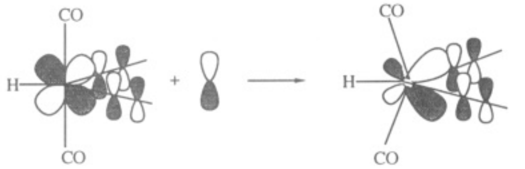

Figure 6. Orbital mixing in $HCo(CO)_4$ (from ref 56).

of 7 with hexafluoro-2-butyne suggested that the reaction had begun with an insertion reaction of the sort characteristic of a metallacyclopropane. PRDDO (partial retention of diatomic differential overlap) calculations (using the Boys localization procedure) on the iron analogue of 1, $Fe(CO)_4(C_2H_4)$ (8), have suggested that the dominant resonance structure of 8 is a metallacyclopropane.[53]

The suggestion[34] that π donation by the bis(trimethylsilyl)acetylene ligand is an important reason for the tilt of the axial carbonyls in $(\eta^2\text{-}Me_3SiC_2SiMe_3)Os(CO)_4$ (**5**) toward the acetylene appears incorrect. While Ball, Burke, and Takats noted a tilt of the axial CO ligands *away* from the coordinated olefin in two $(\eta^2\text{-olefin})Fe(CO)_4$ complexes with bulky olefins,[54] a tilt in this direction is the result of steric effects. The tilt of the axial carbonyls *toward* the unsubstituted ethylene in 1 illustrates that *electronic* effects will bend the axial carbonyls in $LM(CO)_4$ complexes toward *any* L that is a less effective π acceptor than CO. As the calculated energy of distortion to an axial C–Os–C angle of 180° is only 1.4 kcal/mol, it is not surprising that sterically encumbered ligands L can overcome this electronic effect and cause axial carbonyls to bend away from L.

Other workers have also investigated the reasons why axial carbonyls bend toward ligands that are not π acceptors. The seminal work of Elian and Hoffmann on metal carbonyl fragments[55] addressed distortion of $M(CO)_4$ fragments but did not specifically discuss *axial* bending. Ziegler and co-workers have published LCAO-HFS calculations[56] for $HCo(CO)_4$ that describe a mixing of the metal d_{yz} orbital with an empty metal $4p_z$ orbital to give a metal dp hybrid which enhances back-bonding to the equatorial carbonyls (Figure 6). Eisenstein, Crabtree, and co-workers have more recently noted this d–p mixing using EHT.[57]

Conclusions

We have confirmed the dominance of metallacyclopropane character in 1 and provided an explanation for the observed distortion of its axial carbonyl ligands. In addition we have documented, by comparison with its X-ray structure, the geometric accuracy of ab initio calculational methods for third row transition metal complexes and have demonstrated the utility of the Krauss–Stevens[22] carbon and oxygen effective core potentials.

Acknowledgment. This work has been supported by the Department of Energy under Grant DE-FG02-84ER13229-A008 (to J.R.N.) and by the National Science Foundation under Grant CHE-8405399 (to A.K.R.). The authors are grateful to Colonial Metals, Inc., and to Degussa Corp. for the loan of OsO_4. The X-ray diffractometer has been purchased with a grant from the National Science Foundation.

Supplementary Material Available: Tables of anisotropic thermal parameters and H coordinates for 1 (2 pages). Ordering information is given on any current masthead page.

OM920030D

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Double Metalation and Iron–Osmium Bonding Involving Ferrocenyl Moieties on Clusters. Crystal and Molecular Structures of $H_2Os_3(CO)_8[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PPr^i_2)]$ and $H_2Os_3(CO)_8[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PFcEt)]$

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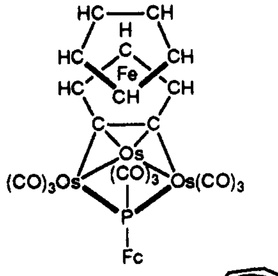
Thermolysis of $Os_3(CO)_{11}(PFcPr^i_2)$ and $Os_3(CO)_{11}(PEtFc_2)$ ($FcH = Fe(\eta\text{-}C_5H_5)_2$) affords the title compounds, $\{\mu_3\text{-}[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PPr^i_2)]\}(\mu\text{-}H)_2Os_3(CO)_8$ (**7**) and $\{\mu_3\text{-}[(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_3PEtFc)]\}(\mu\text{-}H)_2Os_3(CO)_8$ (**8**), in 15 and 25% yield, respectively. The structures of **7** and **8** are very similar and they both contain a doubly metalated ferrocenyl moiety, the iron atom of which is bonded to one osmium atom in the cluster. **7**: triclinic, $a = 10.262$ (3), $b = 15.538$ (2), $c = 9.837$ (3) Å, $\alpha = 98.21$ (2), $\beta = 117.85$ (2), $\gamma = 98.59$ (2)°, $Z = 2$, space group $P\bar{1}$. **8**: monoclinic, $a = 10.356$ (3), $b = 19.514$ (3), $c = 15.630$ (3) Å, $\beta = 102.23$ (2)°, $Z = 4$, space group $P2_1/n$. The structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to $R = 0.025$ and 0.032 for 6294 and 5234 reflections with $I \geq 3\sigma(I)$, respectively.

The thermolysis of tertiary ferrocenylphosphine derivatives of $Os_3(CO)_{12}$ has been used successfully to prepare 1, a cluster derivative of the previously unknown ferrocyne.[1] Other new classes of complexes were also recently characterized,[2,3] including compounds such as 2, which contains a doubly metalated ferrocenyl moiety along with a Fe→Os bond. Dative Fe→M bonding, where Fe is the central metal of a ferrocenyl group, has been observed for only a limited number of metal complexes, e.g. 3–6.[4-7] The metalation of the ferrocene moiety seen in 1, 2, and 4–6 is also little studied. In contrast, the metalation of phenyl groups is very well known.[8] The metalation of the ferrocene moiety in 2a seems surprising because there are two phenyl groups and only one ferrocenyl attached to the phosphorus atom and because phenyl is believed to be more reactive with respect to metalation.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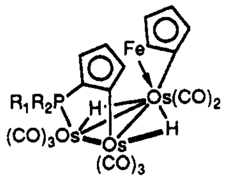
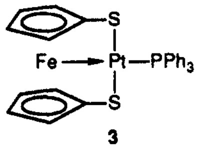

