Thermolysis of $Os_3(CO)_{10}[Fe(\eta\text{-}C_5H_4PPr^i_2)_2]$. Crystal and Molecular Structures of $(\mu\text{-}H)Os_3(CO)_8[\mu\text{-}(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_4PPr^iCHMeCH_2CO)]$, $(\mu\text{-}H)Os_3(CO)_9[\mu\text{-}(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_4PPr^i)]$, and $(\mu\text{-}H)_2Os_3(CO)_8[\eta^3\text{-}\mu\text{-}(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_3PPr^i)]$

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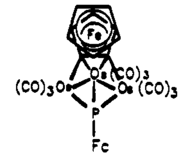
The pyrolysis of $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ ($Fc' = (\eta\text{-}C_5H_4)_2Fe$) in octane for 7.5 h affords $(\mu\text{-}H)Os_3(CO)_8[\mu\text{-}(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_4PPr^iCHMeCH_2CO)]$, **5**, $(\mu\text{-}H)Os_3(CO)_9[\mu\text{-}(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_4PPr^i)]$, **6**, $(\mu\text{-}H)_2Os_3(CO)_8[\mu\text{-}(\eta\text{-}C_5H_4Pr^i_2)Fe(\eta\text{-}C_5H_3PPr^i)]$, **7**, $(\mu\text{-}H)Os_3(CO)_8[\mu\text{-}(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_4PPr^iCHMeCH_2CO)]$, **8**, $(\mu\text{-}H)_2Os_3(CO)_8[(\eta\text{-}C_5H_4PPr^i_2)Fe(\eta\text{-}C_5H_3PPr^i)]$, **9**, and $(\mu\text{-}H)_2Os_3(CO)_8[(\eta\text{-}C_5H_4PPr^i)Fe(\eta\text{-}C_5H_3PPr^i_2)]$, **10**. X-ray data: **5**, monoclinic, space group $P2_1/a$ (No. 14), $a = 16.268$ (2), $b = 11.298$ (3), $c = 20.649$ (3) Å, $\beta = 94.43$ (1)°, $Z = 4$; **6**, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.102$ (3), $b = 17.799$ (4), $c = 9.348$ (2) Å, $\alpha = 101.53$ (2), $\beta = 113.95$ (1), $\gamma = 73.16$ (1)°, $Z = 2$; **7**, monoclinic, space group $P2_1/a$ (No. 14), $a = 14.668$ (2), $b = 14.022$ (2), $c = 15.807$ (3) Å, $\beta = 94.40$ (1)°, $Z = 4$. Final R values of 0.026, 0.029, and 0.031 were obtained by using 4905, 9870, and 4127 unique reflections ($I > 3.00\sigma(I)$), respectively. Compounds **5** and **8** are diastereoisomers, and they are formed by β-C–H activation of one isopropyl group and subsequent CO insertion into the Os–C(alkyl) bond. Compound **6** is formed by β-C–H activation of an isopropyl group with subsequent elimination of propene and the formation of an Os–P bond, while compounds **7**, **9**, and **10** are the results of a further C–H activation of one of the C_5H_4 rings.

Introduction

Coordination unsaturation generated by CO loss in phosphine-substituted Ru_3 or Os_3 carbonyl clusters often leads to C–H and P–C cleavage within the phosphine ligands.[1–4] We have recently made use of these reactions to prepare some unusual metal cluster complexes such as the ferrocyne derivative **1**[2] and the doubly metalated ferrocenyl compounds **2**.[3] We have also studied the thermolysis of $Ru_3(CO)_{10}[Fc'(PPr^i_2)_2]$, $Fc' = Fe(\eta\text{-}C_5H_4)_2$, where the results show, unexpectedly, that C–H and P–C cleavage reactions involve, predominantly, the isopropyl groups rather than the Fc′ moiety.[4] Thermolysis of the osmium analogue $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ affords a variety of products including the novel complexes **3** and **4** previously reported.[2,3] The isolation and characterization of the other products of this thermolysis, **5–10**, constitute the subject matter of this paper.



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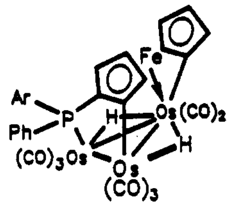

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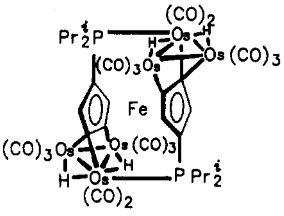

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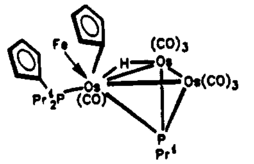

4

Experimental Section

Reactions were carried out under an argon atmosphere. Solvents were predried and distilled prior to use. ^{31}P and ^1H NMR chemical shifts are given in ppm from 85% H_3PO_4 and TMS, respectivley, and the spectra were recorded in $CDCl_3$ at room temperature by using either Bruker AC-200 or Varian XL-300 spectrometer. Elemental analyses were performed by Mr. Peter Borda of this department. Mass spectra (fast atom bombardment, FAB) were recorded by using an AEI MS-9 spectrometer with 3-nitrobenzyl alcohol as the matrix and argon as exciting gas. $Fc'(PPr^i_2)_2$ and $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ were prepared as previously described.[3,4]

Pyrolysis of $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ and Preparation of 5-10. $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ (150 mg, 0.12 mmol) in octane (80 mL) was refluxed for 7.5 h with TLC monitoring. The reaction solvent was removed in vacuo, and the residue was applied directly to a silica column for chromatographic separation: the eluent

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(1) (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. (b) Deeming, A. J.; Kabir, S. E.; Powell, N. I. *J. Chem. Soc., Dalton Trans.* **1987**, 1529. (c) Deeming A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727. (d) Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2589. (e) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Backer-Dirks, J. D. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1879. (f) Brown, S. C.; Evans, J.; Smart, L. *J. Chem. Soc., Chem. Commun.* **1980**, 1021. (g) Bradford, C. W; Nyholm, R.s.; Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1972**, 87. (h) Clucas, J. A.; Foster, D. F.; Harding, M. M.; Smith, A. K. *J. Chem. Soc., Chem. Commun.* **1984**, 949. (i) Bruce, M. I.; Humphrey, P. A.; Shawkataly, O. B.; Snow, M.r.; Tiekink, E. R. T.; Cullen, W. R. *Organometallics* **1990**, *9*, 2910. (j) Cullen, W. R.; Chacon, S. T.; Bruce, M. I.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1988**, *7*, 2273.

(2) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Organometallics* **1992**, *11*, 928.

(3) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Organometallics* **1992**, *11*, 277.

(4) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Organometallics* **1992**, *11*, 853.

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Table I. Crystallographic Data[a]

	compd		
	5·0.5CH_2Cl_2	**6**	**7**
formula	$C_{31}H_{37}FeO_9Os_3P_2\cdot 0.5CH_2Cl_2$	$C_{28}H_{30}FeO_9Os_3P_2$	$C_{27}H_{30}FeO_8Os_3P_2$
fw	1284.49	1198.93	1170.92
color, habit	yellow-orange, prism	red-orange, prism	orange, plate
cryst size, mm	0.08 × 0.17 × 0.20	0.20 × 0.30 × 0.38	0.07 × 0.25 × 0.30
cryst system	monoclinic	triclinic	monoclinic
space group	$P2_1/a$	$P\bar{1}$	$P2_1/a$
a, Å	16.268 (2)	11.102 (3)	14.668 (2)
b, Å	11.298 (3)	17.799 (4)	14.022 (2)
c, Å	20.649 (3)	9.348 (2)	15.807 (3)
α, deg	90	101.53 (2)	90
β, deg	94.43 (1)	113.95 (1)	94.40 (1)
γ, deg	90	73.16 (1)	90
V, Å^3	3784 (1)	1609 (1)	3241.5 (8)
Z	4	2	4
ρ_{calc}, g/cm^3	2.255	2.475	2.399
$F(000)$	2400	1108	2160
μ(Mo Kα), cm^{-1}	106.30	124.12	123.14
rel transm factors	0.72–1.00	0.44–1.00	0.18–1.00
scan type	ω–2θ	ω–2θ	ω–2θ
scan range, deg in ω	1.10 + 0.35 tan θ	1.05 + 0.35 tan θ	1.21 + 0.35 tan θ
scan rate, deg/min	16	32	32
data collcd	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$
$2\theta_{max}$, deg	55	75	55
cryst decay	negligible	3.4%	negligible
tot. no. of reflcns	9438	17 654	8058
no. of unique reflcns	9123	16 893	7762
R_{merge}	0.045	0.038	0.051
reflcns with $I > 3\sigma(I)$	4905	9870	4127
no. of variables	461	389	371
R	0.029	0.031	0.031
R_w	0.026	0.029	0.025
gof	1.25	1.54	1.42
max Δ/σ (final cycle)	0.27[b]	0.07	0.03
resid density, e/Å^3	–0.68 to +0.76	–1.5 to +1.5 (near Os)	–1.10 to 1.25 (near Os)

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.710 69 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B) + (pF^2)^2]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count, p = 0.01 for **5** and **6** and 0.00 for **7**), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof = $[\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I > 3\sigma(I)$. [b] This parameter shift was associated with an off-diagonal thermal parameter of a disordered solvent atom; all shifts associated with the ordered part of the structure were <0.05σ.

was 3/1 petroleum ether/CH_2Cl_2. The first band afforded **9** after evaporation of the solvent in 20% yield, the second **6** (10% yield), the third **10** (10% yield), the fourth **3** (6% yield), the fifth **7** (10% yield), the sixth **4** (8% yield), the seventh **5** (15% yield), and the eighth (last) **8** (3% yield). Suitable crystals of **6** for X-ray analysis were obtained by slow evaporation of the eluted fraction, and crystals of **5** and **7** were obtained from 1/1 hexane/CH_2Cl_2 solutions.

9, yellow solid. $^{31}P\{^1H\}$NMR: δ 76.3, 40.4, J = 2.8. ^1H NMR: δ 4.72 (m, 1H, Cp), 4.43 (m, 2H, Cp), 4.34 (m, 2H, Cp), 4.06 (m, 1H, Cp), 3.84 (m, 1H, Cp), 2.75 (m, 2H, C*H*Me$_2$), 2.20 (m, 1H, C*H*Me$_2$), 1.88 (d, 3H, J = 20.8, CH*Me*$_2$), 1.76 (d, 3H, J = 21.0, CH*Me*$_2$), 1.66 (dd, 3H, CH*Me*$_2$), 1.49 (dd, 3H, CH*Me*$_2$), 1.35 (dd, 3H, CH*Me*$_2$), 1.22 (dd, 3H, CH*Me*$_2$), −17.66 (ddd, 1H, J_1 = 17.7, J_2 = 11.4, J_3 = 1.2, OsH), −19.16 (ddd, 1H, J_1 = 27.6, J_2 = 5.4, J_3 = 1.2, OsH). Mass spectrum (FAB): m/e 1170 (P$^+$, base peak), 1142, 1114, 1086, 1058, 1030, 974, 874, 856, 842, 832, 818. Anal. Calcd for $C_{27}H_{30}FeO_8Os_3P_2$: C, 27.70; H, 2.58. Found: C, 28.03; H, 2.71.

