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Synthesis, Crystal Structure, and Some Reactions of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$

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The dialkylidyne complex $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ is formed, together with $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$, by sequential treatment of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ with PhLi and $MeOSO_2CF_3$. $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ has been characterized by IR, mass, and NMR (^1H and ^{13}C) spectroscopies and by a single-crystal X-ray structure determination. $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 10.6679$ (19) Å, $b = 14.2218$ (12) Å, $c = 14.2097$ (22) Å, $\beta = 99.713$ (13)°, $V = 2124.9$ (5) Å,[3] and $Z = 4$. X-ray diffraction data (Mo Kα, $2\theta = 6\text{–}45°$) were collected on a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved and refined to $R_F = 5.5\%$ and $R_{wF} = 3.7\%$ for all 2798 reflections ($R_F = 2.9\%$ and $R_{wF} = 3.0\%$ for those 1986 reflections with $|F_o| > 6\sigma(|F_o|)$). The molecule consists of three $Os(CO)_3$ groups which are linked by osmium–osmium bonds (Os–Os = 2.797 (1)–2.813 (1) Å) and capped by two alkylidyne ligands. Osmium–carbon distances are 2.061 (13)–2.100 (14) Å to C(1) of the μ_3-COMe ligand and 2.120 (12)–2.139 (13) Å to C(3) of the μ_3-CPh ligand; the C(1)···C(3) distance is 2.688 (18) Å. Protonation of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ gives $[(\mu\text{-}H)Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)^+]$. Treatment of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ with PPh_3 yields $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ and $Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$.

Introduction

Pyrolysis of the alkyne complexes $Cp_3M_3(CO)(C_2R_2)$ (M = Rh, Ir; R = Ph, Tol) leads to the dialkylidyne trinuclear clusters $Cp_3M_3(\mu_3\text{-}CR)_2$,[1] examples of which are also formed by heating CpM(CO)L (L = CO, PPh_3) with RC≡CR.[2] However, attempts to prepare $Os_3(CO)_9(\mu_3\text{-}CR)_2$ by heating the isoelectronic complexes $Os_3(CO)_{10}(C_2R_2)$ (R = Ph, Tol) only lead to the unsaturated species $Os_3(CO)_9(C_2R_2)$ without alkyne ligand cleavage.[3] In contrast, the triiron dialkylidyne complexes $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$,[4] $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$,[5] and $Fe_3(CO)_9(\mu_3\text{-}CF)_2$[6] have been prepared and characterized.

Recently, we found that[7,8] sequential treatment of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ with PhLi and $MeOSO_2CF_3$ yields a benzylidyne complex, $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$,[7] together with a dialkylidyne complex, $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$.[8] Presented in this paper are results concerning the optimized synthesis, crystal structure, and some reactions of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$.

Experimental Section

General Procedures. $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ was prepared from $Os_3(CO)_{12}$ by Keister's method.[9] ^{13}CO-enriched $Os_3({}^*CO)_{12}$ (ca. 50% enriched) was prepared by heating a solution of $Os_3(CO)_{12}$ in decalin at 110 °C for 48 h under 12 equiv of ^{13}CO (90% ^{13}CO, Mound Laboratories) in a pressure bottle. Phenyllithium (Alfa, 1.8 M in ether/benzene), methyl trifluoromethanesulfonate (Aldrich), boron tribromide (Aldrich, 1 M in hexane), trifluoromethanesulfonic acid (Aldrich), triphenylphosphine (Aldrich), and triethylamine (Kodak) were used directly as received. Decane was distilled from sodium, and diethyl ether, THF, and cyclohexane were distilled from sodium benzophenone ketyl before

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use. Dichloromethane and chloroform were dried over phosphorous pentoxide and distilled before use. Dichloromethane-d_2 was dried over phosphorus pentoxide and vacuum distilled before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel GF (Type 60, E. Merck). Melting points were determined in sealed capillaries. ^{1}H and ^{13}C NMR spectra were obtained on a Nicolet NT-360 spectrometer at 360 and 90.56 MHz, respectively. IR spectra were taken on a Perkin-Elmer 281 B spectrometer and were calibrated with polystyrene film and cyclohexane (2138.5 cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. Field desorption mass spectra were obtained by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences (Illinois) on a Varian-MAT 731 mass spectrometer.

Preparation of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) from (μ-H)Os$_3$(CO)$_{10}$(μ-COMe). An oven-dried, 500-mL Schlenk flask was equipped with a magnetic stir bar and a rubber serum stopper. A solution of (μ-H)Os$_3$(CO)$_{10}$(μ-COMe) (500 mg, 0.559 mmol) in freshly distilled diethyl ether (250 mL) was introduced under nitrogen by means of a cannula through the serum stopper. After the mixture was cooled to 0 °C with an ice bath, phenyllithium (778 μL, 1.4 mmol) was added via a syringe over a period of 30 min and methyl trifluoromethanesulfonate (750 μL, 6.63 mmol) then aded via a syringe. The cloudy mixture was concentrated slowly to ca. 30 mL under vacuum at 0 °C, resulting in a clear orange-red solution, which was then placed under nitrogen and stirred at 35 °C for 72 h. The volatile materials were removed under vacuum, and the oily red residue was subjected to TLC, eluting with n-pentane. Isolation of the material forming the first orange-red band gave (μ-H)Os$_3$(CO)$_{10}$(μ_3-CPh)[7] (213 mg, 0.226 mmol, 40%). Crystallization of the material forming the second, orange band from n-hexane afforded air-stable, orange-red crystals of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) (220 mg, 0.23 mmol, 41%), mp 137–139 °C. Anal. Calcd for Os$_3$C$_{18}$H$_8$O$_{10}$: C, 22.64; H, 0.84; Os, 59.76. Found: C, 22.83; H, 0.78; Os, 58.9. Mass spectrum: m/z 960 (M$^+$, ^{192}Os). IR (C$_6$H$_{12}$): ν(CO) 2065 (vs), 2060 (vs), 2024 (s), 2003 (m), 1989 (sh) cm^{-1}. ^{1}H NMR ((CD$_3$)$_2$CO, 20 °C): δ 7.81 (d, 2 H, J(H–H) = 7 Hz, C$_6$H$_5$(ortho)), 7.31 (t, 2 H, J(H–H) = 7 Hz, C$_6$H$_5$ (meta)), 7.21 (tr, 1 H, J(H–H) = 7 Hz, C$_6$H$_5$ (para)), 4.62 (s, 3 H, OCH$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 20 °C): δ 319.4 (s, $\equiv$COMe), 234.6 (s, $\equiv$CPh), 173.9 (s, 9 CO).

The crystal of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) found suitable for X-ray analysis was grown from diethyl ether–hexane at room temperature.

