exponents of which were determined from R_{max} radius of maximum radial density, of the U $7s_{1/2}$ function. For the double-ζ parameters of U 6d and 5f, we used R_{max}, $\langle r \rangle$, and $\langle r^2 \rangle$ of U $6d_{5/2}$ and $6d_{3/2}$ and those of U $5f_{7/2}$ and $5f_{5/2}$, respectively. H_{ii} values were also taken from the Desclaux's functions.[32] In transforming the relativistic functions of U 6d, 5f, and 6p to nonrelativistic ones, weighted averages of each multiplet was used. The parameters for the other elements are standard ones. In the calculations, the weighted H_{ij} formula was used.

Assumed geometries not given in the text are as follows. CpU[(CH₂)(CH₂)PH₂]₃: P–C = 1.8 Å; P–H = 1.42 Å; C–C(Cp)

= 1.42 Å; C–H = 1.09 Å; C–P–C = 109.47°. Cp₃UC≡CH: C≡C = 1.25 Å.

Alkylation of Salts of the Triosmium Anions [Os₃{eq-η¹-C(O)CH₃}(CO)₁₁]⁻, [Os₃{μ-O=C(CH₃)}(CO)₁₀]⁻, and [Os₃{C(O)R}{μ-H;μ-O=C(CH₃)}(CO)₉]⁻, R = CH₃ or C₆H₅. Crystal and Molecular Structure of Os₃{1-η¹-C(OCH₃)CH₃}{1,2-μ-H;1,2-μ-O=C(CH₃)}(CO)₉
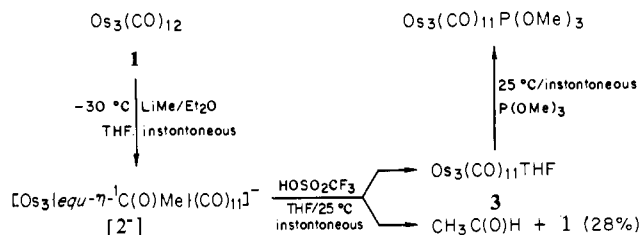
C. M. Jensen, C. B. Knobler, and H. D. Kaesz*

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. Received January 9, 1984

Abstract: Treatment of Os₃(CO)₁₂ with methyl lithium at 0 °C converts it instantly into [Li][Os₃{eq-η¹-C(O)CH₃}(CO)₁₁], [Li][2a]. [Li⁺] or [bis(triphenylphosphine)nitrogen(1+)] N salts of [2a⁻] are resistant to alkylation by CH₃OSO₂CF₃ in tetrahydrofuran solution. Replacement of THF by CHCl₃ is accompanied by loss of CO to give the μ-acyl complex, [Os₃{μ-O=C(CH₃)}(CO)₁₀⁻], [4⁻]. This anion is slowly alkylated by CH₃OSO₂CF₃ in CHCl₃ solution to form a highly unstable bis(acyl) complex Os₃{C(O)CH₃}{μ-O=C(CH₃)}(CO)₉, **5**. Attempts to purify **5** by chromatography on a silica gel column result in its disproportionation to Os₃{1-C(OMe)Me}{1,2-μ-H;1,2-μ-O=C(Me)}(CO)₉, **7a**, and Os₃{1,2-μ-OH;1,2-μ-O=C-(Me)}(CO)₁₀, **8**. Alkylation of [4⁻] with CD₃OSO₂CF₃ produces Os₃{C(O)CD₃}{μ-O=C(CH₃)}(CO)₉, **5**-d_3. Addition of water to a chloroform solution of **5**-d_3 converts it to a mixture of **7a**-d_6, Os₃{1-η¹-C(OCD₃)CD₃}{1,2-μ-H;1,2-μ-O=C(Me)}(CO)₉ and **8**. Due to the presence of halide salts, small amounts of Os₃{1,2-μ-X;1,2-μ-O=C(Me)}(CO)₁₀, **6a**, X = Cl, or **6c**, X = I, are obtained as minor byproducts in these systems. Chromatography of **7a**-d_6 on silica gel is accompanied by H/D exchange of the carbene methyl group to give **7a**-d_3, Os₃{1-η¹-C(OCD₃)CH₃}{1,2-μ-H;1,2-μ-O=C(Me)}(CO)₉. Treatment of Os₃{1,2-μ-H;1,2-μ-O=C(Me)}(CO)₁₀, **9**, with LiR at −30 °C produces [Li][Os₃{η¹-C(O)R}{1,2-μ-H;1,2-μ-O=C(Me)}(CO)₉], [Li][**10a** or **10b**] (a, R = Me, b, R = Ph). Warming the solution to 25 °C and treating it with a slight excess of R′OSO₂CF₃ leads to formation of Os₃{1-η¹-C(OR′)R}{1,2-μ-H;1,2-μ-O=C(Me)}(CO)₉, **7a** (R = R′ = Me), **7b** (R = Me, R′ = Et) and **7c** (R = Ph, R′ = Et) in 68, 80, and 42% yields respectively. A small amount of **6b** (X = Br) is also obtained. The crystal and molecular structure of **7a** was determined at −158 °C: orange crystals are monoclinic of space group $P2_1/n$ with a = 9.578 (4) Å, b = 13.494 (4) Å, c = 15.187 (6) Å, β = 96.30 (3)°, V = 1951 (1) Å³, Z = 4, and ρ_{calcd} = 3.15 g cm⁻³ (Mo Kα = 0.71069 Å³). The structure was solved and refined by using 2728 observed ($I > 3\sigma(I)$) independent reflections measured on a Syntex P1 automated diffractometer in the range 0° < 2θ < 50°. An absorption correction was applied (μ = 195.66 cm⁻¹). Refinement converged at R = 0.050 and R_w = 0.061. The molecule consists of a triangle of osmium atoms, Os(1)–Os(2) = 2.934 (2) Å, Os(1)–Os(3) = 2.852 (1) Å, and Os(2)–Os(3) = 2.892 (1) Å, bridged on the longest edge by an acetyl group and a hydrogen atom on opposite sides of the trimetal plane. The carbene group is terminally bonded on Os(1) to which is also coordinated the oxygen of the bridging acetyl group.