6, yellow solid. $^{31}P\{^1H\}$ NMR: δ 18.0, 16.2, J = 19.3. ^1H NMR: δ 4.41 (m, 1H, C_5H_4), 4.28 (m, 3H, C_5H_4), 4.21 (m, 1H, C_5H_4), 4.13 (m, 2H, C_5H_4), 4.00 (m, 1H, C_5H_4), 2.87 (m, 1H, C*H*Me$_2$), 2.64 (m, 1 H, C*H*Me$_2$), 2.49 (m, 1 H, C*H*Me$_2$), 1.65 (dd, 3H, J_1 = 17.6, J_2 = 7.1, CH*Me*$_2$), 1.32 (dd, 3H, J_1 = 16.7, J = 6.2, CH*Me*$_2$), 1.30 (dd, 3H, J_1 = 15.7, J_2 = 7.6, CH*Me*$_2$), 1.25 (dd, 3H, J_1 = 16.2, J_2 = 7.1, CH*Me*$_2$), 0.97 (dd, 3H, J_1 = 17.1, J_2 = 7.1, CH*Me*$_2$), 0.74 (dd, 3H, J_1 = 11.9, J_2 = 6.7, CH*Me*$_2$), −17.98 (dd, 1H, J_1 = 18.0, J_2 = 8.4, OsH).. Mass spectrum (FAB): m/e 1198 (P$^+$, base peak), 1170, 1142, 1126, 1114, 1099, 1086, 1070, 1058, 1042, 1030, 1002, 974, 960, 946, 930, 903, 887, 860, 818. Anal. Calcd for $C_{28}H_{30}FeO_9Os_3P_2$: C, 28.05; H, 2.52. Found: C, 28.27; H, 2.66.

10, yellow solid. $^{31}P\{^1H\}$ NMR: δ 28.2, 6.0, J = 12.7. ^1H NMR: δ 4.46 (m, 2H, Cp), 4.28 (m, 3H, Cp), 4.17 (m, 1H, Cp), 3.98 (m, 1H, Cp), 2.50 (m, 1H, C*H*Me$_2$), 2.34 (m, 1H, C*H*Me$_2$), 2.20 (m, 1H, C*H*Me$_2$), 1.57 (dd, 3H, CH*Me*$_2$), 1.47 (dd, 3H, CH*Me*$_2$), 1.39 (dd, 3H, CH*Me*$_2$), 1.35 (dd, 3H, CH*Me*$_2$), 1.18 (dd, 3H, CH*Me*$_2$), 1.11 (dd, 3H, CH*Me*$_2$), −17.84 (dd, 1H, J_1 = J_2 = 11.3, OsH), −18.92 (dd, 1H, J_1 = 22.2, J_2 = 6.1, OsH). Mass spectrum (FAB): m/e 1170 (P$^+$, base peak), 1142, 1128, 1114, 1086, 1072, 1058, 1044, 1030, 1016, 1002, 988, 960, 932, 918, 890, 876, 844, 832, 818. Anal. Calcd for $C_{27}H_{30}FeO_8Os_3P_2$: C, 27.70; H, 2.58. Found: C, 27.81; H, 2.82.

7, orange solid. $^{31}P\{^1H\}$ NMR: δ 70.1, 22.6, J = 18.7. ^1H NMR (500 MHz): δ 4.68 (m, 1H, Cp), 4.52 (m, 1H, Cp), 4.40 (m, 1H, Cp), 4.35 (m, 1H, Cp), 4.30 (m, 1H, Cp), 3.97 (m, 1H, Cp), 3.74 (m, 1H, Cp), 2.71 (m, 1H, C*H*Me$_2$), 2.59 (m, 1H, C*H*Me$_2$), 2.50 (m, 1H, C*H*Me$_2$), 1.59 (dd, 3H, CH*Me*$_2$), 1.43 (dd, 3H, CH*Me*$_2$), 1.38 (dd, 3H, CH*Me*$_2$), 1.18 (dd, 3H, CH*Me*$_2$), 1.05 (dd, 3H, CH*Me*$_2$), 0.83 (dd, 3H, CH*Me*$_2$), −15.94 (dd, 1H, J_1 = 18.2, J_2 = 6.3, OsH), −17.27 (dd, 1H, J_1 = 27.0, J_2 = 10.8, OsH). Mass spectrum (FAB): m/e 1170 (P$^+$, base peak), 1142, 1128, 1114, 1086, 1072, 1058, 1044, 1030, 1016, 1002, 988, 974, 960, 946, 932, 918, 890, 876, 858, 844, 832, 818. Anal. Calcd for $C_{27}H_{30}FeO_8Os_3P_2$: C, 27.70; H, 2.58. Found: C, 27.94; H, 2.65.

5, yellow orange solid. $^{31}P\{^1H\}$ NMR: δ 59.2, 19.2, J = 3.8. ^1H NMR: δ 4.62 (m, 1H, C_5H_4), 4.43 (m, 2H, C_5H_4), 4.37 (m, 1H, C_5H_4), 4.28 (m, 2H, C_5H_4), 4.16 (m, 1H, C_5H_4), 3.97 (m, 1H, C_5H_4), 3.08 (m, 1H, C*H*Me$_2$), 2.58 (m, 3H, C*H*Me$_2$ + CHMeC*H*$_2$), 2.33 (m, 1H, C*H*Me$_2$), 2.23 (m, 1H, C*H*Me$_2$), 1.56 (dd, 3H, CH*Me*$_2$), 1.45 (dd, 3H, CH*Me*$_2$), 1.28 (dd, 3H, CH*Me*$_2$), 1.25 (dd, 3H, CH*Me*$_2$), 1.15 (dd, 3H, CH*Me*$_2$), 0.88 (dd, 3H, CH*Me*$_2$), 0.67 (dd, 3H, CH*Me*$_2$), −13.60 (dd, 1H, J_1 = 7.5, J_2 = 6.0, OsH). Mass

Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 5[a]

atom	x	y	z	B_{eq}	occ
Os(1)	0.39007 (2)	0.61226 (3)	0.22111 (2)	2.12 (1)	
Os(2)	0.35385 (2)	0.56189 (3)	0.35491 (2)	2.00 (1)	
Os(3)	0.45297 (2)	0.76260 (3)	0.32489 (2)	2.56 (2)	
Fe(1)	0.24512 (7)	0.2472 (1)	0.22504 (6)	2.53 (5)	
P(1)	0.3383 (1)	0.4787 (2)	0.1380 (1)	2.4 (1)	
P(2)	0.3071 (1)	0.3738 (2)	0.3793 (1)	2.3 (1)	
O(1)	0.4614 (3)	0.4666 (5)	0.2622 (3)	2.4 (3)	
O(2)	0.5280 (5)	0.7030 (7)	0.1445 (4)	5.6 (4)	
O(3)	0.2834 (4)	0.8188 (6)	0.1779 (3)	4.9 (4)	
O(4)	0.1876 (4)	0.6794 (7)	0.3790 (4)	5.9 (4)	
O(5)	0.4412 (5)	0.6040 (7)	0.4879 (3)	5.3 (4)	
O(6)	0.5148 (5)	0.8706 (7)	0.4552 (4)	6.6 (5)	
O(7)	0.5242 (5)	0.9495 (7)	0.2397 (4)	6.3 (5)	
O(8)	0.6007 (4)	0.5926 (7)	0.3306 (4)	6.6 (5)	
O(9)	0.2863 (4)	0.8913 (6)	0.3242 (4)	4.6 (4)	
C(1)	0.3149 (5)	0.3274 (8)	0.1569 (4)	2.5 (4)	
C(2)	0.2494 (5)	0.2537 (9)	0.1268 (4)	3.4 (4)	
C(3)	0.2620 (6)	0.1349 (8)	0.1499 (5)	3.5 (5)	
C(4)	0.3309 (6)	0.1327 (8)	0.1939 (4)	3.2 (4)	
C(5)	0.3638 (5)	0.2483 (8)	0.1978 (4)	2.7 (4)	
C(6)	0.2382 (5)	0.3019 (8)	0.3185 (4)	2.5 (4)	
C(7)	0.1821 (5)	0.3696 (8)	0.2758 (5)	3.0 (4)	
C(8)	0.1266 (5)	0.2927 (9)	0.2426 (5)	3.5 (5)	
C(9)	0.1440 (5)	0.1763 (8)	0.2649 (5)	3.5 (5)	
C(10)	0.2136 (5)	0.1812 (8)	0.3124 (4)	3.0 (4)	
C(11)	0.2468 (6)	0.5281 (8)	0.0880 (4)	3.2 (4)	
C(12)	0.1733 (6)	0.554 (1)	0.1282 (5)	4.3 (5)	
C(13)	0.2620 (7)	0.635 (1)	0.0459 (5)	5.2 (6)	
C(14)	0.4165 (6)	0.4551 (8)	0.0768 (4)	3.2 (4)	
C(15)	0.3835 (7)	0.380 (1)	0.0172 (5)	4.6 (5)	
C(16)	0.4950 (6)	0.4046 (9)	0.1074 (5)	3.6 (5)	
C(17)	0.4044 (5)	0.2863 (8)	0.3955 (4)	3.3 (4)	
C(18)	0.4714 (5)	0.3391 (8)	0.3542 (4)	2.9 (4)	
C(19)	0.4397 (4)	0.4519 (7)	0.3204 (4)	2.3 (4)	
C(20)	0.3995 (6)	0.1543 (9)	0.3921 (6)	4.6 (5)	
C(21)	0.2517 (7)	0.3453 (9)	0.4531 (5)	4.3 (5)	
C(22)	0.2911 (8)	0.407 (1)	0.5133 (5)	6.7 (7)	
C(23)	0.1594 (7)	0.384 (1)	0.4423 (6)	5.9 (7)	
C(24)	0.4746 (6)	0.6685 (8)	0.1732 (5)	3.1 (4)	
C(25)	0.3236 (6)	0.7394 (8)	0.1938 (4)	3.1 (4)	
C(26)	0.2525 (6)	0.6422 (8)	0.3714 (5)	3.5 (5)	
C(27)	0.4065 (6)	0.5853 (8)	0.4379 (4)	3.2 (4)	
C(28)	0.4905 (6)	0.828 (1)	0.4074 (5)	3.9 (5)	
C(29)	0.4982 (6)	0.878 (1)	0.2710 (5)	4.1 (5)	
C(30)	0.5454 (6)	0.6567 (9)	0.3271 (5)	4.1 (5)	
C(31)	0.3469 (6)	0.8403 (8)	0.3243 (4)	3.0 (4)	
C(32)	0.453 (2)	−0.032 (2)	0.029 (1)	9 (2)	0.67
C(33)	0.502 (1)	0.091 (1)	0.0291 (8)	9 (1)	1.13
C(34)	0.557 (3)	0.129 (4)	−0.010 (3)	8 (3)	0.36
C(35)	0.598 (1)	0.069 (2)	−0.065 (1)	8 (1)	0.88
C(36)	0.553 (2)	−0.058 (5)	−0.069 (2)	9 (2)	0.46

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(a_ia_j)$.