2a: R_1 = Fc, R_2 = Ph
b: $R_1 = R_2$ = Ph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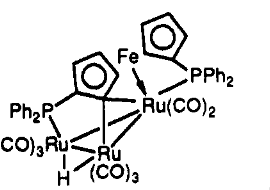
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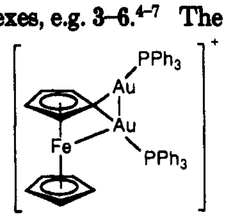
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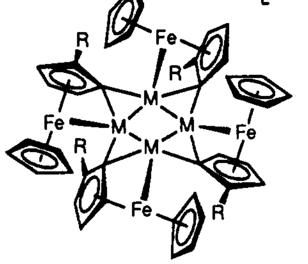
6a: M = Cu
b: M = Ag
R = CH_2NMe_2

In order to gain further insight into these reactions we decided to study the pyrolyses of alkylferrocenylphosphine derivatives of $Os_3(CO)_{12}$. Although some alkyl metalation takes place,[2,3,9] these reactions do give products analogous to 2, and in this paper we describe the preparation and full characterization of two such products, 7 and 8.

Experimental Section

General experimental procedures and instrumentation are the same as previously described.[1-3] All NMR spectra were obtained from $CDCl_3$ solutions.

Preparation of $Os_3(CO)_{11}(PFcPr^i_2)$. To a solution of $Os_3(CO)_{12}$ (272 mg, 0.3 mmol) in CH_2Cl_2 (20 mL) was added CH_3CN (2 mL) and Me_3NO[10] (23 mg, 0.3 mmol), and the mixture was stirred for 1 h, after which $PFcPr^i_2$[11] (100 mg, 0.33 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred for an additional hour, the solvent was then removed in vacuo, and the residue applied directly to a silica column for chromatographic separation (eluent, 3:1 petroleum ether/CH_2Cl_2). The major reddish orange band that eluted was found to contain the pure product $Os_3(CO)_{11}(PFcPr^i_2)$ (250 mg, 70%). $^{31}P\{^1H\}$ NMR: δ 18.5. ^1H NMR: δ 4.48 (m, 2 H), 4.30 (m, 2 H), 4.20 (s, 5 H), 2.40 (m, 2 H), 1.28 (dd, 6 H), 1.04 (dd, 6 H). $^{13}C\{^1H\}$ NMR: δ 77.0 (d, J = 44.6 Hz), 72.2 (d, J = 9.0 Hz), 70.2 (s), 70.0 (d, J = 7.1 Hz), 30.5 (d, J = 31.7 Hz), 18.6 (d, d). FAB mass spectrum: m/e 1182 (P^+) with successive loss of 11 CO's and 2 isopropyl groups. Anal. Calcd for $C_{27}H_{23}FeO_{11}Os_3P$: C, 27.46; H, 1.96. Found: C, 27.81; H, 2.03.

Preparation of $Os_3(CO)_{11}(PEtFc_2)$. A solution of $Os_3(CO)_{12}$ (280 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) was treated with CH_3CN (2 mL) and Me_3NO[10] (23 mg, 0.3 mmol), and the color changed to yellow immediately. After 20 min of stirring, $PEtFc_2$[11] (130 mg, 0.3 mmol) was added to the mixture and it was left stirring for 2 h, after which the solvent was removed in vacuo. The residue was applied directly to a silica column for chromatographic separation (eluent, 3:1 petroleum ether/CH_2Cl_2) and the second band that eluted proved to be the desired product (250 mg, 65%). $^{31}P\{^1H\}$ NMR: δ −21.8. ^1H NMR: δ 4.46 (m, 2 H), 4.42 (m, 2 H), 4.32 (m, 2 H), 4.12 (s + m, 10 + 2 H), 2.66 (m, 2 H), 1.23 (dt, 3 H). FAB mass spectrum: m/e 1308 (P^+) with successive loss of eight CO's (or one ethyl). Anal. Calcd for $C_{33}H_{23}Fe_2O_{11}Os_3P$: C, 30.28; H, 1.77. Found: C, 30.41; H, 1.85.

Preparation of 7. When $Os_3(CO)_{11}(PFcPr^i_2)$ (120 mg, 0.1 mmol) in octane (30 mL) was refluxed for 5 h, TLC investigation of the reaction mixture (3:1 petroleum ether/CH_2Cl_2) showed the complete disappearance of the starting material. The solvent was then removed in vacuo, and the residue was applied to a silica column for chromatographic separation (eluent, 3:1 petroleum ether/CH_2Cl_2). The fifth, orange, band that eluted proved to contain complex 7 (15%), and suitable crystals for X-ray structure analysis were obtained by slow evaporation of the eluent. $^{31}P\{^1H\}$ NMR: δ 2.5. ^1H NMR: δ 5.41 (m, 1 H), 5.11 (m, 1 H), 4.77 (m, 1 H), 4.32 (m, 1 H), 4.24 (m, 1 H), 4.11 (m, 1 H), 3.07 (m, 1 H), 2.55 (m, 1 H), 1.86 (m, 1 H), 1.40 (dd, 3 H), 1.34 (m, 6 H), 1.23 (dd, 3 H), −12.07 (d, 1 H, J = 4.08 Hz), −17.12 (d, 1 H, J = 12.02 Hz). FAB mass spectrum: m/e 1098 (P^+) with successive loss of 5 CO's followed by loss of 2 isopropyl and 3 CO groups. Anal. Calcd for $C_{24}H_{23}FeO_8Os_3P$: C, 26.28; H, 2.11. Found: C, 26.40; H, 2.19.

Preparation of 8. When $Os_3(CO)_{11}(PEtFc_2)$ (130 mg, 0.1 mmol) in octane (50 mL) was refluxed for 12 h, TLC investigation of the reaction mixture (3:1 petroleum ether/CH_2Cl_2) showed that

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[9] The thermolyses of $Os_3(CO)_{11}(PEt_2Fc)$, $Os_3(CO)_{11}(PFcPr^i_2)$, and $Os_3(CO)_{11}(PBu^t_2Fc)$ also result in the metalation of the alkyl groups. For example, the PEt_2Fc complex affords a 65% yield of a complex that is probably similar to those described in the present paper. Cullen, W. R.; Zheng, T. C. Unpublished results.