Protonation of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe). Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) (6 mg, 0.006 mmol) and chloroform-d (0.6 mL) were placed in an oven-dried NMR tube under an atomosphere of nitrogen in a glovebag. Trifluoromethanesulfonic acid (2.5 μL, 5 equiv) was added to the orange solution via a syringe, resulting in a color change to deep red. The tube was then capped with a rubber serum stopper and removed from the glove bag. The product was formulated as {[(μ-H)Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe)$^+$][CF$_3$SO$_3^-$]}, on the basis of NMR data. ^{1}H NMR (17 °C): δ 7.69 (d, 2 H, J(H–H) = 7.9 Hz, C$_6$H$_5$(ortho)), 7.53–7.42 (m, 3 H, C$_6$H$_5$ (meta, para)), 4.80 (s, 3 H, OCH$_3$), –15.56 (s, 1 H, μ-H). The ^{13}C NMR spectrum for {[(μ-H)Os$_3$(*CO)$_9$(μ_3-(*CO)$_9$-(μ_3-*CPh)(μ_3-*COMe)$^+$][CF$_3$SO$_3^-$]} was taken in CD$_2$Cl$_2$ at –75 °C: δ 305.0 (s, $\equiv$COMe), 266.1 (s, $\equiv$CPh), 167.1 (s, 3 CO), 166.1 (s, 2 CO), 165.2 (s, 2 CO), 162.2 (d, ^2J(C–H) = 8 Hz, 2 CO).

The red solution remained stable at room temperature for ca. 24 h and then slowly decomposed to give uncharacterized species over a period of 4 days. The protonation can be reversed to form Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) quantitatively by washing the solution of [(μ-H)Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe)$^+$] with aqueous sodium bicarbonate (10%) in a separatory funnel.

Reaction of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) with Triphenylphosphine. An oven-dried, 100-mL three-necked round-bottomed flask was equipped with a magnetic stir bar. One neck was stoppered, one was fitted with a reflux condenser connected to an oil bubbler, and the third neck had an inlet tube for introduction of gas into the solution. A solution of Os$_3$(CO)$_9$(μ_3-COMe) (26 mg, 0.027 mmol) and triphenylphosphine (36.5 mg, 0.139 mmol) in decane (50 mL) was transfered into the flask. With nitrogen bubbling through the solution, it was heated at 120 °C for 7 h, at which point the IR spectrum showed no absorptions due to Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe). The solvent was removed under vacuum, and the residue was subjected to TLC eluting with n-pentane. Crystallization of the material forming the first, yellow band from dichloromethane–methanol produced air-stable, orange crystals of Os$_3$(CO)$_8$(PPh$_3$)(μ_3-CPh)(μ_3-COMe) (7 mg, 0.006 mmol, 20%). Anal. Calcd for Os$_3$C$_{35}$H$_{23}$O$_9$P: C, 35.34; H, 1.94. Found: C, 34.85; H, 1.99. Mass spectrum: m/z 1194 (M$^+$, ^{192}Os). IR(C$_6$H$_{12}$): ν(CO) 2077 (m), 2052 (vs), 2016 (vs), 2003 (sh) 1988 (s, br), 1974 (m), 1944 (m, br) cm^{-1}. ^{1}H NMR ((CD$_3$)$_2$CO, –20 °C): δ 7.94 (d, 2 H, J = 7 Hz, C$_6$H$_5$ (ortho)), 7.53–7.40 (m, 15 H, PPh$_3$), 7.29 (t, 2 H, J = 7 Hz, C$_6$H$_5$ (meta)), 7.14 (t, 1 H, J = 7 Hz, C$_6$H$_5$ (para)), 3.88 (s, 3 H, OCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, –60 °C): δ 318.9 (s, $\equiv$COMe), 231.5 (d, ^2J(C–P) = 21 Hz, $\equiv$CPh), 183.5 (d, ^2J(C–P) = 3 Hz, 2 CO), 174.8 (s, 6 CO). Crystallization of the material forming the second, yellow band from dichloromethane–methanol yielded air-stable, orange crystals of Os$_3$(CO)$_7$(PPh$_3$)$_2$(μ_3-CPh)(μ_3-COMe) (21 mg, 0.015 mmol, 54%). Anal. Calcd for Os$_3$C$_{52}$H$_{38}$O$_8$P$_2$: C, 43.88; H, 2.67. Found: C, 44.20; H, 2.89. Mass spectrum: m/z 1428 (M$^+$, ^{192}Os). IR (C$_6$H$_{12}$): ν(CO) 2051 (m), 2011 (s), 2000 (m), 1980 (m), 1970 (m, br), 1944 (m, br), 1934 (m, br) cm^{-1}. ^{1}H NMR ((CD$_3$)$_2$CO, 17 °C): δ 7.72 (d, 2 H, J = 7 Hz, C$_6$H$_5$(ortho)), 7.51–7.32 (m, 30 H, PPh$_3$), 7.10–7.01 (m, 3 H, C$_6$H$_5$ (meta, para)), 3.64 (s, 3 H, OCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 17 °C): δ 317.7 (s, $\equiv$COMe), 237.2 (t, ^2J(C–P) = 10 Hz, $\equiv$CPh), 184.1 (d, ^2J(C–P) = 8 Hz, 2 CO), 183.6 (s, 2 CO), 176.9 (s, 3 CO).

Table I. Experimental Data for X-ray Diffraction Study of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe)

(A) Crystal Parameters at 23 °C

cryst system: monoclinic
space group: $P2_1/c$ (C_{2h}^5; No. 14)
a = 10.6679 (19)Å
b = 14.2218 (12) Å
c = 14.2097 (22)Å

β = 99.713 (13)°
V = 2124.9(5)Å^3
Z = 4
M_r 954.85
ρ(calcd) = 2.98 g cm^{-3}

(B) Measurement of Data

diffractometer: Syntex P2$_1$
radiatn: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly orientated (pyrolitic) graphite
scan type: coupled θ(crystal)–2θ(counter)
scan width: symmetrical, [1.8 + $\Delta(\alpha_2 - \alpha_1)$]°
scan speed: 2.5 deg min^{-1}
reflectns collected: $h,k,\pm l$ for 2θ = 6.0–45.0°, 2971 total yielding 2798 unique reflections
absorptn coeff: μ = 190.1 cm^{-1}; corrected by interpolation (in 2θ and ϕ) between experimental ψ scans of four close-to-axial reflections (104, 204, 206, 317)
file name: OSMC-179

Attempted Reaction of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) with Boron Tribromide. A 25-mL Schlenk tube was equipped with a magnetic stir bar and a rubber serum stopper. The tube was evacuated and dried by heating with a heatgun for ca. 5 min. The tube was cooled under vacuum, and nitrogen was admitted. The serum stopper was removed briefly to allow addition of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) (25 mg, 0.026 mmol) against a nitrogen flow. Freshly distilled dichloromethane (5 mL) was introduced by means of a cannula through the serum stopper. Boron tribromide (78 μL 0.078 mmol) was added via a syringe. The solution was placed under nitrogen and stirred at room temperature for 5 h, but no reaction was observed. Even at higher temperatures (40–60 °C, cyclohexane), no reaction occurred.