Table III. Bond Lengths (Å) with Estimated Standard Deviations for 5[a]

Os(1)–Os(2)	2.9250 (6)	P(2)–C(6)	1.809 (9)
Os(1)–Os(3)	2.8610 (6)	P(2)–C(17)	1.87 (1)
Os(1)–P(1)	2.389 (2)	P(2)–C(21)	1.86 (1)
Os(1)–O(1)	2.151 (5)	O(1)–C(19)	1.289 (9)
Os(1)–C(24)	1.87 (1)	O(2)–C(24)	1.16 (1)
Os(1)–C(25)	1.86 (1)	O(3)–C(25)	1.14 (1)
Os(1)–H(1)	1.92	O(4)–C(26)	1.16 (1)
Os(2)–Os(3)	2.8776 (7)	O(5)–C(27)	1.16 (1)
Os(2)–P(2)	2.325 (2)	O(6)–C(28)	1.14 (1)
Os(2)–C(19)	2.039 (8)	O(7)–C(29)	1.14 (1)
Os(2)–C(26)	1.94 (1)	O(8)–C(30)	1.15 (1)
Os(2)–C(27)	1.87 (1)	O(9)–C(31)	1.14 (1)
Os(2)–H(1)	1.80	C(1)–C(2)	1.45 (1)
Os(3)–C(28)	1.91 (1)	C(1)–C(5)	1.43 (1)
Os(3)–C(29)	1.90 (1)	C(2)–C(3)	1.43 (1)
Os(3)–C(30)	1.92 (1)	C(3)–C(4)	1.39 (1)
Os(3)–C(31)	1.93 (1)	C(4)–C(5)	1.41 (1)
Fe(1)–C(1)	2.082 (8)	C(6)–C(7)	1.44 (1)
Fe(1)–C(2)	2.036 (9)	C(6)–C(10)	1.42 (1)
Fe(1)–C(3)	2.040 (9)	C(7)–C(8)	1.39 (1)
Fe(1)–C(4)	2.044 (9)	C(8)–C(9)	1.41 (1)
Fe(1)–C(5)	2.052 (8)	C(9)–C(10)	1.44 (1)
Fe(1)–C(6)	2.038 (8)	C(11)–C(12)	1.54 (1)
Fe(1)–C(7)	2.056 (8)	C(11)–C(13)	1.52 (1)
Fe(1)–C(8)	2.055 (8)	C(14)–C(15)	1.56 (1)
Fe(1)–C(9)	2.057 (8)	C(14)–C(16)	1.49 (1)
Fe(1)–C(10)	2.052 (9)	C(17)–C(18)	1.55 (1)
Fe(1)–Cp(1)	1.655 (4)	C(17)–C(20)	1.49 (1)
Fe(1)–Cp(2)	1.657 (4)	C(18)–C(19)	1.52 (1)
P(1)–C(1)	1.800 (9)	C(21)–C(22)	1.52 (1)
P(1)–C(11)	1.832 (9)	C(21)–C(23)	1.56 (1)
P(1)–C(14)	1.881 (9)		

[a] Here and elsewhere, Cp(1) and Cp(2) refer to the unweighted centroids of the C(1–5) and C(6–10) cyclopentadienyl rings.

spectrum (FAB): *m/e* 1240(P^+, base peak), 1212, 1184, 1156, 1128, 1114, 1100, 1082, 1068, 1054, 1040, 1026, 1012, 984, 956, 942, 928, 914, 886, 872, 858, 844, 830, 816, 788. Anal. Calcd for $C_{31.5}H_{38}ClFeO_9Os_3P_2$, 5·0.5 CH_2Cl_2: C, 29.46; H, 2.98. Found: C, 29.66; H, 3.09.

8, pink solid. $^{31}P\{^1H\}$ NMR: δ 51.0, 18.7, J = 3.6. ^1H NMR: δ 4.67 (m, 1H, C_5H_4), 4.51 (m, 1H, C_5H_4), 4.46 (m, 1H, C_5H_4), 4.32 (m, 1H, C_5H_4), 4.27 (m, 2H, C_5H_4), 4.08 (m, 1H, C_5H_4), 3.91 (m, 1H, C_5H_4), 3.00 (m, 1H, C*H*Me$_2$), 2.60 (m, 2H, CHMeC*H*$_2$), 2.52 (m, 1H, C*H*Me$_2$), 2.36 (m, 1H, C*H*Me$_2$), 2.25 (m, 1H, C*H*Me$_2$), 1.67 (dd, 3H, CH*Me*$_2$), 1.58 (dd, 3H, CH*Me*$_2$), 1.38 (dd, 3H, CH*Me*$_2$), 1.26 (dd, 3H, CH*Me*$_2$), 1.14 (dd, 3H, CH*Me*$_2$), 0.97 (dd, 3H, CH*Me*$_2$), 0.75 (dd, 3H, CH*Me*$_2$), −13.57 (dd, 1H, J_1 = 7.8, J_2 = 6.0, OsH). Mass spectrum (FAB): *m/e* 1240 (P^+), 1212 (base peak), 1184, 1156, 1128, 1114, 1100, 1082, 1068, 1054, 1040, 1026, 1012, 984, 956, 928, 914, 872, 858, 844, 816, 788.

X-ray Crystallographic Analyses. Crystallographic data for 5·0.5CH_2Cl_2, 6, and 7 appear in Table I. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 20.9–29.1, 44.7–47.5, and 33.2–41.2° for 5–7, respectively. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for 5 and 7 and decreased uniformly by 3.4% for 6. The data were processed[5] and corrected for Lorentz and polarization effects, decay (for 6), and absorption (empirical, based on azimuthal scans for four reflections).

The structures were solved by heavy atom methods, the coordinates of the Os and Fe atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The structure analysis of 6 was initiated in the centrosymmetric space group $P\bar{1}$, this choice being confirmed by the subsequent successful solution and refinement of the structure. All non-hydrogen atoms of the three complexes were refined with anisotropic thermal parameters. There is a solvent region in the structure of 5, disordered about a center of symmetry, that appears to consist of both dichloromethane and hexane in an unknown ratio. The crystallographic data in Table I for 5 are calculated by assuming a 2:1 complex:dichloromethane formulation. All resolvable atoms in the solvent region were refined as carbon atoms. The occupancy factors were adjusted to give approximately equal thermal parameters for each site (C(32–36)) with the total number of electrons constrained to equal that expected for half of a dichloromethane molecule.

The metal hydride atoms were included in difference map positions but were not refined. All other hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2 B_{bonded\ atom}$). Corrections for secondary extinction were applied for both structures, the final values of the extinction coefficient being 5.7 (1) × 10^{-8} for 5, 9.8 (1) × 10^{-7} for 6, and 6.4 (1) × 10^{-8} for 7. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 6. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables II–X, respectively. Hydrogen atom

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(5) TEXSAN/TEXRAY structure analysis package (version 5.1). Molecular Structure Corp., 1985.

Table IV. Bond Angles (deg) with Estimated Standard Deviations for 5

Os(2)–Os(1)–Os(3)	59.64 (2)	C(29)–Os(3)–C(31)	94.1 (4)
Os(2)–Os(1)–P(1)	118.01 (6)	C(30)–Os(3)–C(31)	168.4 (4)
Os(2)–Os(1)–O(1)	67.7 (1)	Cp(1)–Fe(1)–Cp(2)	174.7 (2)
Os(2)–Os(1)–C(24)	141.0 (3)	Os(1)–P(1)–C(1)	120.9 (3)
Os(2)–Os(1)–C(25)	106.4 (3)	Os(1)–P(1)–C(11)	116.0 (3)
Os(2)–Os(1)–H(1)	37	Os(1)–P(1)–C(14)	110.7 (3)
Os(3)–Os(1)–P(1)	177.19 (6)	C(1)–P(1)–C(11)	103.6 (4)
Os(3)–Os(1)–O(1)	90.4 (1)	C(1)–P(1)–C(14)	100.1 (4)
Os(3)–Os(1)–C(24)	87.7 (3)	C(11)–P(1)–C(14)	103.1 (4)
Os(3)–Os(1)–C(25)	86.2 (3)	Os(2)–P(2)–C(6)	117.1 (3)
Os(3)–Os(1)–H(1)	90	Os(2)–P(2)–C(17)	103.6 (3)
P(1)–Os(1)–O(1)	87.1 (2)	Os(2)–P(2)–C(21)	121.6 (3)
P(1)–Os(1)–C(24)	93.9 (3)	C(6)–P(2)–C(17)	110.9 (4)
P(1)–Os(1)–C(25)	96.1 (3)	C(6)–P(2)–C(21)	100.2 (4)
P(1)–Os(1)–H(1)	88	C(17)–P(2)–C(21)	102.7 (4)
O(1)–Os(1)–C(24)	94.2 (3)	Os(1)–O(1)–C(19)	106.8 (5)
O(1)–Os(1)–C(25)	174.0 (3)	P(1)–C(1)–C(2)	127.7 (7)
O(1)–Os(1)–H(1)	86	P(1)–C(1)–C(5)	127.2 (7)
C(24)–Os(1)–C(25)	90.6 (4)	C(2)–C(1)–C(5)	104.5 (8)
C(24)–Os(1)–H(1)	178	C(1)–C(2)–C(3)	108.2 (8)
C(25)–Os(1)–H(1)	90	C(2)–C(3)–C(4)	108.8 (8)
Os(1)–Os(2)–Os(3)	59.08 (1)	C(3)–C(4)–C(5)	107.7 (8)
Os(1)–Os(2)–P(2)	118.38 (6)	C(1)–C(5)–C(4)	110.7 (8)
Os(1)–Os(2)–C(19)	66.1 (2)	P(2)–C(6)–C(7)	121.0 (7)
Os(1)–Os(2)–C(26)	108.2 (3)	P(2)–C(6)–C(10)	130.3 (7)
Os(1)–Os(2)–C(27)	136.4 (3)	C(7)–C(6)–C(10)	107.1 (8)
Os(1)–Os(2)–H(1)	40	C(6)–C(7)–C(8)	109.0 (8)
Os(3)–Os(2)–P(2)	164.77 (6)	C(7)–C(8)–C(9)	108.3 (8)
Os(3)–Os(2)–C(19)	89.7 (2)	C(8)–C(9)–C(10)	108.2 (8)
Os(3)–Os(2)–C(26)	99.6 (3)	C(6)–C(10)–C(9)	107.4 (8)
Os(3)–Os(2)–C(27)	82.0 (3)	P(1)–C(11)–C(12)	112.7 (6)
Os(3)–Os(2)–H(1)	92	P(1)–C(11)–C(13)	113.8 (7)
P(2)–Os(2)–C(19)	76.3 (2)	C(12)–C(11)–C(13)	109.0 (8)
P(2)–Os(2)–C(26)	95.4 (3)	P(1)–C(14)–C(15)	113.5 (6)
P(2)–Os(2)–C(27)	93.7 (3)	P(1)–C(14)–C(16)	111.7 (6)
P(2)–Os(2)–H(1)	93	C(15)–C(14)–C(16)	110.9 (8)
C(19)–Os(2)–C(26)	164.5 (4)	P(2)–C(17)–C(18)	108.5 (6)
C(19)–Os(2)–C(27)	97.3 (4)	P(2)–C(17)–C(20)	118.4 (7)
C(19)–Os(2)–H(1)	86	C(18)–C(17)–C(20)	113.3 (8)
C(26)–Os(2)–C(27)	96.2 (4)	C(17)–C(18)–C(19)	110.3 (7)
C(26)–Os(2)–H(1)	82	Os(2)–C(19)–O(1)	119.4 (6)
C(27)–Os(2)–H(1)	174	Os(2)–C(19)–C(18)	124.5 (6)
Os(1)–Os(3)–Os(2)	61.29 (2)	O(1)–C(19)–C(18)	115.3 (7)
Os(1)–Os(3)–C(28)	165.3 (3)	P(2)–C(21)–C(22)	112.9 (7)
Os(1)–Os(3)–C(29)	95.7 (3)	P(2)–C(21)–C(23)	110.9 (7)
Os(1)–Os(3)–C(30)	83.2 (3)	C(22)–C(21)–C(23)	109 (1)
Os(1)–Os(3)–C(31)	89.9 (3)	Os(1)–C(24)–O(2)	178.7 (9)
Os(2)–Os(3)–C(28)	104.9 (3)	Os(1)–C(25)–O(3)	178.8 (8)
Os(2)–Os(3)–C(29)	156.3 (3)	Os(2)–C(26)–O(4)	172.7 (9)
Os(2)–Os(3)–C(30)	87.4 (3)	Os(2)–C(27)–O(5)	176.7 (8)
Os(2)–Os(3)–C(31)	81.1 (3)	Os(3)–C(28)–O(6)	177 (1)
C(28)–Os(3)–C(29)	98.5 (4)	Os(3)–C(29)–O(7)	178 (1)
C(28)–Os(3)–C(30)	91.3 (4)	Os(3)–C(30)–O(8)	178 (1)
C(28)–Os(3)–C(31)	93.1 (4)	Os(3)–C(31)–O(9)	176.7 (8)
C(29)–Os(3)–C(30)	95.9 (4)		