In the 18 years since the isolation of the first heterocarbene complex by Fischer and Maasböl,[1] there had been no report of the synthesis of such a functional group on a cluster complex prior to recent isolation of Os₃{1-η¹-C(OMe)Me}{1,2-μ-H;1,2-μ-O=C-(Me)}(CO)₉ (**7a**, Scheme I).[2a] Di- and trinuclear complexes containing a μ-C(OMe)Ph group have been formed by reaction of M{C(OMe)Ph}(CO)₅ (M = Cr or W) with zerovalent platinum complexes;[2b] this involves migration or transfer of the preformed Fischer carbene group. A triiron complex containing the η¹-

Scheme I

CS₂(CH)₂ group has been obtained in the reaction of 1,3-dithiole-2-thione with Fe₂(CO)₉.[2c]

In the present work, acyl anions are formed instantaneously by attack of a nucleophile on a carbonyl group, but subsequent alkylation is slow and fraught with complications.[3] We here report

(1) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964,** *3,* 580–581.

(2) (a) Jensen, C. M.; Lynch, T. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1982,** *104,* 4679–4680. (b) Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980,** 1615–1624. (c) Benoit, A.; Le Marouille, J.-Y.; Mahe, C.; Patin, H. *J. Organomet. Chem.* **1982,** *233,* C51–C54.

Table I. IR and ^{1}H NMR Spectra of New Compounds

compd	IR,^{a} cm^{-1}	^{1}H NMR,^{b} ppm
Os$_3$\{1-η^1-C(OMe)Me\}\{1,2-μ-H;1,2-μ-O=C(Me)\}(CO)$_9$, **7a**	2093 m, 2052 s, 2022 vs, 2001 m, 1991 m, 1973 m, 1961 w, 1950 m (KBr, ν(C–O)) 1291 m	4.33 (s, 3, OCH_3), 2.56 (s, 3, CCH_3), 2.33 (s, 3, O=CH_3), –15.20 (s, 1, μ-H)
Os$_3$\{1-η^1-C(OEt)Me\}\{1,2-μ-H;1,2-μ-O=C(Me)\}(CO)$_9$, **7b**	2092 m, 2051 s, 2021 vs, 2001 m, 1987 m, 1972 m, 1960 w, 1949 m	4.52 (m, 2, OCH_2CH$_3$), 2.57 (s, 3, CCH_3), 2.33 (s, 3, O=CH_3), 1.64 (t, 3, J = 7.1 Hz, OCH$_2$CH_3, –15.25 (s, 1 μ-*H*)
Os$_3$\{1-η^1-C(OEt)C$_6$H$_5$\}\{1,2-μ-H;1,2-μ-O=C(Me)\}(CO)$_9$, **7c**	2091 m, 2051 s, 2020 vs, 2003 m, 1992 w, 1988 w, 1971 m, 1947 w	(acetone-d_6) 7.75 (m, 5, CC$_6$H$_5$), 4.43 (m, 2, OCH_2CH$_3$), 2.22 (s, 3, O=CH_3), 1.63 (t, 3, J = 7.1 Hz, OCH$_2$CH_3), –14.85 (s, 1, μ-*H*)
Os$_3$\{1,2-μ-OH;1,2-μ-O=C(Me)\}(CO)$_{10}$, **8**	2104 m, 2071 s, 2051 s, 2020 s, 2007 s, 2003 s, 1988 s, 1974 m (KBr, ν(OH)) 3625 w, 3436 w	2.74 (s, O=CH_3)
Os$_3$\{1,2-μ-Cl;1,2-μ-O=C(Me)\}(CO)$_{10}$, **6a**	2109 w, 2077 s, 2058 s, 2026 s, 2010 s, 1996 m, 1987 w, 1981 w	2.68 (s, O=CH_3)
Os$_3$\{1,2-μ-Br;1,2-μ-O=C(Me)\}(CO)$_{10}$, **6b**	2108 w, 2075 s, 2058 s, 2025 s, 2010 s, 1996 m, 1987 w, 1980 w	2.65 (s, O=CH_3)
Os$_3$\{1,2-μ-I;1,2-μ-O=C(Me)\}(CO)$_{10}$, **6c**	2107 w, 2075 s, 2057 s, 2024 s, 2010 s, 1996 m, 1986 w, 1980 w	2.56 (s, O=CH_3)
Os$_3$\{C(O)Me\}\{1,2-μ-O=C(Me)\}(CO)$_9$, **5**	(CHCl$_3$) 2137 w, 2069 s, 2050 s, 2016 m, 2001 m, 1601 (η^1-acyl), 1493 (μ-acyl)	2.57 (s, 1, μ-O=CCH_3), 2.11 (s, 1, n-C(O)CH_3)
[PPN][Os$_3$\{1,2-μ-O=C(Me)\}(CO)$_{10}$], [PPN][**4**]	(CHCl$_3$) 2068 m, i2031 m, 2009 s, 1994 s, 1979 sh, 1941 sh, 1589 vw (PPN), 1483 w (PPN), 1440 m (PPN), 1411 w (μ-acyl)	7.49 (m, 30, [(C$_6$H$_5$)$_3$P]$_2$N), 2.64 (s, 3, O=CH_3)
[Li][Os$_3$\{C(O)Me\}(CO)$_9$\{1,2-μ-H;1,2-μ-O=C(Me)\}], [Li][**10a**]	(Et$_2$O) 2082 m, 2039 s, 2008 s, 1994 vs, 1972 m, 1959 m, 1923 m, 1557 w (μ-acyl)	2.86 (s, 3, μ-O=CCH_3), 2.19 (s, 3, n-C(O)CH_3), –15.54 (s, 1, μ-*H*)
[Li][Os$_3$\{C(O)C$_6$H$_5$\}(CO)$_9$\{1,2-μ-H;1,2-μ-O=C(Me)\}], [Li][**10b**]	(Et$_2$O) 2081 m, 2039 s, 2007 s, 1993 s, 1971 s, 1924 w, 1594 w (μ-acyl)	