Attempted Reaction of (μ-H)Os$_3$(CO)$_{10}$(μ-COMe) with Boron Tribromide. (μ-H)Os$_3$(CO)$_{10}$(μ-COMe) (20 mg) was treated with boron tribromide by the same procedure as described above; no reaction was observed.

Collection of X-ray Diffraction Data and Structure Solution for Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe). A bright red crystal of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) with approximate dimensions 0.07 × 0.17 × 0.20 mm was mounted in a thin-walled glass capillary and aligned on the Syntex P2$_1$ diffractometer. Data were collected as previously described[10] (see Table I). After cooling for absorption and Lorentz and polarization factors, all data were converted to unscaled $|F_o|$ values and placed on an approximate

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Table II. Final Positional Parameters (with Esd's) for $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$

atom	x	y	z	B(iso), Å
Os(1)	0.06213 (5)	0.02562 (4)	0.23243 (4)	
Os(2)	0.28726 (5)	0.12295 (4)	0.30503 (4)	
Os(3)	0.27576 (5)	−0.07229 (4)	0.32566 (4)	
O(1)	0.12978 (92)	0.04118 (58)	0.45478 (64)	
O(11)	−0.1803 (10)	0.02296 (79)	0.32265 (79)	
O(12)	−0.0253 (12)	−0.1371 (10)	0.0994 (11)	
O(13)	−0.0372 (12)	0.1809 (10)	0.09308 (87)	
O(21)	0.3893 (13)	0.19595 (86)	0.50704 (90)	
O(22)	0.5404 (11)	0.15552 (94)	0.2372 (10)	
O(23)	0.1773 (12)	0.30857 (84)	0.22420 (95)	
O(31)	0.1782 (14)	−0.26024 (85)	0.2394 (11)	
O(32)	0.5506 (11)	−0.10033 (93)	0.2948 (11)	
O(33)	0.3116 (14)	−0.1464 (10)	0.53049 (95)	
C(1)	0.1704 (13)	0.03555 (91)	0.3699 (10)	
C(2)	0.0695 (18)	0.1267 (12)	0.4782 (11)	
C(3)	0.2489 (11)	0.01460 (94)	0.20105 (92)	
C(4)	0.2855 (12)	0.00317 (78)	0.10740 (92)	
C(5)	0.2929 (15)	0.0811 (11)	0.0482 (10)	
C(6)	0.3249 (16)	0.0690 (13)	−0.0422 (11)	
C(7)	0.3471 (15)	−0.0184 (14)	−0.0771 (11)	
C(8)	0.3407 (15)	−0.0938 (12)	−0.0187 (12)	
C(9)	0.3108 (15)	−0.0847 (10)	0.0726 (10)	
C(11)	−0.0929 (15)	0.0255 (10)	0.2902 (11)	
C(12)	0.0012 (14)	−0.0706 (13)	0.1444 (12)	
C(13)	−0.0058 (14)	0.1211 (13)	0.1436 (11)	
C(21)	0.3489 (14)	0.1719 (10)	0.4308 (13)	
C(22)	0.4468 (15)	0.1448 (10)	0.2617 (13)	
C(23)	0.2193 (16)	0.2384 (11)	0.2525 (10)	
C(31)	0.2165 (14)	−0.1913 (11)	0.2716 (12)	
C(32)	0.4486 (14)	−0.0932 (12)	0.3060 (13)	
C(33)	0.2977 (17)	−0.1188 (12)	0.4541 (13)	
H(2A)	0.004 (16)	0.109 (12)	0.509 (12)	6.0
H(2B)	0.128	0.164	0.519	6.0
H(2C)	0.037	0.160	0.421	6.0
H(5)	0.276	0.142	0.069	6.0
H(6)	0.331	0.122	−0.080	6.0
H(7)	0.366	−0.025	−0.139	6.0
H(8)	0.357	−0.154	−0.041	6.0
H(9)	0.307	−0.138	0.111	6.0

Table III. Interatomic Distances (in Å) for $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$

(A) Osmium–Osmium Bond Lengths			
Os(1)–Os(2)	2.813 (1)	Os(2)–Os(3)	2.797 (1)
Os(1)–Os(3)	2.805 (1)		
(B) Osmium–Carbyne Distances			
Os(1)–C(1)	2.100 (14)	Os(1)–C(3)	2.120 (12)
Os(2)–C(1)	2.083 (14)	Os(2)–C(3)	2.126 (13)
Os(3)–C(1)	2.061 (13)	Os(3)–C(3)	2.139 (13)
(C) Distances within the Two μ_3-Alkylidyne Ligands			
C(1)–O(1)	1.350 (17)	C(6)–C(7)	1.374 (27)
O(1)–C(2)	1.441 (19)	C(7)–C(8)	1.367 (25)
C(3)–C(4)	1.458 (18)	C(8)–C(9)	1.395 (22)
C(4)–C(5)	1.402 (19)	C(9)–C(4)	1.388 (19)
C(5)–C(6)	1.394 (21)	C(1)···C(3)	2.688 (18)
(D) Osmium–Carbonyl Distances			
Os(1)–C(11)	1.967 (16)	Os(1)–O(11)	3.074 (11)
–C(12)	1.894 (18)	–O(12)	3.033 (14)
–C(13)	1.911 (17)	–O(13)	3.035 (14)
Os(2)–C(21)	1.928 (17)	Os(2)–O(21)	3.074 (13)
–C(22)	1.931 (16)	–O(22)	3.052 (13)
–C(23)	1.896 (16)	–O(23)	3.035 (12)
Os(3)–C(31)	1.921 (16)	Os(3)–O(31)	3.049 (13)
–C(32)	1.934 (15)	–O(32)	3.063 (12)
–C(33)	1.918 (18)	–O(33)	3.059 (13)
(E) Carbon–Oxygen Distances within the Os–CO Groups			
C(11)–O(11)	1.108 (20)	C(23)–O(23)	1.140 (20)
C(12)–O(12)	1.148 (23)	C(31)–O(31)	1.128 (21)
C(13)–O(13)	1.127 (22)	C(32)–O(32)	1.131 (20)
C(21)–O(21)	1.148 (21)	C(33)–O(33)	1.140 (22)
C(22)–O(22)	1.121 (20)		

absolute scale by means of a Wilson plot.

Calculations were performed on the Syntex XTL system[11] as modified at SUNY—Buffalo. The positions of the osmium atoms were determined by using direct methods (MULTAN).[12] A single difference Fourier synthesis revealed the positions of all remaining non-hydrogen atoms. The model was refined by using full-matrix least-squares techniques leading to convergence with[13] discrepancy indices $R_F = 5.5\%$, $R_{wF} = 3.7\%$, and GOF = 1.189 for 283 variables refined against all 2798 observations ($R_F = 3.8\%$ and $R_{wF} = 3.4\%$ for those 2272 reflections with $|F_o| > 3\sigma(|F_o|)$ and $R_F = 2.9\%$ and $R_{wF} = 3.0\%$ for those 1986 reflections with $|F_o| > 6\sigma(|F_o|)$).