parameters, anisotropic thermal parameters, complete tables of bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

Results and Discussion

The pyrolysis of $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ affords eight isolable complexes **3–10**. Complexes **5–10** have now been characterized by spectroscopic and analytical techniques; **5–7** have been subjected to X-ray crystallographic analyses.

Table V. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 6[a]

atom	*x*	*y*	*z*	B_{eq}
Os(1)	0.42378 (2)	0.18486 (1)	0.31454 (2)	1.709 (6)
Os(2)	0.49806 (2)	0.32891 (1)	0.30528 (2)	1.894 (6)
Os(3)	0.70349 (2)	0.19525 (1)	0.45643 (2)	2.307 (7)
Fe(1)	0.03424 (6)	0.36140 (4)	0.17702 (8)	2.11 (2)
P(1)	0.3651 (1)	0.31409 (6)	0.4409 (1)	1.80 (4)
P(2)	0.2101 (1)	0.17046 (6)	0.1237 (1)	1.83 (4)
O(1)	0.4403 (5)	0.0926 (2)	0.5616 (5)	4.5 (2)
O(2)	0.5567 (4)	0.0331 (2)	0.1655 (5)	4.9 (2)
O(3)	0.6607 (5)	0.3281 (3)	0.1068 (6)	6.1 (3)
O(4)	0.2973 (4)	0.4578 (2)	0.1003 (5)	4.2 (2)
O(5)	0.6550 (5)	0.4309 (3)	0.5792 (5)	4.8 (2)
O(6)	0.9371 (4)	0.2786 (3)	0.5888 (5)	5.0 (2)
O(7)	0.8499 (5)	0.0237 (3)	0.5116 (6)	5.4 (2)
O(8)	0.6766 (4)	0.1990 (3)	0.7724 (5)	4.5 (2)
O(9)	0.7212 (5)	0.1485 (3)	0.1295 (5)	5.7 (3)
C(1)	0.4299 (5)	0.1271 (3)	0.4651 (6)	2.8 (2)
C(2)	0.5058 (5)	0.0917 (3)	0.2174 (6)	2.8 (2)
C(3)	0.6036 (5)	0.3230 (3)	0.1812 (6)	3.3 (2)
C(4)	0.3653 (5)	0.4088 (3)	0.1797 (6)	2.6 (2)
C(5)	0.5957 (5)	0.3931 (3)	0.4754 (6)	3.2 (2)
C(6)	0.8496 (5)	0.2491 (3)	0.5389 (6)	3.1 (2)
C(7)	0.7933 (6)	0.0877 (3)	0.4944 (6)	3.4 (2)
C(8)	0.6784 (5)	0.2037 (3)	0.6546 (6)	3.0 (2)
C(9)	0.7113 (5)	0.1696 (4)	0.2469 (7)	3.5 (2)
C(10)	0.1905 (4)	0.3697 (2)	0.3849 (5)	2.1 (2)
C(11)	0.0861 (5)	0.3466 (3)	0.4083 (6)	2.7 (2)
C(12)	−0.0354 (5)	0.4063 (3)	0.3578 (6)	3.2 (2)
C(13)	−0.0068 (5)	0.4670 (3)	0.3058 (7)	3.2 (2)
C(14)	0.1308 (5)	0.4456 (3)	0.3233 (6)	2.5 (2)
C(15)	0.0802 (4)	0.2577 (2)	0.0507 (5)	2.0 (2)
C(16)	−0.0609 (4)	0.2776 (3)	0.0297 (6)	2.6 (2)
C(17)	−0.1232 (5)	0.3504 (3)	−0.0348 (6)	3.0 (2)
C(18)	−0.0210 (5)	0.3778 (3)	−0.0535 (6)	3.1 (2)
C(19)	0.1014 (5)	0.3206 (3)	−0.0015 (5)	2.3 (2)
C(20)	0.4233 (5)	0.3435 (3)	0.6567 (5)	2.6 (2)
C(21)	0.3848 (6)	0.4333 (3)	0.6936 (6)	3.8 (2)
C(22)	0.3740 (7)	0.3006 (4)	0.7407 (6)	4.0 (3)
C(23)	0.2248 (5)	0.1166 (3)	−0.0633 (5)	2.5 (2)
C(24)	0.0916 (6)	0.0999 (4)	−0.1837 (7)	4.0 (3)
C(25)	0.2827 (6)	0.1586 (3)	−0.1396 (6)	3.4 (2)
C(26)	0.1214 (5)	0.1100 (3)	0.1701 (6)	2.7 (2)
C(27)	0.0849 (6)	0.1426 (3)	0.3129 (7)	3.4 (2)
C(28)	0.2028 (7)	0.0240 (3)	0.1823 (7)	3.9 (3)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(a_ia_j)$.

Complex **5** contains two inequivalent phosphorus atoms as indicated by the ^{31}P NMR spectrum, and its mass spectrum corresponds with the loss of one carbonyl from the parent complex. The ^1H NMR spectrum shows eight ferrocenyl protons, four characteristic C*H*Me$_2$ protons, one CH_2 multiplet, seven methyl groups, and one hydride. All these data suggest a formula such as $Os_3(CO)_8(H)[(C_5H_4PPr^i_2)Fe(C_5H_4PPr^iCHMeCH_2CO)]$. An X-ray diffraction study unequivocally established the molecular structure of **5**, and an ORTEP diagram of the structure is shown in Figure 1.

The structure of **5** contains a closed Os_3 metal framework with four carbonyls on Os(3) and two each on Os(1) and Os(2). All the Os centers show a distorted octahedral geometry although, formally, Os(1) and Os(2) are 7-coordinated if the Os(1)–Os(2) bond is included. The whole cluster is electron precise. The acyl group (C(19)–O(1)) and bridging hydride H(1) are on opposite sides of the Os_3 plane. H(1) was located in the structure refinement. As is usual for bridged bonds, Os(1)–Os(2) (2.9250 (6) Å) is longer than Os(1)–Os(3) (2.8610 (6) Å) and Os(2)–Os(3) (2.8776 (7) Å). One compilation lists similarly bridged Os–Os bonds in $Os_3(CO)_{10}H(X)$ as ranging from 2.884 (2) Å (X = $PhCH_2CO$) to 2.945 (1) Å (X = MeC_6H_4NHCO).[7] A unique feature of **5**, however, is the existence of the bridging di(tertiary phosphine) ligand, which occupies two equatorial coordination sites, in addition to the H(X)

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(6) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

(7) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

Table VI. Bond Lengths (Å) with Estimated Standard Deviations for 6[a]

Os(1)–Os(2)	2.9382 (7)	P(1)–C(20)	1.865 (5)
Os(1)–Os(3)	2.8858 (9)	P(2)–C(15)	1.812 (4)
Os(1)–P(1)	2.404 (1)	P(2)–C(23)	1.863 (5)
Os(1)–P(2)	2.368 (1)	P(2)–C(26)	1.861 (5)
Os(1)–C(1)	1.872 (5)	O(1)–C(1)	1.140 (6)
Os(1)–C(2)	1.896 (5)	O(2)–C(2)	1.150 (6)
Os(1)–H(1)	1.88	O(3)–C(3)	1.145 (6)
Os(2)–Os(3)	2.9055 (8)	O(4)–C(4)	1.142 (6)
Os(2)–P(1)	2.395 (1)	O(5)–C(5)	1.142 (6)
Os(2)–C(3)	1.927 (5)	O(6)–C(6)	1.125 (6)
Os(2)–C(4)	1.902 (5)	O(7)–C(7)	1.138 (6)
Os(2)–C(5)	1.898 (5)	O(8)–C(8)	1.129 (6)
Os(2)–H(1)	1.67	O(9)–C(9)	1.126 (6)
Os(3)–C(6)	1.933 (5)	C(10)–C(11)	1.442 (6)
Os(3)–C(7)	1.914 (6)	C(10)–C(14)	1.441 (6)
Os(3)–C(8)	1.954 (6)	C(11)–C(12)	1.424 (7)
Os(3)–C(9)	1.952 (6)	C(12)–C(13)	1.427 (8)
Fe(1)–C(10)	2.026 (5)	C(13)–C(14)	1.411 (7)
Fe(1)–C(11)	2.051 (5)	C(15)–C(16)	1.440 (6)
Fe(1)–C(12)	2.063 (5)	C(15)–C(19)	1.419 (6)
Fe(1)–C(13)	2.058 (5)	C(16)–C(17)	1.406 (7)
Fe(1)–C(14)	2.046 (5)	C(17)–C(18)	1.440 (7)
Fe(1)–C(15)	2.034 (4)	C(18)–C(19)	1.407 (7)
Fe(1)–C(16)	2.037 (5)	C(20)–C(21)	1.536 (7)
Fe(1)–C(17)	2.061 (5)	C(20)–C(22)	1.526 (7)
Fe(1)–C(18)	2.045 (5)	C(23)–C(24)	1.520 (7)
Fe(1)–C(19)	2.020 (4)	C(23)–C(25)	1.532 (7)
Fe(1)–Cp(1)	1.649 (2)	C(26)–C(27)	1.509 (7)
Fe(1)–Cp(2)	1.642 (2)	C(26)–C(28)	1.535 (7)
P(1)–C(10)	1.812 (4)		