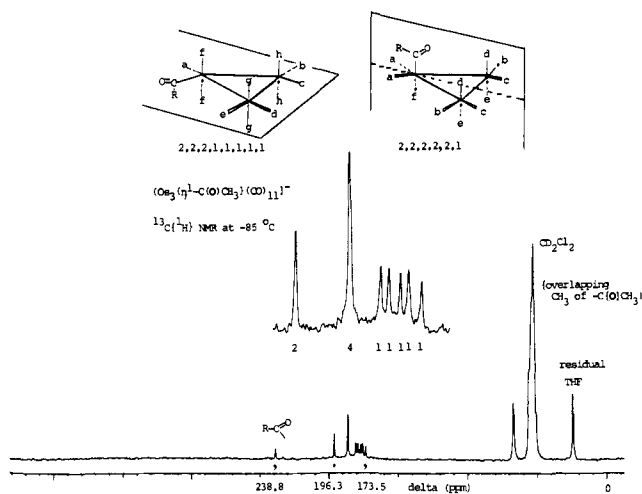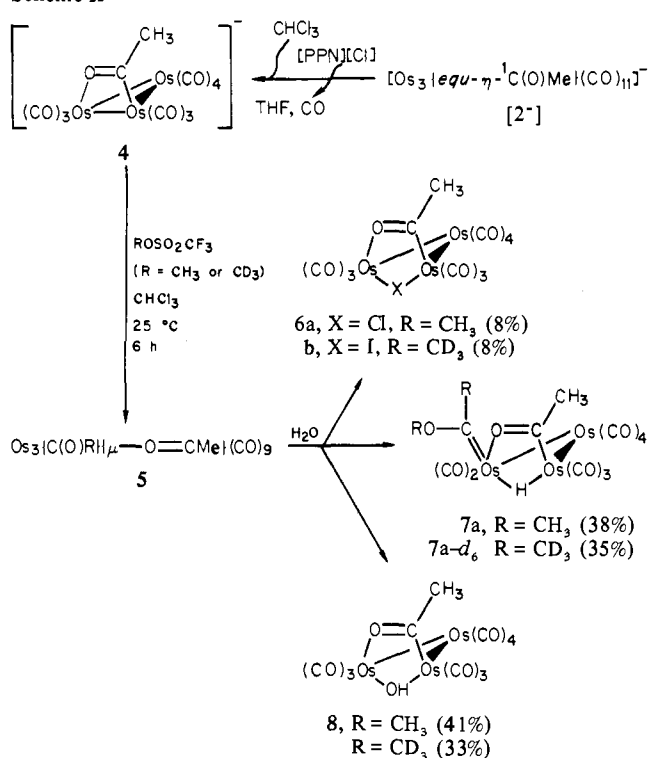^{a} In hexane unless stated otherwise. ^{b} In CDCl$_3$ unless stated otherwise.

Figure 1. ^{13}C NMR spectrum of [Li][Os(CO)$_{11}$-η^1-C(O)Me] in CD$_2$Cl$_2$ solution at –85 °C.

on the preparation of a variety of cluster acyl anions and the products obtained upon their alkylation. We also give the details of a structure determination of **7a**.

Results

The results obtained in the present work are set forth in Schemes I, II, and III, [PPN$^+$] = [bis(triphenylphosphine)nitrogen(1+)]; spectroscopic data for the new complexes either observed in solution or isolated are given in Tables I and II. The anionic complex [**2**$^-$] is obtained by titration of Os$_3$(CO)$_{12}$, **1**, with methyllithium;[4] ^{13}C \{^{1}H\} NMR obtained at –85 °C in CD$_2$Cl$_2$ is shown in Figure 1. The basis for assignment of the acyl group to the *equatorial* position is given in the Discussion. Allowing the CD$_2$Cl$_2$ solution to stand in the NMR tube (sealed under 1 atm of CO) for 3 weeks resulted in no change in the ^{13}C NMR spectrum.

(3) (a) Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem.* **1970**, *82*, 635. (b) Wong, W.; Chiu, K. W.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1557–1563.

(4) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1704–1706.

Scheme II

A THF solution of [Li][**2**] was treated with methyl trifluoromethanesulfonate (methyl triflate) at 25 °C; monitoring by IR shows the reaction is very slow. After about 8 h the principal solution constituents are Os$_3$(CO)$_{11}$(THF), **3**, and in stoichiometric amount, acetaldehyde. Some Os$_3$(CO)$_{12}$ is also obtained as byproduct. Complex **3** is not isolated, but its presence is confirmed by ^{1}H NMR and by its instantaneous reaction with P(OMe)$_3$, as shown in Scheme I. We ascribe the formation of acetaldehyde to protonation of [**2**$^-$] by trifluoromethane sulfonic acid[5] produced in the hydrolysis of the alkylating agent by traces of water in the

(5) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1956**, 173–180.

Table II. Spectroscopic Data

compd	$^{13}C\{^1H\}$ NMR,[a] ppm	MS,[b] m/e
$[Li][Os_3\{\eta^1\text{-}C(O)(Me)\}(CO_{11}], [Li][2]$	238.8 ($C(O)CH_3$), 184.5 (carbonyl carbons), 50.6 ($C(O)CH_3$); carbonyl region at -85 °C in CD_2Cl_2 (relative intensity) 196.2 (2), 186.5 (4), 180.9 (1), 179.5 (1), 177.4 (1), 175.9 (1), 173.5 (1)	
$[PPN][Os_3\{1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}],$ $[PPN][4]$	283.9 ($O{=}C(CH_3)$), 185.1 (carbonyl carbons), 132.7, 130.8, 128.1, 123.3 ($[C_6H_5]_3P_2N$); 50.5 ($O{=}C(CH_3)$), carbonyl region at -55 °C 188.3, 186.1, 185.8, 183.6, 183.3, 180.9, 180.2, 177.8, 175.6, 170.5	
$Os_3\{1\text{-}\eta^1\text{-}C(OMe)Me\}$ $\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9,$ **7a**	282.4 (CMeOMe), 266.7 ($O{=}C(CH_3)$), 186.2, 182.2, 181.7, 178.6, 178.2, 176.5 (approximately double intensity), 175.5, 174.8 (carbonyl carbons), 65.1 (OCH_3), 50.2 ($O{=}C(CH_3)$), 32.3 (CCH_3)	924
$Os_3\{1\text{-}\eta^1\text{-}C(OEt)Me\}$ $\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9,$ **7b**	(C_6D_6) 280.5 (CMeOEt), 267.5 ($O{=}C(CH_3)$), 187.3, 183.0, 182.1, 179.8, 178.9, 177.5, 177.3, 176.3, 175.3 (carbonyl carbons), 74.8 (OCH_2CH_3), 50.3 ($O{=}C(CH_3)$), 32.2 (CCH_3), 13.8 (OCH_2CH_3)	938
$Os_3\{1\text{-}\eta^1\text{-}C(OEt)C_6H_5\}$ $\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9,$ **7c**	(acetone-d_6) 285.5 (CPhOEt), 267.5 ($O{=}C(CH_3)$), 187.4, 184.8, 184.1, 183.0, 181.1, 178.0, 177.5, 177.3, 173.6 (carbonyl carbons), 147.5, 134.9 (approximately double intensity), 129.9, 125.2 (approximately double intensity) (CC_6H_5), 78.7 (OCH_2CH_3), 49.2 ($O{=}C(CH_3)$), 14.8 (OCH_2CH_3)	
$Os_3\{1,2\text{-}\mu\text{-}OH;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10},$ **8**	295.5 ($O{=}C(CH_3)$), 187.3, 183.9, 182.4, 180.1, 178.7, 178.1, 177.5, 175.9, 169.1, 168.5 (carbonyl carbons), 50.8 ($O{=}C(CH_3)$)	910
$Os_3\{1,2\text{-}\mu\text{-}Cl;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10},$ **6a**	292.7 ($O{=}C(CH_3)$), 185.3, 182.1, 181.4, 178.9, 177.4, 176.9, 176.7, 174.7, 168.0 (approximately double intensity) (carbonyl carbons), 52.2 ($O{=}C(CH_3)$)	928
$Os_3\{C(O)Me\}\{1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10},$ **5**	283.8 ($O{=}C(CH_3)$), 269.1 ($C(O)CH_3$), 186.2, 185.6, 180.1, 179.7, 178.8, 178.1, 177.3, 175.5, 173.2 (carbonyl carbons), 50.2 ($O{=}C(CH_3)$), 49.4 ($C(O)CH_3$)	