The analytical form of the scattering factors for the neutral atoms were corrected for the $\Delta P'$ and $i\Delta P'$ terms.[14] The function minimized was $\sum w(|F_o| - |F_o|)^2$, where $w = [\{\sigma(|F_o|)\}^2 + \{0.015|F_o|\}^2]^{-1}$. Hydrogen atoms were placed in calculated positions with d(C–H) = 0.95 Å.[15]

Final positional parameters are listed in Table II; anisotropic thermal parameters appear as supplementary material.

Results and Discussion

Synthesis of $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$. A sequential Ph^-/Me^+ treatment of $(\mu\text{-H})Os_3(CO)_{10}$ $(\mu\text{-COMe})$ effects the transformations of COMe → Ph to form $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$[7] as well as CO(H) → CPh to form $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ (eq 1). The ratio of $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh})$ to $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ depends on the temperature at which the methylation is conducted. It is about 1:1 at 35 °C but increases to ca. 5:3 at lower temperatures (<25 °C). Our recent studies have led to the isolation and characterization of an intermediate, $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-C(OMe)}_2)(\mu_3\text{-CPh})$,[8] in the formation of both compounds; but further details of the reaction are still under investigation.

$$(\mu\text{-H})O_3(CO)_{10}(\mu\text{-COMe}) \xrightarrow[\text{2. MeOSO}_2\text{CF}_3]{\text{1. PhLi}} \begin{array}{c}(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh}) \\ + \\ Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})\end{array} \qquad (1)$$

Crystal Structure of $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$. The crystal consists of an ordered arrangement of discrete $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ molecules, which are separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. The molecular geometry and atomic labeling scheme are illustrated in Figure 1, while Figure 2 provides a stereospecific view of the molecule. Interatomic distances and angles are collected in Tables III and IV.

The overall molecule consists of three $Os(CO)_3$ groups which are linked together by Os–Os bonds to form a triangular $Os_3(CO)_9$ moiety, which in turn is capped on one face by a μ_3-CPh ligand and on the opposite face by a μ_3-COMe ligand.

Since C(1)···C(3) = 2.688 (18) Å, there is no direct interaction between the two alkylidyne fragments. The osmium–osmium bond lengths found for $Os_3(CO)_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$ (average 2.805 ± 0.008 Å) are slightly shorter than values found in the parent compound $Os_3(CO)_{12}$(Os–Os(av) = 2.877 (3) Å).[16] Individual Os-CO bond

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(13) R_F (%) = $100\sum||F_o| - |F_c||/\sum|F_o|$, R_{wF} (%) = $100\,[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and GOF = $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO = number of observations and NV = number of variables.

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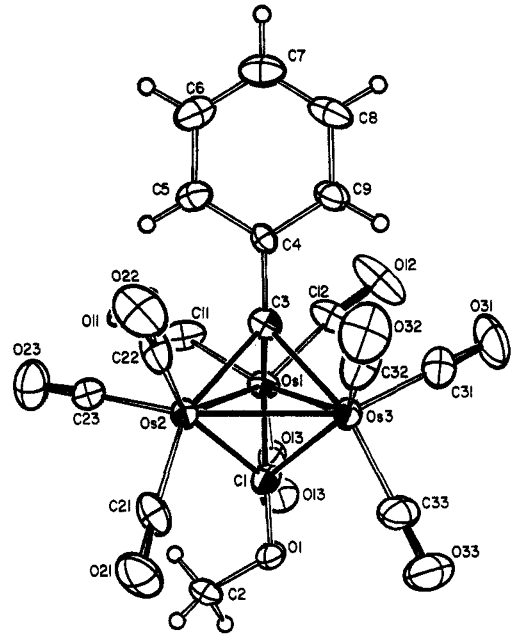

Figure 1. Labeling of atoms in the $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ molecule (ORTEP-II diagram, with hydrogen atoms artificially reduced).

lengths range from 1.894 (18) through 1.967 (16) Å, averaging 1.922 ± 0.022 Å. The C–O distances range from 1.108 (20) through 1.148 (21) Å, averaging 1.132 ± 0.013 Å, while Os–C–O angles are in the range 170.6 (15)–179.6 (16)° (average 177.6 ± 2.7°).

The μ_3-COMe has internal bond lengths of C(1)–O(1) = 1.350 (17) and O(1)–C(2) = 1.441 (19) Å and caps the triosmium core with Os(1)–C(1) = 2.100 (14), Os(2)–C(1) = 2.083 (14), and Os(3)–C(1) = 2.061 (13) Å (average Os–COMe = 2.081 ± 0.019 Å); Os–C(1)–Os angles are 84.5 (5)–84.9 (5)° while Os–C(1)–O(1) angles are slightly less symmetrical with values from 126.2 (9) through 131.8 (10)°.

The μ_3-CPh ligand seems to be slightly less strongly bound to the triosmium core. Thus, Os–CPh distances are longer than Os–COMe distances (Os(1)–C(3) = 2.120 (12), Os(2)–C(3) = 2.126 (13), and Os(3)–C(3) = 2.139 (13) Å; the average Os–CPh distance of 2.128 ± 0.010 Å is 0.047 Å *longer* than the average Os–COMe distance). In keeping with this, Os–C(3)–Os angles are in the range 82.0 (5)–83.0 (5)° and are slightly more acute than the Os–C(1)–Os angles.

Table IV. Selected Interatomic Angles (in deg) for $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$

(A) Intermetallic Angles			
Os(3)–Os(1)–Os(2)	59.72 (2)	Os(2)–Os(3)–Os(1)	60.28 (2)
Os(1)–Os(2)–Os(3)	60.01 (2)		
(B) Osmium–(μ_3-Carbyne) Angles			
Os(1)–C(1)–Os(2)	84.5 (5)	Os(1)–C(3)–Os(2)	83.0 (5)
Os(1)–C(1)–Os(3)	84.8 (5)	Os(1)–C(3)–Os(3)	82.4 (5)
Os(2)–C(1)–Os(3)	84.9 (5)	Os(2)–C(3)–Os(3)	82.0 (5)
Os(1)–C(1)–O(1)	128.7 (9)	Os(1)–C(3)–C(4)	127.3 (9)
Os(2)–C(1)–O(1)	131.8 (10)	Os(2)–C(3)–C(4)	131.7 (9)
Os(3)–C(1)–O(1)	126.2 (9)	Os(3)–C(3)–C(4)	132.3 (9)
(C) Os–Os–CO Angles			
Os(2)–Os(1)–C(11)	125.0 (5)	Os(3)–Os(2)–C(21)	106.0 (5)
–C(12)	140.8 (5)	–C(22)	104.5 (5)
–C(13)	95.6 (5)	–C(23)	151.7 (5)
Os(3)–Os(1)–C(11)	118.4 (5)	Os(1)–Os(3)–C(31)	93.6 (5)
–C(12)	96.6 (5)	–C(32)	136.6 (5)
–C(13)	148.4 (5)	–C(33)	125.4 (5)
Os(1)–Os(2)–C(21)	130.9 (5)	Os(2)–Os(3)–C(31)	148.2 (5)
–C(22)	134.9 (5)	–C(32)	94.5 (5)
–C(23)	92.0 (5)	–C(33)	116.2 (5)
(D) Os–C–O Angles			
Os(1)–C(11)–O(11)	178.2 (14)	Os(3)–C(31)–O(31)	178.0 (15)
–C(12)–O(12)	170.6 (15)	–C(32)–O(32)	176.3 (15)
–C(13)–O(13)	174.7 (15)	–C(33)–O(33)	179.6 (16)
Os(2)–C(21)–O(21)	175.8 (14)		
–C(22)–O(22)	178.4 (15)		
–C(23)–O(23)	177.4 (14)		
(E) Angles within the μ_3-Alkylidyne Ligands			
C(1)–O(1)–C(2)	118.6 (11)	C(7)–C(8)–C(9)	122.4 (16)
C(3)–C(4)–C(5)	120.7 (12)	C(8)–C(9)–C(4)	120.3 (14)
C(4)–C(5)–C(6)	120.2 (14)	C(9)–C(4)–C(5)	117.7 (12)
C(5)–C(6)–C(7)	121.9 (16)	C(9)–C(4)–C(3)	121.6 (12)
C(6)–C(7)–C(8)	117.5 (16)		