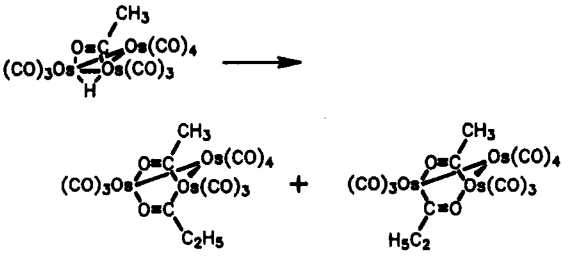
[a] Here and elsewhere, Cp(1) and Cp(2) refer to the unweighted centroids of the C(10–14) and C(15–19) cyclopentadienyl rings, respectively.

Table VII. Bond Angles (deg) with Estimated Standard Deviations for 6

Os(2)–Os(1)–Os(3)	59.84 (2)	C(6)–Os(3)–C(8)	96.1 (2)
Os(2)–Os(1)–P(1)	52.10 (3)	C(6)–Os(3)–C(9)	94.4 (2)
Os(2)–Os(1)–P(2)	114.25 (3)	C(7)–Os(3)–C(8)	85.7 (2)
Os(2)–Os(1)–C(1)	138.3 (2)	C(7)–Os(3)–C(9)	87.7 (2)
Os(2)–Os(1)–C(2)	115.1 (2)	C(8)–Os(3)–C(9)	168.7 (2)
Os(2)–Os(1)–H(1)	32	Cp(1)–Fe(1)–Cp(2)	179.4 (1)
Os(3)–Os(1)–P(1)	88.25 (3)	Os(1)–P(1)–Os(2)	75.50 (3)
Os(3)–Os(1)–P(2)	161.40 (3)	Os(1)–P(1)–C(10)	120.9 (1)
Os(3)–Os(1)–C(1)	96.6 (2)	Os(1)–P(1)–C(20)	126.6 (2)
Os(3)–Os(1)–C(2)	79.4 (1)	Os(2)–P(1)–C(10)	118.4 (1)
Os(3)–Os(1)–H(1)	89	Os(2)–P(1)–C(20)	117.2 (2)
P(1)–Os(1)–P(2)	101.53 (4)	C(10)–P(1)–C(20)	98.8 (2)
P(1)–Os(1)–C(1)	97.3 (2)	Os(1)–P(2)–C(15)	119.3 (1)
P(1)–Os(1)–C(2)	166.1 (2)	Os(1)–P(2)–C(23)	111.6 (2)
P(1)–Os(1)–H(1)	61	Os(1)–P(2)–C(26)	116.9 (2)
P(2)–Os(1)–C(1)	97.7 (2)	C(15)–P(2)–C(23)	100.7 (2)
P(2)–Os(1)–C(2)	88.7 (1)	C(15)–P(2)–C(26)	104.4 (2)
P(2)–Os(1)–H(1)	83	C(23)–P(2)–C(26)	101.4 (2)
C(1)–Os(1)–C(2)	90.5 (2)	Os(1)–C(1)–O(1)	176.4 (5)
C(1)–Os(1)–H(1)	157	Os(1)–C(2)–O(2)	176.2 (5)
C(2)–Os(1)–H(1)	112	Os(2)–C(3)–O(3)	172.6 (5)
Os(1)–Os(2)–Os(3)	59.18 (2)	Os(2)–C(4)–O(4)	172.2 (4)
Os(1)–Os(2)–P(1)	52.40 (3)	Os(2)–C(5)–O(5)	178.9 (5)
Os(1)–Os(2)–C(3)	118.1 (2)	Os(3)–C(6)–O(6)	178.1 (5)
Os(1)–Os(2)–C(4)	119.4 (1)	Os(3)–C(7)–O(7)	176.4 (5)
Os(1)–Os(2)–C(5)	128.6 (2)	Os(3)–C(8)–O(8)	170.6 (5)
Os(1)–Os(2)–H(1)	36	Os(3)–C(9)–O(9)	174.1 (5)
Os(3)–Os(2)–P(1)	87.98 (3)	P(1)–C(10)–C(11)	124.1 (3)
Os(3)–Os(2)–C(3)	87.1 (2)	P(1)–C(10)–C(14)	128.8 (3)
Os(3)–Os(2)–C(4)	172.0 (1)	C(11)–C(10)–C(14)	107.0 (4)
Os(3)–Os(2)–C(5)	86.4 (2)	C(10)–C(11)–C(12)	108.1 (4)
Os(3)–Os(2)–H(1)	92	C(11)–C(12)–C(13)	107.9 (4)
P(1)–Os(2)–C(3)	170.4 (2)	C(12)–C(13)–C(14)	108.7 (4)
P(1)–Os(2)–C(4)	96.9 (1)	C(10)–C(14)–C(13)	108.3 (4)
P(1)–Os(2)–C(5)	93.4 (2)	P(2)–C(15)–C(16)	129.2 (3)
P(1)–Os(2)–H(1)	63	P(2)–C(15)–C(19)	124.5 (3)
C(3)–Os(2)–C(4)	87.1 (2)	C(16)–C(15)–C(19)	106.3 (4)
C(3)–Os(2)–C(5)	94.5 (2)	C(15)–C(16)–C(17)	109.0 (4)
C(3)–Os(2)–H(1)	109	C(16)–C(17)–C(18)	107.6 (4)
C(4)–Os(2)–C(5)	99.5 (2)	C(17)–C(18)–C(19)	107.5 (4)
C(4)–Os(2)–H(1)	85	C(15)–C(19)–C(18)	109.6 (4)
C(5)–Os(2)–H(1)	156	P(1)–C(20)–C(21)	111.9 (4)
Os(1)–Os(3)–Os(2)	60.97 (2)	P(1)–C(20)–C(22)	112.1 (4)
Os(1)–Os(3)–C(6)	155.1 (2)	C(21)–C(20)–C(22)	111.5 (4)
Os(1)–Os(3)–C(7)	101.0 (2)	P(2)–C(23)–C(24)	113.2 (3)
Os(1)–Os(3)–C(8)	84.3 (1)	P(2)–C(23)–C(25)	113.1 (3)
Os(1)–Os(3)–C(9)	87.9 (2)	C(24)–C(23)–C(25)	108.9 (4)
Os(2)–Os(3)–C(6)	94.9 (2)	P(2)–C(26)–C(27)	114.3 (4)
Os(2)–Os(3)–C(7)	158.9 (2)	P(2)–C(26)–C(28)	110.6 (3)
Os(2)–Os(3)–C(8)	102.2 (1)	C(27)–C(26)–C(28)	111.4 (4)
Os(2)–Os(3)–C(9)	81.0 (2)	Os(1)–H(1)–Os(2)	112
C(6)–Os(3)–C(7)	103.9 (2)		

bridge in the Os_3 cluster. We have recently described an analogous Ru_3 cluster in which the bridges comprise OH, Cl, and $Fc'(PPr^i_2)_2$.[4] The carbonyl C–Os distances of 5 show little variation (average 1.90 Å) with Os(1)–C(25) being the shortest at 1.86 (1) Å and Os(2)–C(26) the longest at 1.94 (1) Å. The Os(2)–C(19) bond involving the acyl carbon atom is, as expected, 0.1 Å longer at 2.039 (8) Å. All the carbonyl C–O distances are the same (average 1.15 Å), and again, the acyl C–O distance is 0.1 Å longer at 1.289 (9) Å. The acyl Os(2)–C(19)–O(1) angle is 119.4 (6)°, consistent with sp^2 hybridization at C(19). The Os(1)–P(1) bond distance at 2.389 (2) Å is 0.05 Å longer than Os(2)–P(2) at 2.325 (2) Å probably due to the formation of a stable 5-membered ring at Os(2). The two Cp rings show the common eclipsed configuration.[8] The rings are also opened up slightly, the ring tilt angle being 5.7°, which is comparable with that found in 2 (R = Fc, 5.9°)[3] but smaller than that in 4 (11.8°).[3]

Many Os_3 and Ru_3 acyl complexes analogous to 5 are known,[9] but these are usually synthesized either by the oxidative addition of aldehydes to $M_3(CO)_{12}$ (or to activated derivatives such as $Os_3(CO)_{10}(MeCN)_2$[9c,d]) or by nucleophilic attack of Nu^- (amines, OR^-, R^-) at a CO group of $M_3(CO)_{12}$ followed by decarbonylation and protonation.[9a,e] Insertion of a CO into a M–alkyl bond might be involved in the formation of derivatives such as shown in eq 1 but these reactions involve very forcing conditions (136 atm of C_2H_4/CO (68/1), 140 °C, 48 h).[9e]



(1)

In the present study CO insertation into an Os–alkyl bond occurs under mild conditions (1 atm, 120 °C, 7.5 h) and the result is certainly unprecedented and unexpected because such CO insertion is not a facile process when third row transition metal clusters are involved.[10] However, insertion of CO into the more reactive methylene moiety is known for both Ru_3[11] and Os_3[12] clusters, but these reactions do not afford oxygen-bonded acyl complexes, and therefore the presence of external carbon

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[8] Chacon, S. T.; Cullen, W. R.; Bruce, M. I.; Shawkataly, O. B.; Einstein, F. W. B.; Jones, R. H.; Willis, A. C. *Can. J. Chem.* **1990**, *68*, 2001 and references therein.

[9] (a) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243. (b) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1102. (c) Azam, K. A.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 472. (d) Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 91. (e) Jensen, C. M.; Chen, Y. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4046. (f) Kampe, C. E.; Boag, N. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 2896.