[10] Me_3NO is commonly added to facilitate CO substitution by other ligands such as phosphine and nitrile.[1,2]

[11] The ligands PPr^i_2Fc and $PEtFc_2$ were prepared by using similar procedures to those used for PPh_2Fc or PFc_2Ph, from $ClPPr^i_2$ and Cl_2PEt.[1-3]

Table I. Crystallographic Data[a]

compound	7	8
formula	$C_{24}H_{23}FeO_8Os_3P$	$C_{30}H_{23}Fe_2O_8Os_3P$
formula wt	1096.86	1224.77
color, habit	red-orange, irregular	orange, prism
crystal size, mm	0.20 × 0.25 × 0.35	0.12 × 0.17 × 0.20
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	10.262 (3)	10.356 (3)
b, Å	15.538 (2)	19.514 (3)
c, Å	9.837 (3)	15.630 (3)
α, deg	98.21 (2)	90
β, deg	117.85 (2)	102.23 (2)
γ, deg	98.59 (2)	90
V, Å^3	1330.2 (6)	3086.8 (9)
Z	2	4
ρ_{calc}, g/cm^3	2.738	2.635
$F(000)$	1000	2248
μ(Mo Kα), cm^{-1}	149.37	133.36
transmission factors[b]	0.57–1.00	0.65–1.00
scan type	$\omega - 2\theta$	$\omega - 2\theta$
scan range, deg in ω	$1.21 + 0.35 \tan\theta$	$1.31 + 0.35 \tan\theta$
scan rate, deg/min	32	16
data collected	$+h, \pm k, \pm l$	$+h, +k, \pm l$
$2\theta_{max}$, deg	65	65
crystal decay	negligible	5.3%
total no. reflcns	10069	11987
no. unique reflcns	9599	11457
R_{merge}	0.028	0.050
reflcns with $I \geq 3\sigma(I)$	6294	5234
no. of variables	355	398
R	0.025	0.032
R_w	0.025	0.025
gof	1.32	1.33
max Δ/σ (final cycle)	0.01	0.03
residual density e/Å^3	−0.93 to +0.85	−1.09 to +1.43 (near Os)

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.71069 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 7, 0.00 for 8), 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 $I \geq 3\sigma(I)$. [b] Relative.

Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 7[a]

atom	x	y	z	B_{eq}
Os(1)	0.36941 (2)	0.25989 (1)	0.76229 (2)	1.916 (6)
Os(2)	0.24367 (2)	0.12914 (1)	0.43880 (2)	2.014 (6)
Os(3)	0.48837 (2)	0.28531 (1)	0.55791 (3)	2.256 (6)
Fe(1)	0.16969 (8)	0.37454 (4)	0.64564 (8)	2.05 (2)
P(1)	0.0743 (2)	0.21937 (8)	0.3040 (2)	2.18 (4)
O(1)	0.6173 (5)	0.3964 (3)	1.0549 (5)	4.4 (1)
O(2)	0.4180 (5)	0.1161 (3)	0.9428 (5)	4.5 (2)
O(3)	0.3193 (7)	0.0817 (3)	0.1769 (6)	5.6 (2)
O(4)	−0.0012 (6)	−0.0405 (3)	0.3449 (6)	5.3 (2)
O(5)	0.4813 (6)	0.0382 (3)	0.6515 (6)	5.0 (2)
O(6)	0.4455 (7)	0.3298 (4)	0.2515 (6)	5.9 (2)
O(7)	0.7422 (6)	0.4541 (3)	0.7698 (7)	6.3 (2)
O(8)	0.6949 (6)	0.1643 (3)	0.5501 (7)	5.6 (2)
C(1)	0.3196 (6)	0.3546 (3)	0.5582 (6)	2.1 (1)
C(2)	0.1585 (6)	0.3312 (3)	0.4351 (6)	1.9 (1)
C(3)	0.0996 (6)	0.4089 (3)	0.4335 (6)	2.5 (2)
C(4)	0.2170 (7)	0.4801 (3)	0.5573 (6)	2.6 (2)
C(5)	0.3478 (6)	0.4486 (3)	0.6338 (6)	2.5 (2)
C(6)	0.2033 (6)	0.2998 (3)	0.8001 (6)	2.4 (2)
C(7)	0.0456 (6)	0.2729 (3)	0.6820 (7)	2.7 (2)
C(8)	−0.0171 (7)	0.3504 (4)	0.6797 (7)	3.0 (2)
C(9)	0.0976 (7)	0.4230 (4)	0.8017 (7)	2.9 (2)
C(10)	0.2300 (7)	0.3921 (4)	0.8795 (6)	2.7 (2)
C(11)	0.0591 (7)	0.2371 (4)	0.1141 (6)	3.5 (2)
C(12)	0.005 (1)	0.1515 (6)	−0.0181 (8)	6.4 (3)
C(13)	−0.028 (1)	0.3056 (5)	0.0480 (9)	5.7 (3)
C(14)	−0.1222 (6)	0.1772 (4)	0.2687 (6)	3.1 (2)
C(15)	−0.2107 (9)	0.0949 (5)	0.135 (1)	6.2 (3)
C(16)	−0.2191 (7)	0.2428 (5)	0.2528 (8)	4.3 (2)
C(17)	0.5195 (7)	0.3458 (4)	0.9448 (7)	2.9 (2)
C(18)	0.4034 (7)	0.1713 (4)	0.8732 (7)	3.0 (2)
C(19)	0.2910 (7)	0.1000 (4)	0.2747 (7)	3.1 (2)
C(20)	0.0855 (7)	0.0245 (4)	0.3798 (6)	2.9 (2)
C(21)	0.3935 (7)	0.0723 (4)	0.5719 (7)	3.2 (2)
C(22)	0.4561 (7)	0.3124 (4)	0.3636 (7)	3.4 (2)
C(23)	0.6469 (7)	0.3917 (4)	0.6882 (8)	3.6 (2)
C(24)	0.6194 (7)	0.2095 (4)	0.5541 (7)	3.4 (2)

[a] $B_{eq} = (^8/_3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(a_i \cdot a_j)$

there was no starting material left. The solvent was then removed in vacuo, and the residue was applied to a silica column for chromatographic separation (eluent 3:1 petroleum ether/CH_2Cl_2). The fourth, yellow, band was found to contain compound 8 (25%), and suitable crystals for X-ray structure analysis were obtained as above. $^{31}P\{^1H\}$ NMR: δ −27.5. ^1H NMR: δ 4.98 (m, 2 H), 4.62 (m, 1 H), 4.54 (m, 1 H), 4.42 (m, 2 H), 4.33 (m, 1 H), 4.28 (m, 1 H), 4.24 (m, 5 H), 4.02 (m, 1 H), 3.26 (m, 1 H), 3.00 (m, 1 H), 2.66 (m, 2 H), 1.22 (dt, 3 H), −12.13 (d, 1 H, J = 3.9 Hz), −17.04 (d, 1 H, J = 12.3 Hz). FAB mass spectrum: m/e 1224 (P^+) with successive loss of 7 CO's and 1 ferrocenyl. Anal. Calcd for $C_{30}H_{23}Fe_2O_8Os_3P$: C, 29.42; H, 1.89. Found: C, 29.59; H, 2.07.