^{13}C NMR of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$. The variable-temperature ^{13}C NMR spectra for $Os_3(\text{*}CO)_9(\mu_3\text{-*}CPh)(\mu_3\text{-*}COMe)$ (ca. 50% ^{13}C enrichment) are shown in Figure 3. The spectrum at 20 °C shows the alkylidyne carbons at δ 319.4 and 234.6 and the carbonyl carbons at δ 173.9. By comparing the alkylidyne carbon resonances measured for $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}COMe)$ (δ 205.5)[9] and $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CPh)$ (δ 153.7),[7] the signals at δ 319.4 and 234.6 can be assigned to the methoxycarbyne and the benzylidyne carbons, respectively. Interestingly, this significant difference between the two alkylidyne carbon resonances is in sharp contrast to the analogous triiron complex $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ (δ 359.8 (COMe), 334.6 (CMe).[4]

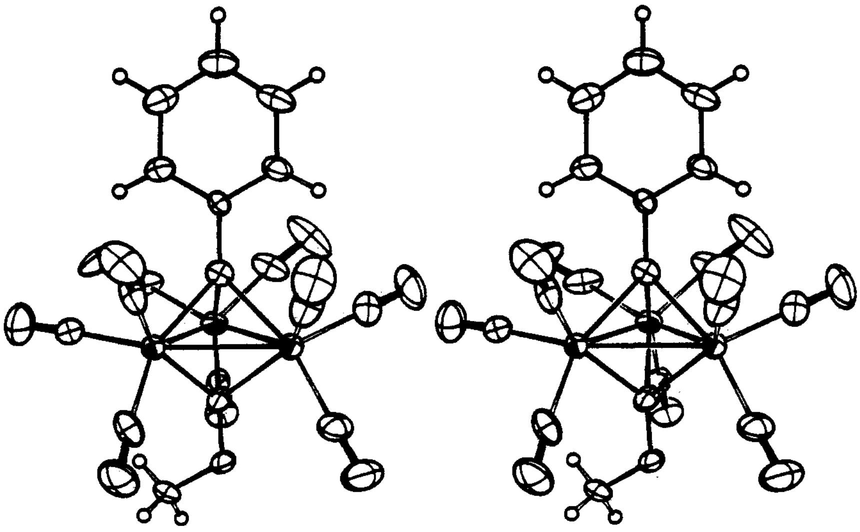

Figure 2. Stereoscopic view of the $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ molecule.

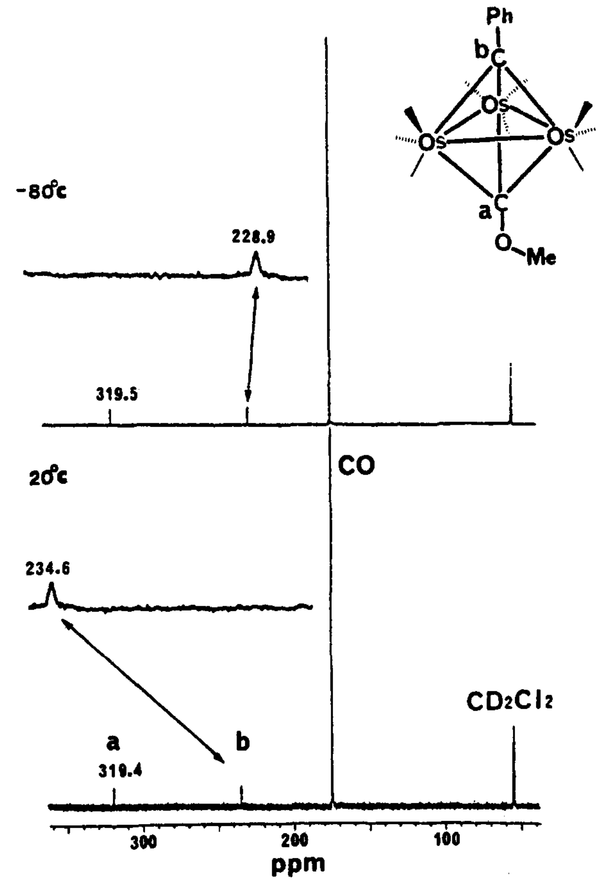

Figure 3. 90-MHz ^{13}C NMR spectra of $Os_3({}^*CO)_9(\mu_3\text{-}{}^*CPh)(\mu_3\text{-}{}^*COMe)$ in CD_2Cl_2.

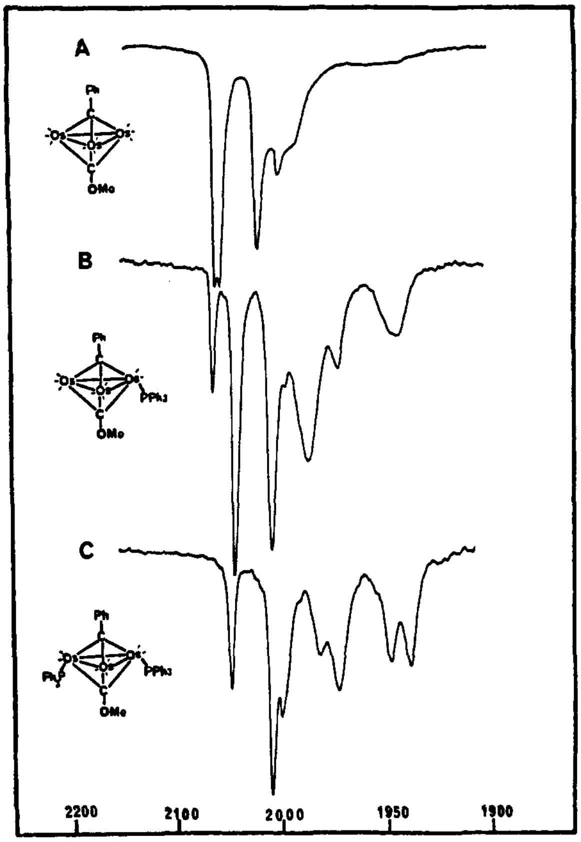

Figure 4. IR spectra in the carbonyl region for $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (A), $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (B), and $Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$(C) (all obtained in C_6H_{12}).