Table VIII. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å²) for 7[a]

atom	*x*	*y*	*z*	B_{eq}
Os(1)	0.21027 (2)	0.05006 (2)	0.19178 (2)	2.67 (1)
Os(2)	0.39695 (2)	0.01770 (3)	0.29397 (3)	4.24 (2)
Os(3)	0.37797 (2)	−0.00107 (2)	0.11189 (3)	3.37 (2)
Fe(1)	0.24505 (9)	−0.1809 (1)	0.3594 (1)	4.24 (7)
P(1)	0.2618 (1)	−0.1045 (1)	0.1528 (2)	2.7 (1)
P(2)	0.0995 (1)	0.0021 (2)	0.2846 (1)	3.1 (1)
O(1)	0.0767 (4)	0.0805 (5)	0.0383 (5)	5.6 (4)
O(2)	0.1985 (5)	0.2641 (5)	0.2262 (6)	9.0 (6)
O(3)	0.5977 (5)	−0.0394 (7)	0.2926 (6)	9.7 (6)
O(4)	0.4036 (6)	0.0366 (7)	0.4857 (6)	10.2 (6)
O(5)	0.4242 (6)	0.2322 (6)	0.2697 (8)	12.7 (7)
O(6)	0.5243 (4)	−0.1541 (5)	0.1164 (5)	7.3 (5)
O(7)	0.3287 (5)	−0.0056 (6)	−0.0797 (5)	7.4 (5)
O(8)	0.5111 (5)	0.1670 (6)	0.1004 (6)	8.6 (5)
C(1)	0.3606 (5)	−0.1297 (6)	0.3051 (5)	3.3 (4)
C(2)	0.2995 (5)	−0.1743 (6)	0.2434 (6)	3.2 (4)
C(3)	0.2844 (6)	−0.2725 (6)	0.2685 (7)	4.3 (5)
C(4)	0.3366 (7)	−0.2868 (7)	0.3460 (7)	5.0 (6)
C(5)	0.3832 (6)	−0.2017 (8)	0.3690 (6)	5.0 (6)
C(6)	0.1369 (6)	−0.0877 (7)	0.3615 (6)	4.1 (5)
C(7)	0.1997 (7)	−0.0743 (8)	0.4338 (6)	5.5 (6)
C(8)	0.2078 (9)	−0.160 (1)	0.4801 (8)	7.6 (8)
C(9)	0.1522 (9)	−0.227 (1)	0.440 (1)	7.6 (9)
C(10)	0.1062 (6)	−0.1858 (8)	0.3663 (7)	5.6 (6)
C(11)	0.2088 (5)	−0.1914 (6)	0.0780 (6)	3.5 (4)
C(12)	0.1565 (6)	−0.1488 (7)	0.0004 (7)	4.8 (5)
C(13)	0.2825 (6)	−0.2592 (6)	0.0475 (7)	5.1 (5)
C(14)	−0.0085 (5)	−0.0476 (6)	0.2371 (6)	3.9 (4)
C(15)	−0.0738 (6)	0.0253 (8)	0.1928 (7)	6.0 (6)
C(16)	0.0075 (6)	−0.1309 (7)	0.1762 (7)	5.9 (6)
C(17)	0.0603 (7)	0.1013 (6)	0.3482 (6)	4.7 (5)
C(18)	−0.0179 (8)	0.0748 (9)	0.4027 (8)	8.1 (8)
C(19)	0.1359 (8)	0.1499 (9)	0.4052 (8)	7.9 (8)
C(20)	0.1246 (5)	0.0665 (6)	0.0987 (6)	3.6 (4)
C(21)	0.2026 (6)	0.1851 (7)	0.2145 (7)	5.3 (6)
C(22)	0.5238 (7)	−0.0165 (8)	0.2922 (7)	6.1 (6)
C(23)	0.4003 (8)	0.028 (1)	0.413 (1)	7.4 (7)
C(24)	0.4160 (7)	0.1517 (9)	0.2791 (9)	7.3 (7)
C(25)	0.4703 (6)	−0.0952 (7)	0.1144 (6)	4.4 (5)
C(26)	0.3465 (6)	−0.0050 (7)	−0.0092 (7)	4.5 (5)
C(27)	0.4607 (6)	0.1050 (8)	0.1043 (7)	5.8 (6)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(a_ia_j)$.

Table IX. Bond Lengths (Å) with Estimated Standard Deviations for 7

Os(1)–Os(2)	3.1038 (6)	Fe(1)–Cp(2)	1.657
Os(1)–Os(3)	2.9387 (6)	P(1)–C(2)	1.788 (9)
Os(1)–P(1)	2.392 (2)	P(1)–C(11)	1.828 (9)
Os(1)–P(2)	2.369 (2)	P(2)–C(6)	1.81 (1)
Os(1)–C(20)	1.87 (1)	P(2)–C(14)	1.837 (8)
Os(1)–C(21)	1.93 (1)	P(2)–C(17)	1.834 (9)
Os(1)–H(1)	1.89	O(1)–C(20)	1.16 (1)
Os(1)–H(2)	1.83	O(2)–C(21)	1.13 (1)
Os(2)–Os(3)	2.8823 (8)	O(3)–C(22)	1.13 (1)
Os(2)–C(1)	2.145 (9)	O(4)–C(23)	1.16 (1)
Os(2)–C(22)	1.92 (1)	O(5)–C(24)	1.15 (1)
Os(2)–C(23)	1.88 (1)	O(6)–C(25)	1.14 (1)
Os(2)–C(24)	1.92 (1)	O(7)–C(26)	1.13 (1)
Os(2)–H(1)	1.69	O(8)–C(27)	1.15 (1)
Os(3)–P(1)	2.365 (2)	C(1)–C(2)	1.42 (1)
Os(3)–C(25)	1.89 (1)	C(1)–C(5)	1.45 (1)
Os(3)–C(26)	1.93 (1)	C(2)–C(3)	1.45 (1)
Os(3)–C(27)	1.93 (1)	C(3)–C(4)	1.41 (1)
Os(3)–H(2)	1.78	C(4)–C(5)	1.41 (1)
Fe(1)–C(1)	2.085 (8)	C(6)–C(7)	1.42 (1)
Fe(1)–C(2)	2.057 (9)	C(6)–C(10)	1.45 (1)
Fe(1)–C(3)	2.042 (9)	C(7)–C(8)	1.41 (1)
Fe(1)–C(4)	2.024 (9)	C(8)–C(9)	1.37 (2)
Fe(1)–C(5)	2.041 (8)	C(9)–C(10)	1.43 (2)
Fe(1)–C(6)	2.057 (8)	C(11)–C(12)	1.52 (1)
Fe(1)–C(7)	2.04 (1)	C(11)–C(13)	1.54 (1)
Fe(1)–C(8)	2.05 (1)	C(14)–C(15)	1.53 (1)
Fe(1)–C(9)	2.05 (1)	C(14)–C(16)	1.54 (1)
Fe(1)–C(10)	2.049 (9)	C(17)–C(18)	1.53 (1)
Fe(1)–Cp(1)	1.651	C(17)–C(19)	1.53 (1)

monoxide is necessary to drive the reaction. The formation of 5 from its probable precursors C and D (Scheme III) is an isomerization reaction.

Complex 6 shows the parent ion at 1198 in the mass spectrum, corresponding to the loss of one CO and one Pr^i group from the parent complex. The ^1H NMR spectrum shows the presence of eight ferrocenyl protons, three isopropyl groups, and one hydride. The two ^{31}P NMR resonances are close in chemical shift, but they are nevertheless consistent with the determined structure. The formulation of 6 as $Os_3(CO)_9(H)[(C_5H_4PPr^i_2)Fe(C_5H_4PPr^i)]$ has been confirmed by an X-ray crystallographic study, and an ORTEP diagram of the molecular structure of 6 is depicted in Figure 2.

The structure of 6 also contains a closed Os_3 metal framework with four carbonyls on Os(3), three on Os(2), and two on Os(1). One end of the phosphine ligand (P(2)) is still attached to Os(1), while at the other end P(1) has lost an isopropyl group and now bridges the Os(1)–Os(2) bond as a phosphido moiety. Again, all the Os centers show distorted octahedral geometry if the Os(1)–Os(2) bond is excluded and the whole cluster is electron precise. The hydride was located in the refinement. The phosphido P(1) and hydride H(1) are on opposite sides of the Os_3 plane. As in 5, C(9) is displaced toward Os(2) (Os(2)–Os(3)–C(9) = 81.0 (2)°) and C(8) toward Os(1) (Os(1)–Os(3)–C(8) = 84.3 (1)°). Again the bridged Os–Os bond (2.9382 (7) Å) is longer than Os(1)–Os(3) (2.8858 (9) Å) and Os(2)–Os(3) (2.9055 (8) Å). The carbonyl C–Os distances show some variation (the data for 6 are better than for 5) with two axial carbonyls at Os(3) being the longest (1.954 (6) and 1.952 (6) Å) and Os(1)–C(1) being the shortest at 1.872 (5) Å; the others average to 1.912 Å. All the C–O distances are effectively the same (average 1.137 Å), but the Os–C–O angles are not. The Os(2)–C(4)–O(4), Os(2)–C(3)–O(3), and Os(3)–C(8)–O(8) angles average to 171.8°, smaller than the others (average 176.7°), but there is no obvious explanation for this bending. The phosphido P(1) bridges Os(1) and Os(2) symmetrically (P(1)–Os(1) = 2.404 (1) Å and P(1)–Os(2) = 2.395 (1) Å), and these bond lengths are longer than P(2)–Os(1) at 2.368 (1) Å. The two Cp rings have a small ring tilt angle of 2.1°, and overall the data indicate that there is much less distortion of the phosphine ligand in 6 compared to 5 and that there is little strain in this structure.

Complex 7 shows ^{31}P resonances at 70.1 and 22.6 ppm with a coupling of 18.7 Hz. The mass spectrum gives the parent ion at 1170, corresponding to the loss of two CO and one Pr^i group from the parent complex. The ^1H NMR spectrum shows the presence of only seven ferrocenyl protons, three intact isopropyl groups and two hydrides. A formula such as $H_2Os_3(CO)_8[(C_5H_4PPr^i)Fe(C_5H_3PPr^i_2)]$ or $H_2Os_3(CO)_8[(C_5H_3PPr^i)Fe(C_5H_4PPr^i_2)]$ is indicated by the data, but the exact structure was only established by an X-ray diffraction study. An ORTEP diagram of the molecular structure of 7 is shown in Figure 3.

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(10) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 371.

(11) Nucciarone, D.; Taylor, N. J.; Carty, A. J.; Tiripicchio, A.; Camellini, M. T.; Sappa, E. *Organometallics* 1988, *7*, 118.

(12) Stevert, A. C.; Strictland, D. S.; Shapley, J. R.; Steinmetz, G. R. Geoffroy, G. L. *Organometallics* 1982, *1*, 214.