X-ray Crystallographic Analyses. Crystallographic data for $\{\mu_3\text{-}[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_3)]P(i\text{-}C_3H_7)_2\text{-}Fe,P,C,C\}(\mu\text{-}H)_2Os_3(CO)_8$ (7) and $\{\mu_3\text{-}[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_3)]P[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](C_2H_5)\text{-}Fe,P,C,C\}(\mu\text{-}H)_2Os_3(CO)_8$ (8) appear in Table I. The final unit cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 48.5–52.4° for 7 and 29.3–39.7° for 8. The intensities of 3 standard reflections, measured every 200 reflections throughout the data collections, remained constant for 7 and decreased uniformly by 5.3% for 8. The data were processed[12] and corrected for Lorentz and polarization effects, decay (for 8), and absorption (empirical, based on azimuthal scans for 4 reflections).

Both 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 7 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 both complexes were refined with anisotropic thermal parameters. The metal hydride atoms in both complexes were included in difference map positions, but were not refined. All other hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{bonded\ atom}$). Corrections for secondary extinction were applied for both structures, the final values of the extinction coefficient being 6.16×10^{-7} for 7 and 1.43×10^{-8} for 8. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography*.[13] Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles for 7 and 8 appear in Tables II–VII. Hydrogen-atom parameters, anisotropic thermal parameters, and complete tables of bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

Results and Discussion

The complexes 7 and 8 are the thermal decomposition

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[12] TEXSAN/TEXRAY is a structure analysis package that includes versions of the following: DIRDIF, direct methods for difference structures, by P.T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

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

[14] The reaction in octane for 19 h produced 7 in 15% yield (determined by NMR integration), but it is more difficult to separate the product from the reaction mixture.

Table III. Bond Lengths (Å) with Estimated Standard Deviations for 7[a]

atom	atom	distance	atom	atom	distance
Os(1)	Os(2)	3.075 (1)	Fe(1)	Cp(2)	1.652 (3)
Os(1)	Os(3)	2.8398 (7)	P(1)	C(2)	1.817 (5)
Os(1)	Fe(1)	2.858 (1)	P(1)	C(11)	1.865 (6)
Os(1)	C(6)	2.067 (5)	P(1)	C(14)	1.872 (6)
Os(1)	C(17)	1.869 (6)	O(1)	C(17)	1.142 (7)
Os(1)	C(18)	1.851 (6)	O(2)	C(18)	1.156 (6)
Os(2)	Os(3)	2.861 (1)	O(3)	C(19)	1.139 (7)
Os(2)	P(1)	2.419 (1)	O(4)	C(20)	1.131 (7)
Os(2)	C(19)	1.907 (6)	O(5)	C(21)	1.143 (7)
Os(2)	C(20)	1.917 (6)	O(6)	C(22)	1.133 (7)
Os(2)	C(21)	1.927 (6)	O(7)	C(23)	1.141 (7)
Os(3)	C(1)	2.173 (5)	O(8)	C(24)	1.130 (6)
Os(3)	C(22)	1.903 (6)	C(1)	C(2)	1.469 (7)
Os(3)	C(23)	1.915 (6)	C(1)	C(5)	1.459 (6)
Os(3)	C(24)	1.925 (6)	C(2)	C(3)	1.427 (6)
Fe(1)	C(1)	2.123 (5)	C(3)	C(4)	1.416 (7)
Fe(1)	C(2)	2.028 (5)	C(4)	C(5)	1.403 (8)
Fe(1)	C(3)	2.046 (5)	C(6)	C(7)	1.430 (8)
Fe(1)	C(4)	2.061 (5)	C(6)	C(10)	1.451 (7)
Fe(1)	C(5)	2.071 (5)	C(7)	C(8)	1.446 (7)
Fe(1)	C(6)	1.977 (5)	C(8)	C(9)	1.413 (8)
Fe(1)	C(7)	2.057 (5)	C(9)	C(10)	1.411 (8)
Fe(1)	C(8)	2.086 (6)	C(11)	C(12)	1.542 (9)
Fe(1)	C(9)	2.089 (5)	C(11)	C(13)	1.517 (9)
Fe(1)	C(10)	2.046 (5)	C(14)	C(15)	1.500 (9)
Fe(1)	Cp(1)	1.667 (3)	C(14)	C(16)	1.501 (8)