The carbonyl carbon signal at δ 173.9 remains sharp down to -110 °C, implying a low threefold rotational barrier for the carbonyls in the $Os(CO)_3$ unit. It has been shown that the energy barrier for the carbonyl threefold exchange at the $Os(CO)_4$ center decreases significantly from the six-coordinate osmium center in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ ($\Delta G^\ddagger$ = 17 kcal/mol)[17] to the pseudo-seven-coordinate osmium center in $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CR)$ ($\Delta G^\ddagger$ = 9 kcal/mol for R = H,[18] Ph[7]). In $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, the osmium centers are seven coordinate. The chemical shift of the benzylidyne carbon is quite temperature-dependent, changing from δ 234.6 at 20 °C to δ 228.9 at -80 °C, whereas the methoxycarbyne carbon resonance remains unchanged. It is unclear at presence why the two alkylidyne moieties behave differently. A similar temperature dependence of the alkylidyne carbon shifts was noted for $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$,[7] $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$,[8] and $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CCH_2CHMe_2)$.[19]

The methoxycarbyne carbon resonance position at δ 314.5 is comparable with that measured for $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ (δ 352.2)[17] but well downfield of that for $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}COMe)$ (δ 205.2).[9] Furthermore, the chemical shift of the benzylidyne carbon at δ 234.6 is considerably upfield of those measured for $Os_3(CO)_9(\mu_3\text{-}CPh)_2$ (δ 274.7)[20] and $Os_3(CO)_8(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)_2$ (δ 270.0).[20] The presence of a resonance interaction, $(M)_3^- {=}C{=}{}^+OMe$, has been proposed for the methoxycarbyne complexes $HM_3(CO)_{10}(\mu\text{-}COMe)$ (M = Fe,[21] Ru,[9,22] Os[9,17]). A similar resonance interaction might be operative in $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, leading to transfer of negative charge to the benzylidyne carbon and hence shielding. Support for this suggestion comes from a survey of the difference between C–O distances involving the alkylidyne carbon and the methoxy carbon in the complexes studied so far.[22] The difference is maximized in the μ_2-alkylidyne complex $(\mu\text{-}H)Ru_3(CO)_{10}(\mu\text{-}COMe)$[22b] in which C(alkylidyne)–O is 1.305 (5) Å as compared to O–C(Me) = 1.467 (8) Å yielding a difference of 0.162 (10) Å. In the present complex the C(alkylidyne)–O–Me system is defined by the bonds C(1)–O(1) = 1.350 (17) and O(1)–C(2) = 1.441 (19) Å; the difference is 0.091 (26) Å. Finally, in the complex $(\mu\text{-}H)Ru_3(CO)_8(\eta^4\text{-}C_6H_8)(\mu_3\text{-}COMe)$,[22b] we have C(alkylidyne)–O = 1.357 (3) and O–C(Me) = 1.399 (6) Å; the difference here is only 0.042 (7) Å.

IR and ^{1}H NMR Spectra of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$. The IR spectrum in the carbonyl region of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ is shown in Figure 4A. Such a simple absorption pattern reflects the highly symmetrical structure of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$. Unexpectedly, the analogous complex $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ was found to display a more complex pattern, in which eight absorption peaks were recorded.[4]

The ^{1}H NMR spectrum of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ is shown in Figure 5. Resonances between δ 7.82 and 7.20 are due to the phenyl protons. On the basis of the couplings, the 2 H doublet at δ 7.81, the 2 H triplet at δ 7.31 and the 1 H triplet at δ 7.21 (J = 7 Hz) can be assigned to the ortho, meta, and para protons, respectively. This

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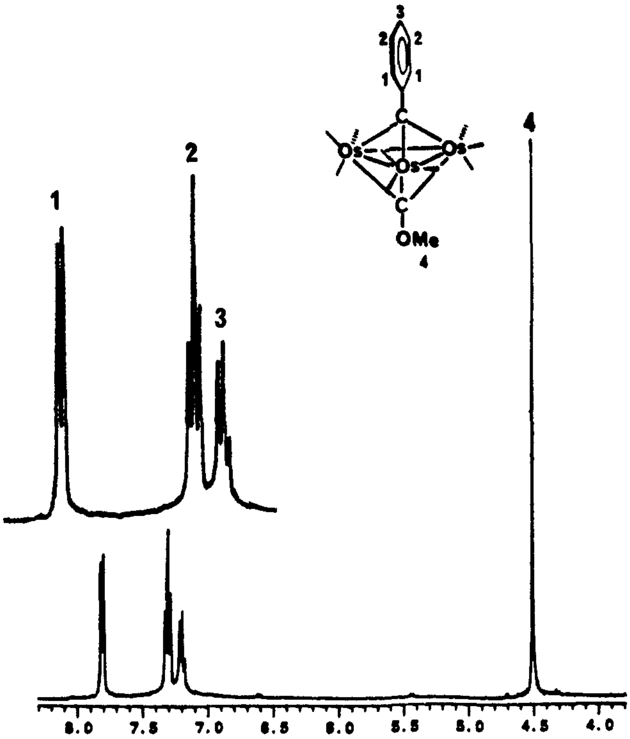

Figure 5. 360-MHz ^{1}H NMR spectrum of $Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-COMe) in $(CD_3)_2CO$.

type of pattern, in which the ortho protons are considerably downfield of the meta and para protons, has been noted for the phenyl groups in a variety of metal cluster benzylidyne complexes, such as $(\mu$-$H)Os_3(CO)_{10}(\mu_3$-CPh),[7] $(\mu$-$H)_3Os_3(CO)_9(\mu_3$-CPh),[7,23] and $Cp_3M_3(\mu_3$-$CPh)_2$ (M = Co,[2b] Rh,[1] Ir[1]). The methyl resonance at δ 4.62 is downfield of that measured for $(\mu$-$H)_3Os_3(CO)_9(\mu_3$-COMe) (δ 3.80)[23,24] but comparable with that for $(\mu$-$H)Os_3(CO)_{10}(\mu$-COMe) (δ 4.56).[17] Again, deshielding of the methyl protons may result from the resonance form $(M)_3{}^-{=}C{=}{}^+OMe$.