Table X. Bond Angles (deg) with Estimated Standard Deviations for 7

Os(2)–Os(1)–Os(3)	56.90 (2)	Os(1)–P(1)–Os(3)	76.31 (6)
Os(2)–Os(1)–P(1)	73.63 (5)	Os(1)–P(1)–C(2)	112.0 (3)
Os(2)–Os(1)–P(2)	104.81 (5)	Os(1)–P(1)–C(11)	130.1 (3)
Os(2)–Os(1)–C(20)	159.7 (3)	Os(3)–P(1)–C(2)	111.7 (3)
Os(2)–Os(1)–C(21)	96.2 (3)	Os(3)–P(1)–C(11)	120.8 (3)
Os(3)–Os(1)–P(1)	51.43 (5)	C(2)–P(1)–C(11)	104.0 (4)
Os(3)–Os(1)–P(2)	146.46 (5)	Os(1)–P(2)–C(6)	115.3 (3)
Os(3)–Os(1)–C(20)	103.0 (3)	Os(1)–P(2)–C(14)	117.7 (3)
Os(3)–Os(1)–C(21)	112.4 (3)	Os(1)–P(2)–C(17)	112.5 (3)
P(1)–Os(1)–P(2)	98.51 (7)	C(6)–P(2)–C(14)	102.6 (4)
P(1)–Os(1)–C(20)	96.6 (3)	C(6)–P(2)–C(17)	104.6 (4)
P(1)–Os(1)–C(21)	163.7 (3)	C(14)–P(2)–C(17)	102.4 (4)
P(2)–Os(1)–C(20)	94.1 (3)	Os(2)–C(1)–C(2)	121.1 (6)
P(2)–Os(1)–C(21)	96.3 (3)	Os(2)–C(1)–C(5)	133.2 (7)
C(20)–Os(1)–C(21)	88.9 (4)	C(2)–C(1)–C(5)	105.7 (8)
Os(1)–Os(2)–Os(3)	58.66 (2)	P(1)–C(2)–C(1)	116.7 (6)
Os(1)–Os(2)–C(1)	88.2 (2)	P(1)–C(2)–C(3)	133.9 (7)
Os(1)–Os(2)–C(22)	147.6 (3)	C(1)–C(2)–C(3)	109.4 (8)
Os(1)–Os(2)–C(23)	117.5 (3)	C(2)–C(3)–C(4)	106.7 (9)
Os(1)–Os(2)–C(24)	85.6 (3)	C(3)–C(4)–C(5)	109.0 (8)
Os(3)–Os(2)–C(1)	89.4 (2)	C(1)–C(5)–C(4)	109.2 (9)
Os(3)–Os(2)–C(22)	89.0 (3)	P(2)–C(6)–C(7)	126.3 (8)
Os(3)–Os(2)–C(23)	175.9 (4)	P(2)–C(6)–C(10)	128.1 (8)
Os(3)–Os(2)–C(24)	88.3 (4)	C(7)–C(6)–C(10)	105.5 (9)
C(1)–Os(2)–C(22)	90.4 (4)	C(6)–C(7)–C(8)	109 (1)
C(1)–Os(2)–C(23)	89.0 (5)	C(7)–C(8)–C(9)	109 (1)
C(1)–Os(2)–C(24)	173.8 (4)	C(8)–C(9)–C(10)	109 (1)
C(22)–Os(2)–C(23)	94.8 (5)	C(6)–C(10)–C(9)	108 (1)
C(22)–Os(2)–C(24)	95.3 (4)	P(1)–C(11)–C(12)	115.0 (6)
C(23)–Os(2)–C(24)	92.9 (6)	P(1)–C(11)–C(13)	109.8 (6)
Os(1)–Os(3)–Os(2)	64.44 (2)	C(12)–C(11)–C(13)	108.2 (8)
Os(1)–Os(3)–P(1)	52.26 (5)	P(2)–C(14)–C(15)	115.0 (6)
Os(1)–Os(3)–C(25)	141.6 (3)	P(2)–C(14)–C(16)	112.0 (6)
Os(1)–Os(3)–C(26)	106.7 (3)	C(15)–C(14)–C(16)	109.8 (9)
Os(1)–Os(3)–C(27)	113.0 (3)	P(2)–C(17)–C(18)	113.9 (8)
Os(2)–Os(3)–P(1)	78.44 (6)	P(2)–C(17)–C(19)	114.6 (6)
Os(2)–Os(3)–C(25)	91.6 (3)	C(18)–C(17)–C(19)	108 (1)
Os(2)–Os(3)–C(26)	171.0 (3)	Os(1)–C(20)–O(1)	174.9 (8)
Os(2)–Os(3)–C(27)	88.8 (3)	Os(1)–C(21)–O(2)	179 (1)
P(1)–Os(3)–C(25)	95.5 (3)	Os(2)–C(22)–O(3)	178 (1)
P(1)–Os(3)–C(26)	97.5 (3)	Os(2)–C(23)–O(4)	179 (1)
P(1)–Os(3)–C(27)	163.7 (3)	Os(2)–C(24)–O(5)	178 (1)
C(25)–Os(3)–C(26)	96.7 (4)	Os(3)–C(25)–O(6)	178.0 (8)
C(25)–Os(3)–C(27)	95.0 (4)	Os(3)–C(26)–O(7)	179 (1)
C(26)–Os(3)–C(27)	93.6 (4)	Os(3)–C(27)–O(8)	179 (1)
Cp(1)–Fe(1)–Cp(2)	177.2		

The structure of 7 consists of a closed Os_3 triangle with one face capped by the bidentate phosphine–phosphido moiety and by the metalated Cp(1) ring to which the phosphido group is attached. Os(2) and Os(3) are each bonded to three carbonyls, and Os(1) is bonded to two. The Os–Os bond distances show a large variation with Os(1)–Os(2) at 3.1038 (6) Å being the longest, Os(2)–Os(3) at 2.8823 (8) Å being the shortest, and Os(1)–Os(3) being of intermediate length at 2.9387 (6) Å. As expected, the two hydrides, which were located in the structure refinement, bridge the two longer Os–Os bonds. The phosphido moiety bridges the Os(1)–Os(3) bond approximately symmetrically (Os(1)–P(1) = 2.392 (2) Å, Os(3)–P(1) = 2.365 (2) Å), and the Os(1)Os(3)P(1) plane is almost perpendicular to the Os_3 plane (84.87°). The C(1)–Os(2) bond is trans to carbonyl C(24)O(5), and the length of 2.145 (9) Å is typical of an Os–C σ bond. The phosphine occupies a pseudo-axial coordination site (P(2) is 1.1811 Å above the Os_3 plane). The Os–C(carbonyl) bond lengths range from 1.87 (1) to 1.93 (1) Å, and all Os–C–O angles are linear.

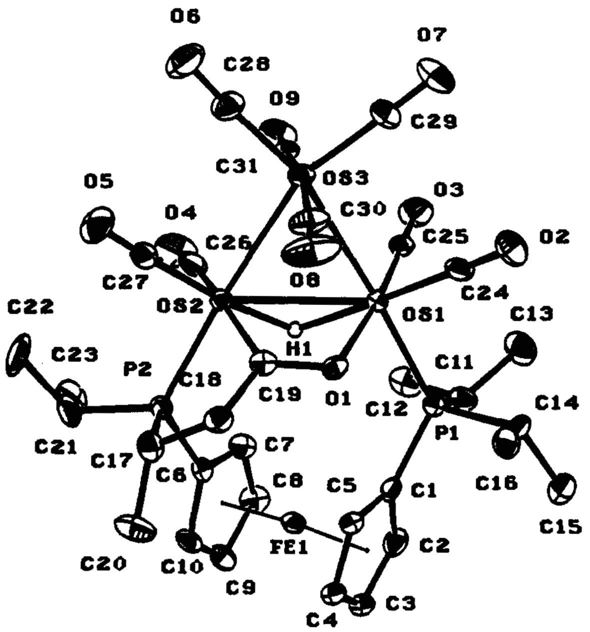
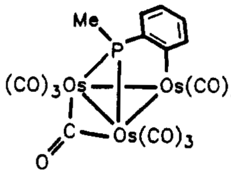


Figure 1. ORTEP diagram for 5, with 33% probability thermal ellipsoids.

In the ferrocenyl moiety, all the Fe–C bonds are equal and normal (average 2.05 Å). The Cp(1) plane is nearly perpendicular to the Os_3 plane (86.88°), and the two Cp rings are parallel with a small ring tilt angle of 2.58°. P(2), P(1), and Os(2) (0.0749 Å) are essentially coplanar with the Cp planes to which they are bound.

This structure may be compared with that of $Os_3(CO)_9(\mu\text{-}CO)(PMe)(C_6H_4)$, 11, which was obtained by pyrolyzing $Os_3(CO)_{11}(PMePh_2)$.[1b] The notable differences are as follows: (1) The bridging carbonyl in 11 is replaced by two bridging hydrides in 7. (2) The six-membered C_6H_4 ring in 11 is replaced by a C_5H_3 ring which is also coordinated to a $Fe(C_5H_4PPr^i_2)$ moiety with the phosphine replacing one carbonyl. (3) The formation of 11 involves an orthometalation of a C_6H_5 group followed by the reductive elimination of a benzene molecule, while 7 is unlikely to be formed by way of a ferrocenyl C–H activation as the first step as is discussed below (Scheme IV).

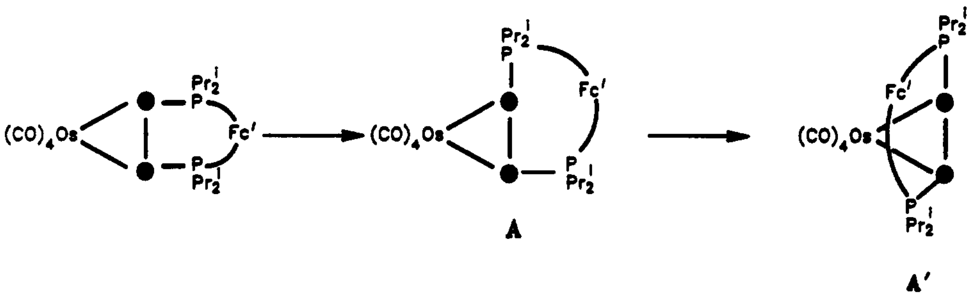


11

Complex 8 shows ^{31}P resonances at 51.0 and 18.7 ppm with a coupling of 3.6 Hz. Its mass spectrum is identical with that of complex 5, while the ^1H NMR spectrum shows eight ferrocenyl protons, four $CHMe_2$ protons, seven methyl groups, one CH_2 multiplet, and one hydride at −13.57 ppm. These data suggest that 8 is a diastereoisomer of 5 differing in the configuration of the CHMe group (Scheme III). Complex 5 is the major isomer (5:1) present in the pyrolysis mixture, and this may be understood if steric interactions between the methyl and the isopropyl group in the Os(2)P(2)C(17)C(18)C(19) 5-membered ring are considered. Also in 5 and 8, the P(1) resonances have almost the same chemical shifts (Δ = 0.5 ppm), while the P(2) resonances differ by 8.2 ppm; this seems to be consistent with the change in the configuration at the C(17) atom.