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

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

atom	atom	atom	angle	atom	atom	atom	angle
Os(2)	Os(1)	Os(3)	57.70 (2)	C(22)	Os(3)	C(23)	94.6 (3)
Os(2)	Os(1)	Fe(1)	95.64 (3)	C(22)	Os(3)	C(24)	92.1 (3)
Os(2)	Os(1)	C(6)	113.8 (1)	C(23)	Os(3)	C(24)	96.3 (2)
Os(2)	Os(1)	C(17)	154.5 (2)	Os(1)	Fe(1)	Cp(1)	96.2 (1)
Os(2)	Os(1)	C(18)	94.2 (2)	Os(1)	Fe(1)	Cp(2)	84.9 (1)
Os(3)	Os(1)	Fe(1)	92.75 (2)	Cp(1)	Fe(1)	Cp(2)	178.4 (1)
Os(3)	Os(1)	C(6)	136.4 (1)	Os(2)	P(1)	C(2)	105.2 (2)
Os(3)	Os(1)	C(17)	99.0 (2)	Os(2)	P(1)	C(11)	117.1 (2)
Os(3)	Os(1)	C(18)	122.6 (2)	Os(2)	P(1)	C(14)	112.2 (2)
Fe (1)	Os(1)	C(6)	43.8 (1)	C(2)	P(1)	C(11)	103.6 (2)
Fe(1)	Os(1)	C(17)	95.8 (2)	C(2)	P(1)	C(14)	109.9 (2)
Fe(1)	Os(1)	C(18)	142.7 (2)	C(11)	P(1)	C(14)	108.3 (3)
C(6)	Os(1)	C(17)	90.0 (2)	Os(3)	C(1)	C(2)	125.4 (3)
C(6)	Os(1)	C(18)	99.7 (2)	Os(3)	C(1)	C(5)	126.6 (4)
C(17)	Os(1)	C(18)	90.4 (2)	C(2)	C(1)	C(5)	103.6 (4)
Os(1)	Os(2)	Os(3)	57.03 (2)	P(1)	C(2)	C(1)	119.0 (3)
Os(1)	Os(2)	P(1)	91.74 (4)	P(1)	C(2)	C(3)	131.3 (4)
Os(1)	Os(2)	C(19)	141.1 (2)	C(1)	C(2)	C(3)	109.5 (4)
Os(1)	Os(2)	C(20)	118.0 (2)	C(2)	C(3)	C(4)	107.8 (5)
Os(1)	Os(2)	C(21)	80.2 (2)	C(3)	C(4)	C(5)	108.7 (4)
Os(3)	Os(2)	P(1)	87.35 (4)	C(1)	C(5)	C(4)	110.3 (5)
Os(3)	Os(2)	C(19)	84.9 (2)	Os(1)	C(6)	C(7)	122.6 (4)
Os(3)	Os(2)	C(20)	174.5 (2)	Os(1)	C(6)	C(10)	119.6 (4)
Os(3)	Os(2)	C(21)	86.4 (2)	C(7)	C(6)	C(10)	105.8 (5)
P(1)	Os(2)	C(19)	94.1 (2)	C(6)	C(7)	C(8)	108.2 (5)
P(1)	Os(2)	C(20)	95.4 (2)	C(7)	C(8)	C(9)	108.3 (5)
P(1)	Os(2)	C(21)	171.7 (2)	C(8)	C(9)	C(10)	107.8 (5)
C(19)	Os(2)	C(20)	99.6 (2)	C(6)	C(10)	C(9)	109.6 (5)
C(19)	Os(2)	C(21)	90.9 (2)	P(1)	C(11)	C(12)	115.9 (5)
C(20)	Os(2)	C(21)	90.3 (2)	P(1)	C(11)	C(13)	114.8 (4)
Os(1)	Os(3)	Os(2)	65.27 (2)	C(12)	C(11)	C(13)	110.1 (6)
Os(1)	Os(3)	C(1)	59.8 (1)	P(1)	C(14)	C(15)	112.6 (5)
Os(1)	Os(3)	C(22)	147.5 (2)	P(1)	C(14)	C(16)	118.2 (4)
Os(1)	Os(3)	C(23)	99.1 (2)	C(15)	C(14)	C(16)	109.8 (5)
Os(1)	Os(3)	C(24)	115.3 (2)	Os(1)	C(17)	O(1)	176.1 (5)
Os(2)	Os(3)	C(1)	83.1 (1)	Os(1)	C(18)	O(2)	176.5 (5)
Os(2)	Os(3)	C(22)	99.8 (2)	Os(2)	C(19)	O(3)	179.3 (5)
Os(2)	Os(3)	C(23)	164.3 (2)	Os(2)	C(20)	O(4)	175.3 (5)
Os(2)	Os(3)	C(24)	89.5 (2)	Os(2)	C(21)	O(5)	179.2 (6)
C(1)	Os(3)	C(22)	91.0 (2)	Os(3)	C(22)	O(6)	176.1 (6)
C(1)	Os(3)	C(23)	90.4 (2)	Os(3)	C(23)	O(7)	177.9 (6)
C(1)	Os(3)	C(24)	172.4 (2)	Os(3)	C(24)	O(8)	179.1 (6)

Table V. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 8[a]

atom	*x*	*y*	*z*	B_{eq}
Os(1)	0.08910 (3)	0.17129 (2)	0.13651 (2)	2.38 (1)
Os(2)	0.27736 (3)	0.25881 (2)	0.24649 (2)	2.40 (1)
Os(3)	0.32910 (3)	0.10483 (2)	0.21435 (2)	2.82 (1)
Fe(1)	0.4440 (1)	0.13171 (6)	0.06841 (7)	2.72 (4)
Fe(2)	0.5788 (1)	0.41971 (6)	0.15507 (7)	2.88 (4)
P(1)	0.3416 (2)	0.2913 (1)	0.1132 (1)	2.13 (7)
O(1)	−0.0740 (6)	0.0544 (3)	0.0377 (4)	4.7 (3)
O(2)	−0.0570 (6)	0.2794 (3)	0.0136 (4)	4.7 (3)
O(3)	−0.0975 (6)	0.1927 (4)	0.2616 (4)	5.5 (3)
O(4)	0.4797 (6)	0.3415 (3)	0.3761 (3)	4.9 (3)
O(5)	0.0640 (6)	0.3693 (4)	0.2178 (4)	5.8 (3)
O(6)	0.1683 (7)	0.2005 (4)	0.3976 (4)	7.1 (4)
O(7)	0.2558 (7)	−0.0383 (3)	0.1519 (4)	5.6 (3)
O(8)	0.3774 (7)	0.0602 (4)	0.4014 (4)	7.2 (4)
C(1)	0.2444 (6)	0.1597 (4)	0.0626 (4)	2.2 (3)
C(2)	0.3278 (6)	0.2158 (4)	0.0462 (4)	2.2 (3)
C(3)	0.3818 (7)	0.2011 (4)	−0.0282 (5)	2.9 (3)
C(4)	0.3378 (7)	0.1348 (4)	−0.0586 (5)	3.1 (3)
C(5)	0.2567 (7)	0.1085 (4)	−0.0039 (5)	2.9 (3)
C(6)	0.5143 (7)	0.0934 (4)	0.1869 (5)	3.3 (3)
C(7)	0.5928 (7)	0.1515 (4)	0.1747 (5)	3.1 (3)
C(8)	0.6489 (7)	0.1417 (5)	0.0997 (6)	4.0 (4)
C(9)	0.6112 (8)	0.0735 (5)	0.0676 (6)	4.6 (4)
C(10)	0.5347 (8)	0.0447 (5)	0.1213 (6)	4.3 (4)
C(11)	0.5069 (6)	0.3237 (4)	0.1199 (4)	2.2 (3)
C(12)	0.6154 (7)	0.3211 (4)	0.1942 (5)	2.8 (3)
C(13)	0.7279 (7)	0.3488 (4)	0.1682 (5)	3.6 (4)
C(14)	0.6905 (8)	0.3708 (5)	0.0813 (6)	3.8 (4)
C(15)	0.5543 (7)	0.3550 (4)	0.0500 (5)	3.0 (3)
C(16)	0.439 (1)	0.4783 (5)	0.1965 (8)	5.6 (5)
C(17)	0.554 (1)	0.4754 (5)	0.2603 (7)	6.1 (6)
C(18)	0.657 (1)	0.5027 (6)	0.2273 (8)	6.5 (6)
C(19)	0.603 (1)	0.5215 (5)	0.1387 (8)	5.7 (5)
C(20)	0.472 (1)	0.5070 (5)	0.1205 (6)	4.9 (5)
C(21)	0.2360 (7)	0.3540 (4)	0.0424 (5)	3.4 (3)
C(22)	0.2039 (8)	0.3415 (4)	−0.0558 (5)	4.2 (4)
C(23)	−0.0113 (7)	0.0977 (4)	0.0743 (5)	2.9 (3)
C(24)	0.0007 (7)	0.2390 (4)	0.0595 (5)	3.1 (3)
C(25)	−0.0302 (7)	0.1850 (5)	0.2137 (5)	3.6 (4)
C(26)	0.4094 (7)	0.3097 (4)	0.3240 (5)	3.4 (4)
C(27)	0.1452 (7)	0.3277 (5)	0.2289 (5)	3.6 (4)
C(28)	0.2104 (8)	0.2210 (6)	0.3421 (5)	4.5 (4)
C(29)	0.2873 (8)	0.0151 (5)	0.1750 (6)	4.2 (4)
C(30)	0.3555 (9)	0.0770 (5)	0.3300 (6)	4.7 (4)

