMeFe(CO)_3$ crystallizes in the monoclinic system. The crystallographic parameters are as follows: space group $P2_1/c$, $a = 11.163$ (3) Å, $b = 16.191$ (2) Å, $c = 15.165$ (3) Å, $\beta = 109.02$ (2)°, $V = 2591$ Å^3, $Z = 4$, $d_{calcd} = 1.461$ g cm^{-3}, $d_{obsd} = 1.45$ (1) g cm^{-3}. The molecule has an approximate twofold axis. The important bond lengths are Fe–Fe′ 2.517 (1) Å, Fe–C(CO) average 1.785 Å, Fe–C(σ bonded) average 2.003 Å, and Fe–C(π bonded) 2.093 (5)–2.191 (4) Å. The structures were solved by the heavy-atom method and refined by full-matrix least squares to $R = 0.047$ and 0.038, respectively, for 1962 and 2105 independent observed data.

Introduction

Our current interest in the use of organosilyl–transition metal complexes in organic synthesis[1,2] led us to investigate the reactivity of these complexes with organic molecules. The silicon–transition metal bond is usually very stable. It can be cleaved by nucleophiles or electrophiles.[3] Since we were interested in more reactive silicon–metal bonds, we set out to prepare dinuclear complexes containing μ-SiR_2 ligands. Only a few complexes of this type have been reported, and little attention has been paid to their chemical reactivity.[4,5] We

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