Reactivity of $Os_3(CO)_9(\mu_3$-CPh$)(\mu_3$-COMe) toward Boron Tribromide. Attempts at converting the methoxy group into a bromo substituent by treating $Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-COMe) with boron tribromide were unsuccessful. This is in contrast to the results concerning $(\mu$-$H)_3M_3(CO)_9(\mu_3$-COMe) (M = Os, Ru), where a facile reaction leading to $(\mu$-$H)_3M_3(CO)_9(\mu_3$-CBr)[23,24] was observed. It is not surprising that $(\mu$-$H)Os_3(CO)_{10}(\mu$-COMe) is also inert to boron tribromide, since the resonance interaction $(M)_3{}^-{=}C{=}{}^+OMe$ would decrease the nucleophilicity of the methoxy oxygen toward Lewis acids.

Protonation of $Os_3(CO)_9(\mu_3$-CPh$)(\mu_3$-COMe). Treatment of $Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-COMe) with CF_3SO_3H in chloroform solution causes a color change in the solution from orange to deep red, forming $\{[(\mu$-$H)Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-$COMe)^+][CF_3SO_3{}^-]\}$. This reaction can be reversed by treating the solution of $[(\mu$-$H)Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-$COMe)^+]$ with aqueous base, which affords $Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-COMe) quantitatively. Solutions of $[(\mu$-$H)Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-$COMe)^+]$ are stable at room temperature for ca. 24 h but decompose over a period of few days.

Although the crystal structure of $\{[(\mu$-$H)Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-$COMe)^+][CF_3SO_3{}^-]\}$ has not been determined, it has been carefully characterized by ^{1}H and ^{13}C NMR spectroscopy and apparently retains the dialkylidyne framework of the parent complex. The ^{1}H NMR spectrum of $\{[(\mu$-$H)Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-$COMe)^+][CF_3SO_3{}^-]\}$ shows a doublet at δ 7.69 with ^3J(H–H) = 7.9 Hz assigned to the orthoprotons, and a multiplet in δ 7.43 7.42 to overlapping of the meta and para protons of the phenyl ring. The methyl resonance at δ 4.80 is deshielded slightly compared to the parent complex $Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-COMe) (δ 4.62). The 1 H singlet at δ −15.56 is typical for bridging hydride resonances in metal clusters.[25]

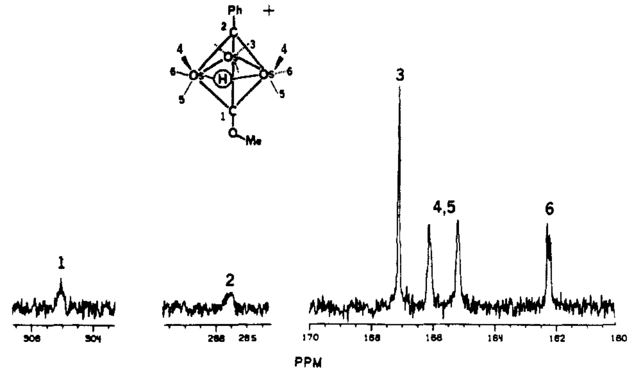

Figure 6. 90-MHz ^{13}C NMR spectrum of $\{[(\mu$-$H)Os_3(*CO)_9(\mu_3$-$*CPh)(\mu_3$-$*COMe)^+][CF_3SO_3{}^-]\}$ in CD_2Cl_2 at −70 °C.

The ^{13}C NMR spectrum of $\{[(\mu$-$H)Os_3(*CO)_9(\mu_3$-$*CPh)(\mu_3$-$*COMe)^+][CF_3SO_3{}^-]\}$ in CD_2Cl_2 is illustrated in Figure 6. Resonances at δ 305.1 and 265.4 are assigned to the methoxycarbyne and the benzylidyne carbon, respectively. The carbonyl carbons split into a 3:2:2:2 pattern in the range of δ 167–164. The benzylidyne carbon at δ 265.4 is shifted downfield significantly compared to that of $Os_3(*CO)_9(\mu_3$-$*CPh)(\mu_3$-$*COMe)$ (δ 230), whereas the remaining signals move slightly upfield. Thus, incorporation of the proton effects considerable deshielding of the benzylidyne carbon. The average resonance of δ 165.4 for the carbonyl carbons is 8.5 ppm upfield of that for $Os_3(*CO)_9(\mu_3$-$*CPh)(\mu_3$-$*COMe)$ (δ 173.9), apparently due to the positive charge on the metal framework. The 3 C signal at δ 167.1 is assigned to the $Os(CO)_3$ group facing the briding hydride. The hydride ligand, which presumably lies nearly in the Os_3 plane, hinders threefold rotation of carbonyls in the two bridged $Os(CO)_3$ groups and splits the resonances into three sets of two each. Thus, the 2 C signals at δ 166.1 and 165.2 can be assigned to two sets of carbonyls, with one set above and one set below the Os_3 plane. Finally, the 2 C signal at δ 162.2, which shows coupling to the hydride ligand (^2J(C–H) = 8 Hz), is assigned to the remaining two carbonyls located *trans* to the bridging hydride.

A similar protonation reaction on the tricobalt dialkylidyne complex $Cp_3Co_3(\mu_3$-$CR)_2$, yielding $[(\mu$-$H)$-$Cp_3Co_3(\mu_3$-$CR)_2{}^+]$ (R = *n*-Bu), was previously described by Vollhardt.[26] These results are consistent with theoretical indications[1] that the HOMO in these bicapped trimetal complexes is derived largely from metal–metal bonding.

Carbonyl Substitution by Triphenylphosphine. Treatment of $Os_3(CO)_9(\mu_3$-$CPh)(\mu_3$-COMe) with PPh_3 leads to CO substitution, forming $Os_3(CO)_8(PPh_3)(\mu_3$-$CPh)(\mu_3$-COMe) and $Os_3(CO)_7(PPh_3)_2(\mu_3$-$CPh)(\mu_3$-COMe), which have been characterized by microanalysis and IR, ^{1}H and ^{13}C NMR, and mass spectroscopies. The ^{1}H NMR spectra of both substituted complexes show that the benzylidyne protons have the same pattern as that for the unsubstituted complex, with the addition that the tri-

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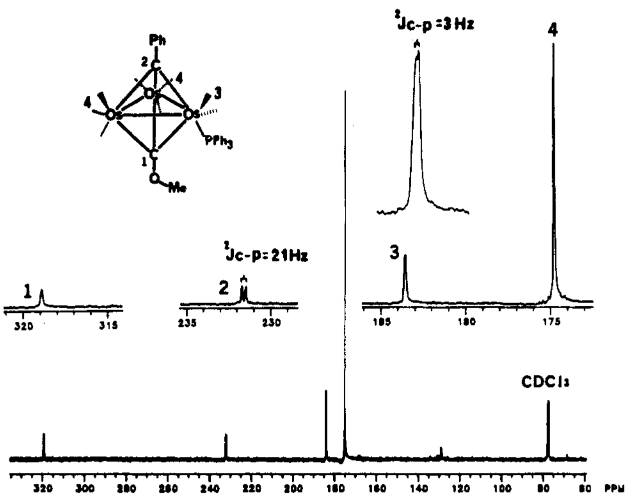

Figure 7. 90-MHz $^{13}C\{^1H\}$ NMR spectrum of $Os_3(^*CO)_8(PPh_3)(\mu_3\text{-}^*CPh)(\mu_3\text{-}^*COMe)$ in $CDCl_3$ at -60 °C.

phenylphosphine protons give rise to a complicated multiplet in the range δ 7.53–7.32. The phosphine ligands have a considerable shielding effect on the methoxy proton resonance, such that it appears at δ 4.62, 3.88, and 3.64 for $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, and $Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, respectively. The IR spectra in the carbonyl region for all three compounds are shown in Figure 4; it is apparent that the absorptions are shifted to lower energy with increasing substitution, consistent with the stronger net donor capability of the PPh_3 ligand compared with CO.