[a] $B_{eq} = (^8/_3)\pi^2\sum\sum U_{ij}a_i{}^*a_j{}^*(a_i \cdot a_j)$

products of $Os_3(CO)_{11}(PFcPr^i_2)$ and $Os_3(CO)_{11}(PEtFc_2)$, respectively. Their formation involves metalation of both cyclopentadiene rings with concomitant formation of a Fe→Os bond. Each metalation and Fe→Os bond formation is accompanied by CO loss; however, the sequence of these three steps is not clear at present, although the first is probably metalation of the C_5H_4P ring.

The structures of 7 and 8 are depicted in Figures 1 and 2. Their essential features are similar, so they will not be discussed separately. Each complex contains two bridging hydrides, which were located in the structure refinement, eight terminal carbonyls, one phosphine, and the metalated ferrocenyl moiety. Each osmium center has a distorted octahedral geometry if the bridged Os–Os bonds are not included. The whole cluster is electron precise if the metal–metal bonds are counted, and the coordination number at one osmium atom is eight (Os(3) in 8, Os(1) in 7). One Os–Os bond is long (3.075 (1) Å in 7 and 3.1117 (4) Å in 8). The other two Os–Os bonds in each structure are normal at 2.8398 (7) and 2.861 (1) Å for 7 and 2.8386 (7) and 2.8727 (6) Å for 8. The hydrides are in different environments, e.g. in 7 H(1) is almost coplanar with the Os_3 plane, 0.10 Å to one side, while H(2) is 0.9350 Å away on the other side of that plane. In 8, H(1) is 0.73 Å and H(2) 0.49 Å away from the Os_3 plane, again on

Table VI. Bond Lengths (Å) with Estimated Standard Deviations for 8[a]

atom	atom	distance	atom	atom	distance
Os(1)	Os(2)	2.8727 (6)	Fe(2)	C(20)	2.04 (1)
Os(1)	Os(3)	2.8386 (7)	Fe(2)	Cp(3)	1.646 (4)
Os(1)	C(1)	2.181 (7)	Fe(2)	Cp(4)	1.659 (5)
Os(1)	C(23)	1.913 (8)	P(1)	C(2)	1.796 (7)
Os(1)	C(24)	1.888 (9)	P(1)	C(11)	1.807 (7)
Os(1)	C(25)	1.920 (8)	P(1)	C(21)	1.846 (8)
Os(2)	Os(3)	3.1117 (7)	O(1)	C(23)	1.142 (9)
Os(2)	P(1)	2.402 (2)	O(2)	C(24)	1.145 (9)
Os(2)	C(26)	1.904 (8)	O(3)	C(25)	1.135 (9)
Os(2)	C(27)	1.896 (9)	O(4)	C(26)	1.152 (9)
Os(2)	C(28)	1.924 (9)	O(5)	C(27)	1.16 (1)
Os(3)	Fe(1)	2.836 (1)	O(6)	C(28)	1.123 (9)
Os(3)	C(6)	2.065 (8)	O(7)	C(29)	1.13 (1)
Os(3)	C(29)	1.88 (1)	O(8)	C(30)	1.14 (1)
Os(3)	C(30)	1.851 (9)	C(1)	C(2)	1.45 (1)
Fe(1)	C(1)	2.121 (7)	C(1)	C(5)	1.47 (1)
Fe(1)	C(2)	2.021 (7)	C(2)	C(3)	1.42 (1)
Fe(1)	C(3)	2.029 (8)	C(3)	C(4)	1.42 (1)
Fe(1)	C(4)	2.056 (7)	C(4)	C(5)	1.42 (1)
Fe(1)	C(5)	2.078 (7)	C(6)	C(7)	1.43 (1)
Fe(1)	C(6)	1.987 (7)	C(6)	C(10)	1.45 (1)
Fe(1)	C(7)	2.050 (7)	C(7)	C(8)	1.43 (1)
Fe(1)	C(8)	2.084 (8)	C(8)	C(9)	1.45 (1)
Fe(1)	C(9)	2.074 (8)	C(9)	C(10)	1.39 (1)
Fe(1)	C(10)	2.030 (9)	C(11)	C(12)	1.435 (9)
Fe(1)	Cp(1)	1.661 (3)	C(11)	C(15)	1.43 (1)
Fe(1)	Cp(2)	1.645 (4)	C(12)	C(13)	1.42 (1)
Fe(2)	C(11)	2.049 (7)	C(13)	C(14)	1.40 (1)
Fe(2)	C(12)	2.030 (7)	C(14)	C(15)	1.42 (1)
Fe(2)	C(13)	2.051 (8)	C(16)	C(17)	1.38 (1)
Fe(2)	C(14)	2.036 (8)	C(16)	C(20)	1.42 (1)
Fe(2)	C(15)	2.046 (7)	C(17)	C(18)	1.38 (2)
Fe(2)	C(16)	2.05 (1)	C(18)	C(19)	1.43 (1)
Fe(2)	C(17)	2.03 (1)	C(19)	C(20)	1.35 (1)
Fe(2)	C(18)	2.04 (1)	C(21)	C(22)	1.52 (1)
Fe(2)	C(19)	2.024 (9)			

[a] Here and elsewhere Cp(1), Cp(2), Cp(3), and Cp(4) refer to the unweighted centroids of the C(1–5), C(6–10), C(11–15), and C(16–20) cyclopentadienyl rings.