[a] In $CDCl_3$ at 25 °C unless stated otherwise with 10 mg of $Cr(acac)_3$ added to increase resolution of the carbonyl region. [b] ^{190}Os parent ion MS parent ion for $Os_3\{1,2\text{-}\mu\text{-}Br;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **6b**, and $Os_3\{1,2\text{-}\mu\text{-}I;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **6c**: m/e 973 and 1020, respectively.

Scheme III

7a, R = Me, R' = Me (68%)   6b (8%)
b, R = Me, R' = Et (80%)
c, R = Ph, R' = Et (42%)
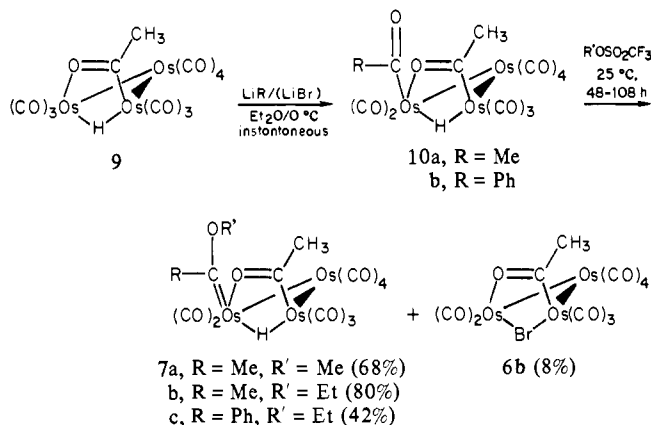
system; protonation of metal acylates is known to give aldehydes.[6] In support of this conclusion, addition of a stoichiometeric amount of trifluoromethanesulfonic acid to a THF solution of [2⁻] is found to result in the instantaneous formation of 3 and a stoichiometric amount of acetaldehyde.

Under rigorously anhydrous conditions, no alkylation is seen. After 16 h, polymerization of the THF solution[7] is seen for either the [Li⁺] or the [PPN⁺] salts of [2⁻].

We next sought to perform the alkylation in chloroform. We were however unable to achieve the substitution of solvents without appreciable conversion of [2⁻] into $[Os_3\{\mu\text{-}O{=}C(CH_3)\}(CO)_{10}^-]$, [4⁻];[4] see Scheme II. A part of this transformation occurs during the removal of the THF under reduced pressure, and additionally, we observe an enhanced rate for the conversion of [2⁻] to [4⁻] in chloroform. Methyl triflate is next added to this solution, and after 2 h [4⁻] is completely converted to the bis(acyl) derivative $Os_3\{C(O)CH_3\}\{1,2\text{-}\mu\text{-}O{=}C(CH_3)\}(CO)_9$, **5**. The reactivity of [4⁻] toward alkylating agents is greater than that of [2⁻]; in THF where we saw no alkylation of [2⁻] before polymerization of the THF

set in, [4⁻] showed partial alkylation to 5 in about the same time.

Attempts to purify 5 by silica gel column chromatography results in its disproportionation to $Os_3\{1\text{-}\eta^1\text{-}C(OMe)Me\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$, **7a**, and $Os_3\{1,2\text{-}\mu\text{-}OH;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **8** (Scheme II). $Os_3\{1,2\text{-}\mu\text{-}Cl;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **6a**, is a minor byproduct in this reaction. This arises from the presence of chloride ion in the mixture owing to incomplete precipitation of LiCl in metathesis of [PPN][Cl] with [Li][2].

In order to trace the origin of the methyl group in the disproportionation of 5 to 7a and 8, we alkylated [4⁻] with $CD_3O\text{-}SO_2CF_3$ (Scheme II). The bis(acyl) complex **5-d_3** was examined by ^2H NMR and found to contain the deuterium label only in the η^1-acyl group, i.e., $Os_3\{\eta^1\text{-}O{=}C(CD_3)\}\{\mu\text{-}H;\mu\text{-}O{=}C(Me)\}(CO)_{10}$. No scrambling of the deuterium label is observed in this complex over 1 week at room temperature (under N_2 gas). Addition of water to the sample at this point followed by the removal of the chloroform solvent and extraction with petroleum ether results in the disappearance of the resonance corresponding to the η^1-acyl group in the ^2H NMR and its replacement by resonances corresponding to CD_3 and OCD_3 groups of the carbene moiety of **7a-d_6**. Chromatography of the petroleum ether extracts on silica gel produces **7a-d_3**: $Os_3\{\eta^1\text{-}C(OCD_3)CH_3\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$. Loss of the label on the carbene methyl group results from the acidic nature of these protons[8] leading to H/D exchange on silica gel. No label is detected in complex 8 that is also produced in this reaction. In transformations of the CD_3-labeled materials, the minor byproduct is $Os_3\{1,2\text{-}\mu\text{-}I;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **6c**. This arises from reaction of residual [I⁻] introduced in the preparation of the methyl-d_3 triflate by the reaction of silver triflate with CD_3I.