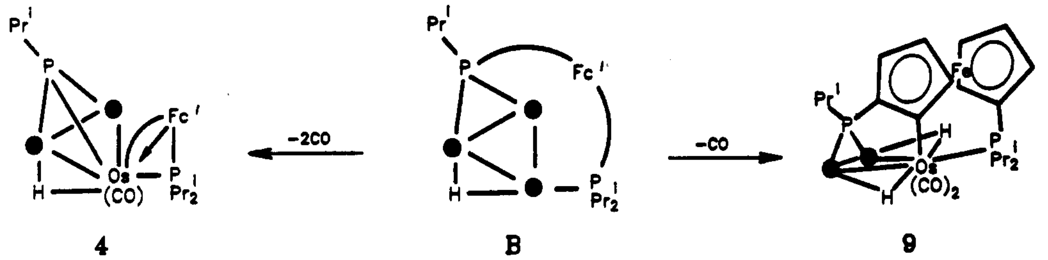
Complex 9 shows a mass spectrum identical with that of 7. The ^{31}P resonances are at 76.3 and 40.4 ppm with

Scheme I[a]



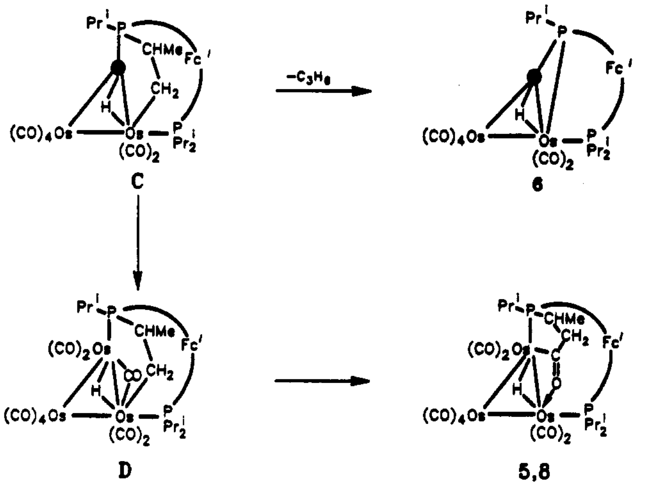
[a] ● = $Os(CO)_3$.

Scheme II[a]



[a] ● = $Os(CO)_3$.

Scheme III[a]



[a] ● = $Os(CO)_3$.

a coupling of 2.8 Hz. The ^1H NMR spectrum shows the presence of only seven ferrocenyl protons, three intact isopropyl groups, and two hydrides. The exact structure can only be determined from an X-ray diffraction study, but it is believed to have that shown in Scheme II.

Complex **10** also shows a mass spectrum that is identical with **7** and with **9**. The ^{31}P NMR spectrum shows resonances at 28.2 and 6.0 ppm with a coupling of 12.8 Hz. The ^1H NMR spectrum again shows the presence of seven ferrocenyl protons, three intact isopropyl groups, and two hydrides. Clearly, this is another isomer of **7** and **9**. A probable structure is shown in Scheme IV.

Two reaction pathways seem to account for the products of the thermolysis of $Ru_3(CO)_{10}[Fc'(PPr^i_2)_2]$.[4] Both of these involve initial β-C–H activation of an isopropyl group followed by propene elimination and concomitant formation of a Ru–P bond, the essential first step being the movement of one end of the ligand from an equatorial to an axial position. The thermolysis of $Os_3(CO)_{10}[Fc'(PPr^i_2)_2]$ is more complicated; more products are produced

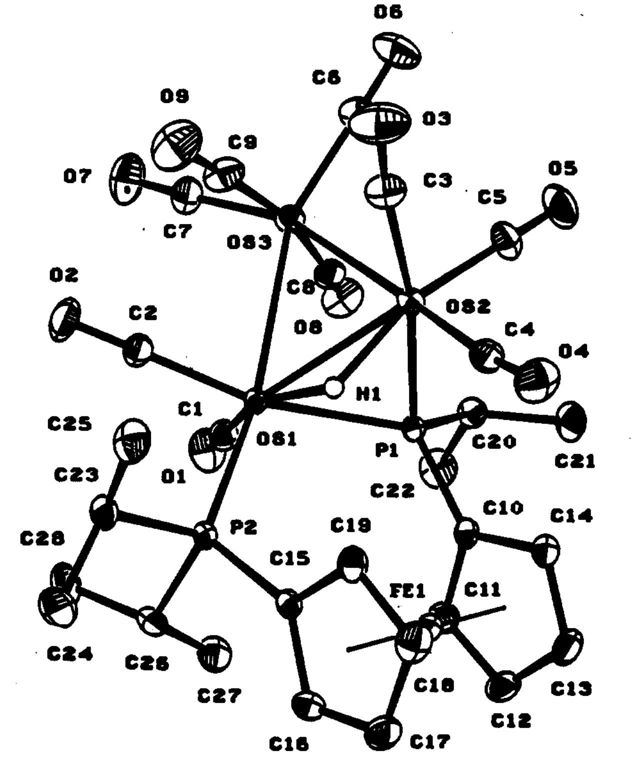


Figure 2. ORTEP diagram for **6**, with 33% probability thermal elipsoids.

some involving CO insertion and metalation of Cp rings. The first step of the reaction appears not only to involve movement of one phosphorus atom to form A, the analogue of the initial ruthenium intermediate, but also movement of both phosphorus atoms to form A′ (Scheme I). *In this scheme and those after it, compounds designated by letters are proposed intermediates and have not been isolated.*

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(13) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Can. J. Chem.*, in press.
(14) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. *Organometallics* **1992**, *11*, 3434.

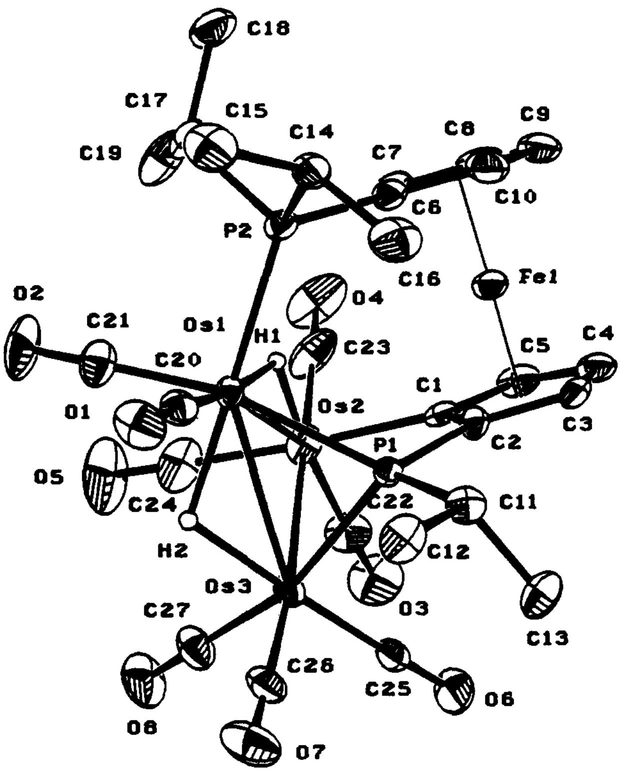


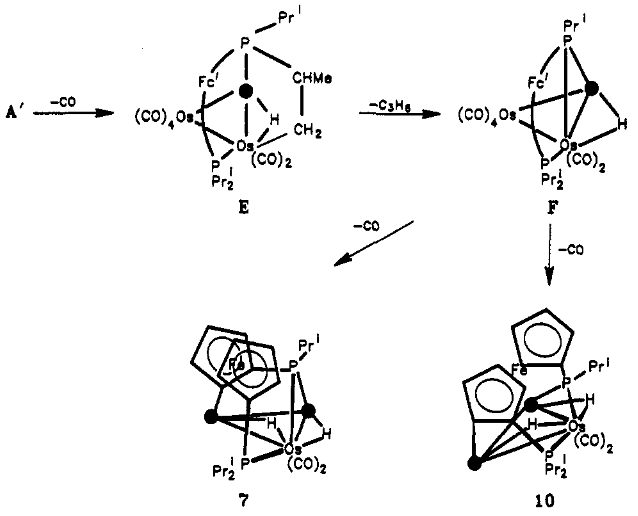
Figure 3. ORTEP diagram for 7, with 33% probability thermal elipsoids.

The osmium complex **4** (structurally characterized)[2] is probably produced from A via B in a reaction sequence that is very similar to the one described for its ruthenium analogue;[4] the intermediate B is well set up for the necessary P–C_5(ring) bond clevage and Fe→Os bond formation. The Fc′ group of B is also held close to an osmium center; this allows metalation to afford **9** (not structurally characterized).

Activation of the other isopropyl group on the axial phosphorus atoms of A leads to intermediate C, which is the precursor to **6** (Figure 2) and **5**/**8** (Figure 1) (Scheme III) via propene elimination or CO insertion. As described above the diastereomeric pair **5** and **8** are isolated in a 5:1 molar ratio and it is possible that **5** originates predominantly from one of the diastereomers of intermediate C and **6** from the other. A ruthenium analogue of **6** was not isolated because in this case the isopropyl group on the phosphido bridge is easily activated and the end product is **12**. It may be that the osmium reaction stops at **6** because the isopropyl group is too far away from the $Os(CO)_4$ moiety, even though it points in the right direction.

The isolation of **7** and **10** from the thermolysis reaction indicates the involvement of other intermediates in which the Fc′ moiety lies over the Os_3 triangle. The structures of **7** (Figure 3) and **10** (proposed structure) require the movement of both phosphorus atoms, and a likely initial precursor is shown as A′. Scheme IV shows how this could produce both **7** and **10** by propene elimination followed by metalation of one or other of the C_5 rings of the Fc′ moiety. Apparently a ruthenium analogue of A′ (or an equivalent precursor) is not produced to any extent in the thermolysis of $Ru_3(CO)_{10}[Fc'(PPr^i_2)]$.[4]

Scheme IV[a]



[a] ● = $Os(CO)_3$.

Overall, the proposed schemes account reasonably well for the formation of the isolated complexes. Although H–C(sp^3) activation is involved in forming all the isolated complexes, we believe that ferrocenyl C–H activation is in general a more facile process in these metal cluster assisted reactions, and it is only because the C_5 rings are held in a less accessible rigid bridge that the metalation of the rings is not the predominant reaction. The thermolytic studies of $Os_3(CO)_{11}(PFcEt_2)$[13] and $Os_3(CO)_{11}(PFcPr^i_2)$[14,15] seem to support this view, but further work is needed in order to make better comparisons.

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, complete bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes and ORTEP drawings for 5–7 (39 pages). Ordering information is given on any current masthead page.

OM920178X

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(15) Cullen, W. R.; Rettig, S. J.; Zheng, T. C. Unpublished results.