Table VII. Bond Angles (deg) with Estimated Standard Deviations for 8

atom	atom	atom	angle	atom	atom	atom	angle
Os(2)	Os(1)	Os(3)	66.02 (2)	Os(3)	Fe(1)	Cp(2)	85.2 (1)
Os(2)	Os(1)	C(1)	84.0 (2)	Cp(1)	Fe(1)	Cp(2)	177.8 (2)
Os(2)	Os(1)	C(23)	167.8 (2)	Cp(3)	Fe(2)	Cp(4)	177.6 (2)
Os(2)	Os(1)	C(24)	98.1 (2)	Os(2)	P(1)	C(2)	106.7 (2)
Os(2)	Os(1)	C(25)	89.2 (2)	Os(2)	P(1)	C(11)	118.4 (2)
Os(3)	Os(1)	C(1)	60.2 (2)	Os(2)	P(1)	C(21)	117.2 (3)
Os(3)	Os(1)	C(23)	102.0 (2)	C(2)	P(1)	C(11)	106.1 (3)
Os(3)	Os(1)	C(24)	148.8 (2)	C(2)	P(1)	C(21)	103.3 (3)
Os(3)	Os(1)	C(25)	114.6 (2)	C(11)	P(1)	C(21)	103.6 (3)
C(1)	Os(1)	C(23)	92.0 (3)	Os(1)	C(1)	C(2)	123.3 (5)
C(1)	Os(1)	C(24)	92.7 (3)	Os(1)	C(1)	C(5)	129.1 (5)
C(1)	Os(1)	C(25)	172.8 (3)	C(2)	C(1)	C(5)	104.1 (6)
C(23)	Os(1)	C(24)	93.6 (3)	P(1)	C(2)	C(1)	119.5 (5)
C(23)	Os(1)	C(25)	94.1 (3)	P(1)	C(2)	C(3)	130.2 (6)
C(24)	Os(1)	C(25)	90.8 (3)	C(1)	C(2)	C(3)	110.2 (6)
Os(1)	Os(2)	Os(3)	56.46 (1)	C(2)	C(3)	C(4)	107.6 (7)
Os(1)	Os(2)	P(1)	85.14 (5)	C(3)	C(4)	C(5)	108.6 (6)
Os(1)	Os(2)	C(26)	175.0 (2)	C(1)	C(5)	C(4)	109.4 (6)
Os(1)	Os(2)	C(27)	87.6 (2)	Os(3)	C(6)	C(7)	121.4 (6)
Os(1)	Os(2)	C(28)	85.8 (2)	Os(3)	C(6)	C(10)	120.0 (6)
Os(3)	Os(2)	P(1)	91.48 (5)	C(7)	C(6)	C(10)	104.7 (7)
Os(3)	Os(2)	C(26)	118.8 (2)	C(6)	C(7)	C(8)	110.1 (7)
Os(3)	Os(2)	C(27)	143.6 (2)	C(7)	C(8)	C(9)	106.3 (8)
Os(3)	Os(2)	C(28)	81.8 (3)	C(8)	C(9)	C(10)	108.0 (8)
P(1)	Os(2)	C(26)	96.9 (2)	C(6)	C(10)	C(9)	110.5 (8)
P(1)	Os(2)	C(27)	90.6 (3)	P(1)	C(11)	C(12)	127.2 (6)
P(1)	Os(2)	C(28)	170.7 (3)	P(1)	C(11)	C(15)	125.5 (5)
C(26)	Os(2)	C(27)	97.0 (3)	C(12)	C(11)	C(15)	107.3 (6)
C(26)	Os(2)	C(28)	92.0 (3)	C(11)	C(12)	C(13)	107.8 (7)
C(27)	Os(2)	C(28)	91.0 (4)	C(12)	C(13)	C(14)	108.6 (6)
Os(1)	Os(3)	Os(2)	57.51 (1)	C(13)	C(14)	C(15)	108.6 (7)
Os(1)	Os(3)	Fe(1)	92.82 (3)	C(11)	C(15)	C(14)	107.8 (7)
Os(1)	Os(3)	C(6)	136.7 (2)	C(17)	C(16)	C(20)	107 (1)
Os(1)	Os(3)	C(29)	99.5 (3)	C(16)	C(17)	C(18)	109 (1)
Os(1)	Os(3)	C(30)	119.2 (3)	C(17)	C(18)	C(19)	107 (1)
Os(2)	Os(3)	Fe(1)	93.85 (3)	C(18)	C(19)	C(20)	109 (1)
Os(2)	Os(3)	C(6)	109.7 (2)	C(16)	C(20)	C(19)	108 (1)
Os(2)	Os(3)	C(29)	156.7 (3)	P(1)	C(21)	C(22)	118.3 (6)
Os(2)	Os(3)	C(30)	96.9 (3)	Os(1)	C(23)	O(1)	178.4 (7)
Fe(1)	Os(3)	C(6)	44.5 (2)	Os(1)	C(24)	O(2)	177.6 (7)
Fe(1)	Os(3)	C(29)	90.9 (3)	Os(1)	C(25)	O(3)	177.8 (7)
Fe(1)	Os(3)	C(30)	147.0 (3)	Os(2)	C(26)	O(4)	172.9 (7)
C(6)	Os(3)	C(29)	89.5 (4)	Os(2)	C(27)	O(5)	179.4 (7)
C(6)	Os(3)	C(30)	102.7 (4)	Os(2)	C(28)	O(6)	178 (1)
C(29)	Os(3)	C(30)	91.3 (4)	Os(3)	C(29)	O(7)	176.5 (8)
Os(3)	Fe(1)	Cp(1)	96.9 (1)	Os(3)	C(30)	O(8)	177.1 (9)