Having obtained 7a by the aforementioned disproportionation on silica gel, we were led to attempt its direct synthesis from $Os_3\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_{10}$, **9**; this proved successful as summarized in Scheme III. Titration of 9 in diethyl ether at -30 °C with LiMe (also in diethyl ether, low bromide content) produces $[Li][Os_3\{\eta^1\text{-}C(O)Me\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$, $[Li][10a]$. Warming the solution to 25 °C and treating it with a slight excess of $CH_3OSO_2CF_3$ lead after 36 h of stirring to 7a in 68% yield. Longer reaction time does not increase the amount of 7a produced. Instead increasing amounts of the *ethoxy* carbene derivative $Os_3\{1\text{-}\eta^1\text{-}C(OEt)Me\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9$, **7b**, are obtained in yields approaching 10% in 70 h. Formation of this product results from the trans-alkylation reaction between

(6) (a) The formation of aldehyde may result from either protonation at the metal followed by reductive elimination of aldehyde as in: Cooke, M. P. *J. Am. Chem. Soc.* **1970**, *92*, 6080–6082, or (b) from protonation at oxygen to give a hydroxycarbene followed by rearrangement to aldehyde as in: Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2444–2456.

(7) Meerwein, H.; Delfs, D.; Morschel, H. *Angew. Chem.* **1960**, *74*, 927–934.

(8) Kreiter, C. G. *Angew. Chem.* **1968**, *80*, 402–404.

$CH_3OSO_2CF_3$ and the diethyl ether.[5] When [Li][10a] is alkylated directly with ethyl triflate, 7b is obtained in 80% yield (48-h reaction time). In these reaction sequences, the minor byproduct is the bromide complex $Os_3\{1,2-\mu-Br;1,2-\mu-O=C(Me)\}(CO)_{10}$, 6b, arising from reaction of LiBr originating in the LiMe solution.

Titration of 9 with LiC_6H_5 in diethyl ether at -30 °C produces a solution of [Li][10b]; see Scheme III. Alkylation at 25 °C with a slight excess of $EtOSO_2CF_3$ requires 108 h to form $Os_3\{1-\eta^1-C(OEt)C_6H_5\}\{1,2-\mu-H;1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_9$, 7c, in 42% yield. Again, a minor amount of 6b (8%) is obtained.

Discussion

Structure Assignment for $[Os_3\{eq-\eta^1-C(O)Me\}(CO)_{11}^-]$, $[2^-]$. The ^{13}C NMR of this anion at -85 °C is shown in Figure 1. An intensity pattern of 2:4:1:1:1:1:1 is observed in the carbonyl region. To interpret this, we consider two possible isomers shown in schematic form at the top of the figure. To avoid repulsions between the acyl group atoms and the carbonyl groups on the metal to which the acyl group is attached, we choose a staggered conformation in each structure.[9] This would create a plane of symmetry in the *axial* ligand but would remove all symmetry in the *equatorial* isomer. The observed pattern rules out the *axial* isomer as a 2:2:2:2:2:1 pattern would be expected in the carbonyl region. The groups may of course be rotating; this would not affect the pattern expected for the *axial* isomer but, in the *equatorial* isomer, would introduce mirror symmetry for the carbonyl groups above and below the trimetal plane. In that event, an intensity pattern of 2:2:2:1:1:1:1:1 would be expected, which is close to that observed. If two pairs of carbonyls are accidentally equivalent in such an *equatorial* isomer, the observed pattern is exactly reproduced.

Alkylation of $[4^-]$. This reaction shown in Scheme II is seen to lead to the bis(acyl) derivative 5. This transformation suggests that alkylation takes place at the metal center(s) on the cluster. This, rather than O-alkylation, is thought to be prevalent in carbonyl acylates of iron.[10,11] A metal-akylated intermediate has been observed in the reaction of CH_3OCO_2F with $[Fe\{C(O)-OMe\}(CO)_4][C(NMe_2)_3]$.[12]

Metal alkylation in $[4^-]$ must be followed by migration to coordinated CO to give the bis(acyl) derivative 5. A similar pattern of metal alkylation and migration leads to formation of $[Fe\{\eta^1-C(O)Me\}(CO)_2\{\mu-P(C_6H_5)_2\}Fe(CO)_3^-]$ in the reaction of $[Fe(CO)_3\{\mu-P(C_6H_5)_2\}Fe(CO)_3^{2-}]$ with CH_3I.[13]

It is noted that the μ-acyl complex $[4^-]$ undergoes alkylation while the η^1-acyl complex $[2^-]$ does not. This indicates that O-alkylation is not at all favored and that the metal framework is more accessible in the former than in the latter. This is contrasted by O-alkylation in two cases: (1) the reaction of the anion containing a triply bridging acyl group, $[Fe_3(CO)_9-\mu_3-O=C(Me)^-]$, with a tenfold excess of methyl fluorosulfate that (in a week's time) gives the O-alkylated product $Fe_3(CO)_9(\mu_3-OMe)(\mu_3-CMe)$;[3b] and (2) the immediate alkylation of $[HOs_3(CO)_{11}^-]$ at the oxygen of a bridging carbonyl group when treated with an 80-fold excess of $MeOSO_2F$, giving $HOs_3(\mu-C-(OMe))(CO)_{10}$.[14]

Alkylation with $CD_3OSO_2CF_3$. Two conclusions may be drawn from the results of this experiment summarized in Scheme II. No scrambling is observed for the deuterium label in $5-d_3$ over a week's time. This demonstrates that equilibration of the $C(O)CD_3$ and the μ-acyl groups is either very slow or nonexistent. The dis-

(9) Casey, C. P.; Bunnell C. A. *J. Am. Chem. Soc.* 1976, 98, 436–441.
(10) (a) Collman, J. P. *Acc. Chem. Res.* 1975, 8, 342–356. (b) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* 1983, 105, 4099–4100.
(11) (a) O-alkylation has been found to occur in special systems where the acylate complexes are phosphine substituted: Conder, H. L.; Darensbourg, M. Y. *Inorg. Chem.* 1974, 13, 506–511, or (b) where the acylate contains a C_6Cl_5, C_6F_5, or $N(Me)_2$ group: Fischer, E. O.; Beck, H. J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, H. *Chem. Ber.* 1972, 105, 162, or where HMPA is utilized as a cosolvent as in 10b.
(12) Petz, W. *Organometallics* 1983, 2, 1044–1046.
(13) (a) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Rose-Munch, F. *J. Am. Chem. Soc.* 1977, 99, 7381–7383.
(14) Gavens, P. D.; Mays, M. J. *J. Organomet. Chem.* 1978, 162, 389–401.