The ^{13}C NMR spectrum of $Os_3(^*CO)_8(PPh_3)(\mu_3\text{-}^*CPh)(\mu_3\text{-}^*COMe)$ is illustrated in Figure 7. It shows a signal at δ 318.9 for the methoxycarbyne carbon and a doublet at δ 231.5 with $^2J(C\text{-}P) = 21$ Hz for the benzylidyne carbon, together with resonances at δ 183.5 and 174.8 2:6 ratio for the carbonyl carbons. These data strongly suggest that the dialkylidyne framework is retained in $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$. On the basis of the strong $^{13}C\text{-}^{31}P$ coupling observed for the benzylidyne carbon at δ 231.5 ($^2J(C\text{-}P) = 21$ Hz), the triphenylphosphine ligand appears to replace a carbonyl ligand trans to the Os–CPh vector. The 2 C doublet at δ 183.5, which shows a small cis $^{13}C\text{-}^{31}P$ coupling constant of 3 Hz, is assigned to the two carbonyls in the $Os(CO)_2P$ group. The remaining 6 C resonance at δ 174.8 is assigned to the carbonyls in the two identical $Os(CO)_3$ units.

The ^{13}C NMR spectrum of $Os_3(^*CO)_7(PPh_3)_2(\mu_3\text{-}^*CPh)(\mu_3\text{-}^*COMe)$ is shown in Figure 8. Signals at δ 317.7 and 237.7 are assigned to the methoxycarbyne and to the benzylidyne carbons, respectively, whereas those signals forming a 2:2:3 pattern between δ 184.1 and 176.9 are assigned to the carbonyl carbons. The triphenylphosphine ligands apparently substitute for one carbonyl on each of two $Os(CO)_3$ units. The benzylidyne carbon appears as a triplet with $^2J(C\text{-}P) = 10$ Hz. The decrease in the $^{13}C\text{-}^{31}P$ coupling constant compared to that in $Os_3(^*CO)_8(PPh_3)(\mu_3\text{-}^*CPh)(\mu_3\text{-}^*COMe)$ (21 Hz) may reflect a static structural distortion, i.e., a smaller P–Os–CPh angle due to repulsion between two bulky phosphine ligands on the same side of the Os_3 plane. However, the decrease also may be due to a time average over several conformations, some of which do not have both substituted sites trans to the benzylidyne carbon atom. The 2 C signals at δ 184.1 and 183.6 are assigned to the diastereotopic carbonyls of the two $Os(CO)_2P$ groups; the differential in germinal $^{13}C\text{-}^{31}P$ coupling constants again implies a difference in either static or dynamic $P\text{-}Os(CO)_2$ relationships. Finally, the remaining 3 C signal at δ 176.9 is assigned to the carbonyls in the $Os(CO)_3$ unit. Note that in both substituted compounds the signal for a $Os(CO)_2P$ unit is ca. 7–9 ppm downfield of that for a corresponding $Os(CO)_3$ unit.

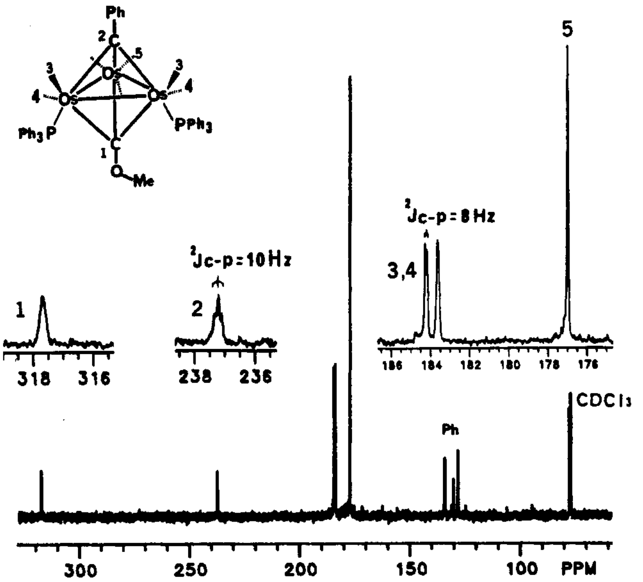

Figure 8. 90-MHz $^{13}C\{^1H\}$ NMR spectrum of $Os_3(^*CO)_7(PPh_3)_2(\mu_3\text{-}^*CPh)(\mu_3\text{-}^*COMe)$ in $CDCl_3$ at 17 °C.

Our observations that the reaction of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ with PPh_3 leads to direct CO substitution are in sharp contrast to the results recently reported[27] on the reaction of $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$ with PPh_3, wherein alkylidyne–alkylidyne coupling occurs to afford the alkyne complex $Fe_3(CO)_9(PPh_3)(\mu_3\text{-}\eta^2\text{-}C_2(OEt)Me)$. Moreover, $Fe_3(CO)_9(PPh_3)(\mu_3\text{-}\eta^2\text{-}C_2(OEt)Me)$ readily reverts to form both $Fe_3(CO)_8(PPh_3)(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$ and $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COEt)$.[27] The relatively weaker metal–metal and metal–ligand bonds for the triiron system undoubtedly contribute to this difference in reactivity. We have obtained evidence for alkylidyne–alkylidyne coupling in the triosmium system at moderately high temperatures;[20] these results will be described in a separate report.

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Registry No. $OS_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, 98015-27-1; $(\mu\text{-}H)OS_3(CO)_{10}(\mu\text{-}COMe)$, 69048-01-7; $(\mu\text{-}H)OS_3(CO)_{10}(\mu_3\text{-}CPh)$, 95122-80-8; $[(\mu\text{-}H)OS_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)^+][CF_3SO_3^-]$, 103258-05-5; $OS_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, 103240-46-6; $OS_3(CO)_7(PPh_3)_2(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, 103240-47-7; phenyllithium, 591-51-5; methyl triflouromethanesulfonate, 333-27-7; boron tribromide, 10294-33-4.

Supplementary Material Available: A table of anisotropic thermal parameters for $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (1 page); a listing of observed and calculated structure factors for $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (14 pages). Ordering information is given on any current masthead page.

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[27] Nuel, D.; Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436.