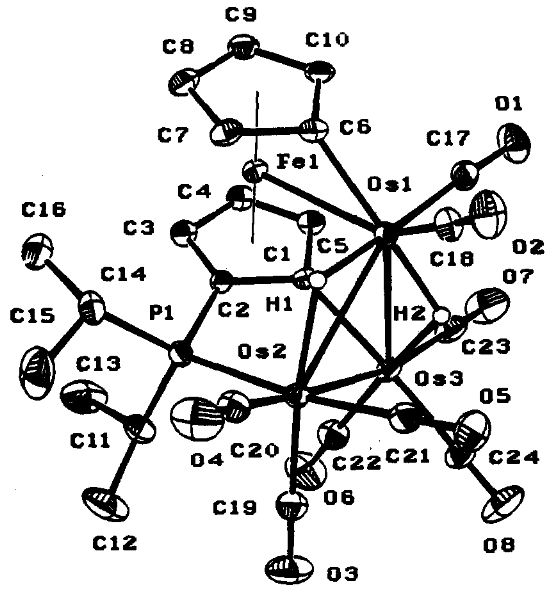

Figure 1. Perspective view of 7; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

opposite sides. Os–C(1) distances (2.173 (5) Å in 7 and 2.181 (7) Å in 8) are longer than Os–C(6) distances (2.067 (5) Å in 7 and 2.065 (8) Å in 8). The Fe→Os distances are 2.858 (1) Å for 7 and 2.836 (1) Å for 8, which are comparable with the bond lengths measured for 2 (2.826 (1) Å for **2a** and 2.830 (1) Å for **2b**).[2] The Os–CO bond lengths show some variation, the shortest ones involve the 8-coordinated osmium atom Os(1) in 7 (av 1.860 Å) and Os(3) in 8 (av 1.866 Å). The longest ones involve the axial carbonyls on the remaining two osmium metal centers (av 1.926 Å for 7, C(21) and C(24); and av 1.922 Å for 8, C(25) and C(28)).

The metalated ferrocenyl moieties have a slightly staggered configuration (torsion angle of 5.1 (3)° for 7 and 12.4 (4)° for 8), and the Cp rings are nearly parallel, with very small ring tilt angles (1.26° for 7 and 1.85° for 8). It is interesting to note that the second ferrocenyl group in 8 has a slightly larger ring tilt angle at 2.84°, and the same phenomenon was also noted for 2.[2] Although the Fe–Cp (centroid) distances are similar, the Fe–C bonds do show different lengths, probably the result of a slight motion of the iron atom in order to form the Fe→Os bond. Thus for the dangling ferrocenyl group in 8, all Fe–C distances are the same (av 2.042 Å), but for the metalated ferrocenyl moiety, Fe(1)–C(1) (2.121 (7) Å) is longer than the other four in Cp(1) (av 2.046 Å), and Fe(1)–C(6) (1.987 (7) Å) is appreciably shorter than the other four in Cp(2) (av 2.060 Å). Similar variations are also observed for 1 and 2.[2] The phosphorus atoms are almost in the Cp planes, but the osmium atoms directly bonded to the Cp rings are, like those in 2, quite removed from these planes. For

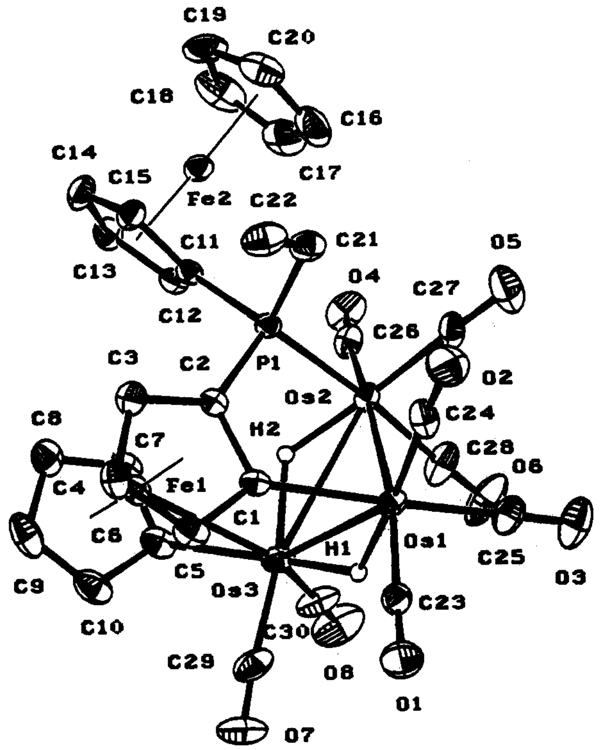

Figure 2. Perspective view of 8; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.

example, in 7, Os(3) is 0.765 Å away from the Cp(1) plane, and Os(1) is 1.22 Å away from the Cp(2) plane; Fe(1) is 1.649 Å from Cp(2), so the movement of Os(1) away from the anticipated coplanarity with Cp(2) is remarkable.

The spectroscopic data for 7 and 8 are in accord with their solid-state structures. In particular, the seven protons on each metalated ferrocenyl moiety are inequivalent and are seen as well-resolved resonances in the ^1H NMR spectra. The two bridging hydrides in each complex have very similar chemical shifts and coupling constants, and there is no indication of any exchange process involving the noncarbonyl ligands.

The isolation of these two alkylferrocenylphosphine derivatives indicates that the ease of metalation of ferrocenyl C–H bonds by Os_3 cluster is at least comparable with that of both aryl and alkyl C–H bonds and that Fe→Os bonding involving a ferrocene moiety is not just a curiosity. Indeed, these bonds are the shortest Fe(ferrocene)→M bonds known,[4-7] and they appear to be formed as long as there is one ferrocenyl group on the phosphine, thus providing a general route to this type of complex.

The formation of 7 and 8 is in accord with the generally held belief that metalation of a $C(sp^2)$–H bond is easier than a $C(sp^3)$–H.[15] However, this is not always the case. The thermolysis of $Ru_3(CO)_{10}[Fe(\eta\text{-}C_5H_4PPr^i_2)_2]$ affords products that result from $C(sp^3)$–H and P–$C(sp^3)$ cleavage with only one product showing a P–ferrocenyl cleavage.[3] Our more recent results with molecules that contain alkyl, aryl, and ferrocenyl moieties indicate that both accessibility and the number of particular C–H bonds play an important role in determining which group will be metalated. Further work is in progress to better understand these C–H activations, and the pyrolytic studies are being extended to Ru_3 clusters and to other ligands such as ferrocenylarsines and ferrocenyl sulfides.

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Supplementary Material Available: Stereo ORTEP diagrams of 7 and 8 and listings of hydrogen atom parameters and complete tables of bond lengths and bond angles, torsion or conformation angles, intermolecular contacts, and least-squares planes for 7 and 8 (22 pages). Ordering information is given on any current masthead page.

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[15] Garrou, P. E. *Chem. Rev.* 1985, *85*, 171.