Table III. Crystal and Intensity Collection Data for $Os_3\{1-\eta^1-C(OMe)Me\}\{1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_9$

formula	$C_{14}H_{10}O_{11}Os_3$
fw	924.8
a/Å	9.578 (4)
b/Å	13.494 (4)
c/Å	15.187 (6)
β/deg	96.30 (3)
V/Å	1951 (1)
Z	4
ρ(calcd)/g cm^{-3}	3.15
space group	$P2_1/n$
cryst size/mm^3	0.0087
indices of faces	$\{001\}$, $\{010\}$, $(\bar{1}\bar{1}1)$, $(102)^a$
temp/°C	-158
radiatn source $(\lambda/\text{Å})$	Mo $K\alpha$ (0.710 69)
abs coeff (μ/cm^{-1})	195.66
transmissn factors	0.0537–0.1759
scan rate/deg min^{-1}	8
scan range:	
deg below $K\alpha_1$	1.0
deg above $K\alpha_2$	1.0
2θ limits/deg	0–50
takeoff angle/deg	4.0
observns	$+h,+k,\pm l$
total obsd data	4001
no. of unique data $(I_o > 3\sigma I_o))$	2728
final no. of variables	257
goodness of fit^b	1.84
R^c	0.050
R_w^d	0.061

^{a} Perpendicular distances from a common point of 0.0, 0.11, 0.0, 0.18, 0.20, and 0.0 mm, respectively. ^{b} GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where $w = 1/[\sigma(|F_o|)^2$. $^c R = \sum||F_o| - |F_c||/|F_o|$. $^d R_w = [\sum w-(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.
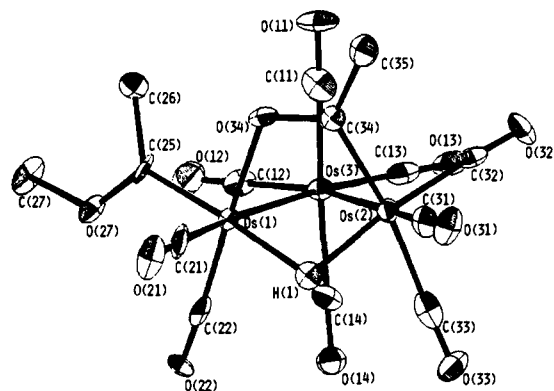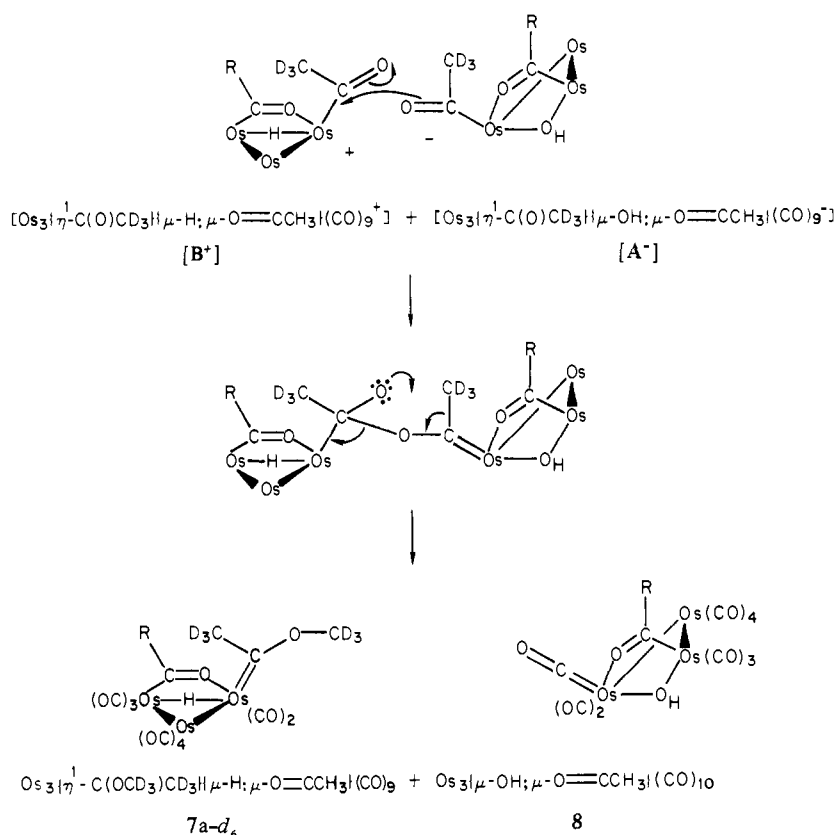

Figure 2. ORTEP diagram of 7a (ellipsoids at 50% probability).

proportionation of $5-d_3$ to $7a-d_6$ and 8 in the presence of water does not involve the μ-acyl group. The disproportionation requires transfer of a pair of electrons *as well as* CD_3 from the $C(O)CD_3$ group of one bis(acyl) derivative to the oxygen of a $C(O)CD_3$ group in another. These requirements can be met through the proposed sequence shown in Scheme IV.

For the bis(acyl) derivative $Os_3\{C(O)Me\}\{\mu-O=CMe\}(CO)_9$, 5, a count of 48 electrons is achieved if the $C(O)Me$ group were η^2 coordinated.[15] A formal count of 46 electrons (and electronic unsaturation) results if the $C(O)Me$ group is η^1 coordinated. Attack of water on 5 followed by proton transfer to another molecule of 5 would lead to the ionic species $[A^-]$ and $[B^+]$ as shown in Scheme IV. The transfer of CD_3 would take place between these species giving the products observed.

Synthesis of the Carbene Complexes 7a–c from 9. The reaction of 9 with methyllithium is shown in Scheme III. This is remarkable in view of the Brønsted acidity of cluster hydrides.[16]

(15) Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* 1979, 182, C46–C48.

Table IV. Atomic Positional Parameters

atom	x	y	z	atom	x	y	z
Os(1)	0.3809 (1)	0.2358 (1)	0.5248 (1)	C(14)	0.087 (2)	0.370 (2)	0.540 (1)
Os(2)	0.3265 (1)	0.3903 (1)	0.3894 (1)	C(11)	0.140 (2)	0.185 (2)	0.349 (1)
Os(3)	0.1012 (1)	0.2722 (1)	0.4465 (1)	C(31)	0.483 (2)	0.459 (2)	0.354 (1)
O(13)	−0.162 (2)	0.354 (1)	0.340 (1)	C(22)	0.337 (2)	0.280 (1)	0.635 (1)
O(11)	0.153 (2)	0.130 (1)	0.292 (1)	C(25)	0.337 (2)	0.097 (2)	0.554 (1)
O(27)	0.311 (1)	0.0738 (9)	0.6366 (9)	C(21)	0.579 (2)	0.228 (1)	0.567 (2)
O(12)	−0.013 (2)	0.109 (1)	0.558 (1)	C(33)	0.261 (2)	0.510 (2)	0.451 (1)
O(21)	0.690 (2)	0.225 (1)	0.596 (1)	C(12)	0.025 (2)	0.172 (1)	0.515 (1)
O(22)	0.308 (2)	0.302 (1)	0.7033 (8)	C(26)	0.328 (2)	0.013 (1)	0.488 (1)
O(33)	0.233 (2)	0.580 (1)	0.484 (1)	C(13)	−0.062 (2)	0.325 (1)	0.379 (1)
O(31)	0.580 (1)	0.4984 (9)	0.330 (1)	C(27)	0.282 (2)	−0.027 (1)	0.663 (2)
O(14)	0.083 (2)	0.4288 (9)	0.5933 (9)	O(34)	0.436 (1)	0.1908 (9)	0.3983 (8)
O(32)	0.129 (2)	0.435 (1)	0.2231 (9)	C(34)	0.409 (2)	0.263 (1)	0.344 (1)
C(32)	0.204 (2)	0.417 (1)	0.283 (1)	H(1)	0.45 (2)	0.38 (2)	0.51 (2)
C(35)	0.459 (2)	0.243 (2)	0.253 (1)				

Scheme IV

$[Os_3\{\eta^1\text{-}C(O)CD_3\}\mu\text{-}H;\mu\text{-}O\!\equiv\!\!CCH_3\}(CO)_9^+]$ + $[Os_3\{\eta^1\text{-}C(O)CD_3\}\mu\text{-}OH;\mu\text{-}O\!\equiv\!\!CCH_3\}(CO)_9^-]$

[B⁺]   [A⁻]

$Os_3\{\eta^1\text{-}C(OCD_3)CD_3\}CD_3\}\mu\text{-}H;\mu\text{-}O\!\equiv\!\!CCH_3\}(CO)_9$ + $Os_3\{\mu\text{-}OH;\mu\text{-}O\!\equiv\!\!CCH_3\}(CO)_{10}$

7a-d_6 8

The salt Li[**10a**] is found to undergo O-alkylation in diethyl ether. This contrasts the chemistry of iron acylates[11b] that undergo alkylation at the metal center with this combination of solvent and counterion. The long reaction time and/or excess of reagent required for completion are generally observed in the alkylation of cluster anions.[3b,14] This is presumably due to delocalization of charge on the cluster framework. The tendency toward O-alkylation is even lower in the phenacyl anion [**10b⁻**] as evidenced by the threefold increase required in its reaction time and the decrease observed in the yield.

Discussion of Structure. The crystal consists of discrete molecular units of Os₃{1-η¹-C(OMe)Me}{1,2-μ-H;1,2-μ-O=C-(Me)}(CO)₉, **7a**. A crystal packing diagram viewed down the *a* axis is available as a supplementary figure. Closest intermolecular approaches are between oxygen atoms; those below 3.00 Å are as follows [Å (±0.02)]: O(13)···O(22) = 2.95, O(22)···O(31) =

(16) (a) Fontal, B. Ph.D Thesis, University of California at Los Angeles, 1969. (b) Pearson, R. G.; Ford, P. C. *Comments Inorg. Chem.* **1982**, *1*, 279–291. (c) Cluster hydrogen is removed as proton in reaction of hydrido cluster complexes with H⁻: Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444–1445.

Table V. Selected Interatomic Distances (Å)

Os(1)–Os(2)	2.934 (1)	C(14)–O(14)	1.14 (2)
Os(1)–Os(3)	2.852 (2)	C(31)–O(31)	1.16 (3)
Os(2)–Os(3)	2.892 (1)	C(12)–O(12)	1.15 (2)
Os(1)–C(21)	1.94 (2)	C(13)–O(13)	1.14 (3)
Os(1)–C(22)	1.86 (2)	C(21)–O(21)	1.10 (2)
Os(2)–C(31)	1.89 (3)	C(22)–O(22)	1.15 (2)
Os(2)–C(32)	1.92 (2)	C(11)–O(11)	1.16 (3)
Os(2)–C(33)	1.99 (2)	C(33)–O(33)	1.12 (2)
Os(3)–C(11)	1.95 (2)	C(32)–O(32)	1.12 (2)
Os(3)–C(12)	1.90 (2)	C(25)–O(27)	1.34 (2)
Os(3)–C(13)	1.91 (2)	C(25)–C(26)	1.51 (3)
Os(3)–C(14)	1.95 (2)	O(27)–C(27)	1.45 (2)
Os(2)–C(34)	2.05 (2)	C(34)–C(35)	1.53 (3)
Os(1)–C(25)	1.99 (2)	C(34)–O(34)	1.28 (2)
Os(1)–O(34)	2.13 (1)		
Os(1)–H(1)	2.0 (2)		
Os(2)–H(1)	2.0 (2)		

2.96, and O(13)···O(33) = 2.97.

Molecular Geometry. The molecular structure and numbering of the atoms are depicted in Figure 2.[17] Selected interatomic

$Os_3\{1-\eta^1-C(OCH_3)CH_3\}\{1,2-\mu-H;1,2-\mu-O\!=\!C(CH_3)\}(CO)_9$

J. Am. Chem. Soc., Vol. 106, No. 20, 1984 5931

Table VI. Selected Interatomic Angles (deg)

Os(3)-Os(1)-Os(2)	59.94 (4)	Os(1)-Os(2)-Os(3)	58.61 (4)	Os(1)-Os(3)-Os(2)	61.44 (4)
"trans"		"trans"		"trans"	
O(34)-Os(1)-C(22)	177.8 (6)	C(34)-Os(2)-C(33)	171.7 (7)	C(11)-Os(3)-C(14)	171.4 (9)
C(25)-Os(1)-H(1)	174 (6)	H(1)-Os(2)-C(32)	174 (6)	Os(1)-Os(3)-C(13)	164.3 (6)
C(21)-Os(1)-Os(3)	171.3 (6)	C(31)-Os(2)-Os(3)	175.4 (6)	Os(2)-Os(3)-C(12)	154.3 (6)
"cis"		"cis"		"cis"	
O(34)-Os(1)-C(25)	90.7 (7)	C(34)-Os(2)-H(1)	90 (6)	C(11)-Os(3)-Os(1)	87.8 (6)
O(34)-Os(1)-C(21)	87.6 (7)	C(34)-Os(2)-C(31)	88.0 (8)	C(11)-Os(3)-Os(2)	83.9 (6)
O(34)-Os(1)-H(1)	89.9 (7)	C(34)-Os(2)-C(32)	95.7 (7)	C(11)-Os(3)-C(13)	91.9 (8)
O(34)-Os(1)-Os(3)	89.2 (3)	C(34)-Os(2)-Os(3)	88.2 (5)	C(11)-Os(3)-C(12)	95.9 (9)
C(25)-Os(1)-C(21)	95.7 (8)	H(1)-Os(2)-C(31)	83 (7)	Os(1)-Os(3)-C(12)	92.8 (6)
C(25)-Os(1)-Os(3)	92.4 (6)	H(1)-Os(2)-Os(3)	94.4 (7)	Os(1)-Os(3)-C(14)	87.1 (6)
C(25)-Os(1)-C(22)	91.3 (8)	H(1)-Os(2)-C(33)	82 (6)	Os(2)-Os(3)-C(13)	102.9 (6)
C(21)-Os(1)-H(1)	78.0 (6)	C(31)-Os(2)-C(32)	95.7 (8)	Os(2)-Os(3)-C(14)	87.6 (6)
C(21)-Os(1)-C(22)	91.5 (9)	C(31)-Os(2)-C(33)	92.3 (8)	C(12)-Os(3)-C(13)	102.8 (9)
H(1)-Os(1)-Os(3)	94 (6)	C(32)-Os(2)-Os(3)	87.1 (5)	C(12)-Os(3)-C(14)	91.2 (8)
H(1)-Os(1)-C(22)	88 (7)	C(32)-Os(2)-C(33)	92.6 (7)	C(13)-Os(3)-C(14)	91.1 (8)
Os(3)-Os(1)-C(22)	91.5 (6)	C(33)-Os(2)-Os(3)	91.1 (5)		
carbonyls		carbene		acyl	
O(22)-C(22)-Os(1)	177 (1)	C(26)-C(25)-Os(1)	124 (1)	C(35)-C(34)-Os(2)	128 (1)
O(21)-C(21)-Os(1)	176 (2)	O(27)-C(25)-Os(1)	120 (1)	O(34)-C(34)-Os(2)	118 (1)
O(31)-C(31)-Os(2)	178 (2)	O(27)-C(25)-C(26)	116 (1)	O(34)-C(34)-C(35)	113 (2)
O(32)-C(32)-Os(2)	177 (2)	C(25)-O(27)-C(27)	122 (1)	C(34)-O(34)-Os(1)	108 (1)
O(33)-C(33)-Os(2)	174 (2)	hydride			
O(11)-C(11)-Os(3)	175 (2)	Os(1)-H(1)-Os(2)	94 (9)		
O(12)-C(12)-Os(3)	176 (2)				
O(13)-C(13)-Os(3)	177 (2)				
O(14)-C(14)-Os(3)	178 (2)				

distances and angles are presented in Tables V and VI, respectively.

The molecule consists of a triangle of osmium atoms in which the nonbridged osmium–osmium separations (see Table V) are nearly identical with the mean osmium–osmium separation in $Os_3(CO)_{12}$ of 2.877 (3) Å.[18] The remaining edge, bridged by an acetyl group and a hydrogen atom on opposite sides of the plane defined by the metal triangle, is significantly longer than that of the nonbridged edges. This is still within bonding range but is influenced by the steric requirements of the bridging groups.[19] The bond angles C(25)–Os(2)–H(1) and H(1)–Os(3)–C(31) (both 174 (6)°), as well as the bond lengths Os(2)–H(1) and Os(3)–H(1) (both 2.0 (2) Å) fall well within what is expected for the bridging hydrogen.[20]

The disposition of terminal and bridging groups around the metal triangle follows a pattern seen in a large number of structures of general formula $M_3(\mu$-X:μ-Y)(CO)$_{10}$, M = Os, and in a smaller number of similar ruthenium complexes.[21] For the closest comparison we cite $Os_3\{\mu$-H:μ-O$=\!$CCH$_2$Ph$\}$(CO)$_{10}$, **11**.[22] An approximately octahedral geometry may be recognized for the bonding of terminal or bridging groups coordinated to each of the osmium atoms. Interatomic angles in Table VI have been organized to illustrate this point.

The metal–carbon and carbon–oxygen separations of the nine terminally bonded CO groups fall within typical ranges: Os–C = 1.86–1.99 (2) Å;[19,23] C–O = 1.10–1.16 (2) Å.[24] The metal–carbon–oxygen angles of these terminally bonded groups are close to linear: Os–C–O = 174–177 (2)° (see Table VI).

Structural Features of the Carbene Group. This group is terminally bonded to Os(1) in a position approximately trans to the bridging hydride (see Figure 2 and Table VI). The separation between the carbene carbon atom to the metal, C(25)–Os(1) = 1.99 (2) Å, is at the upper limit of the range observed for Os–C separations for the terminally bonded CO groups. The distance from the carbene carbon to the methoxy oxygen, C(25)–O(27) = 1.34 (2) Å, is intermediate between that expected for carbon-oxygen single and double bonds, 1.426 (5) and 1.215 (5) Å, respectively,[24] reflecting intermediate bond order. This is attributable to a substantial electron donation from the lone pair of O(27) to C(25), typically found in Fischer-type carbene complexes.[25] The angles C(26)–C(25)–Os(1) = 124 (1)°, O(27)–C(25)–Os(1) = 120 (1)°, and O(27)–C(25)–C(26) = 116 (1)° are also comparable with those previously reported for Fischer-type carbene complexes.[25] While η^1-bonding for carbene groups is seen in some dimeric metal complexes[26] and one tri-iron complex,[2c] bridge bonding is observed in all other previously reported cluster-bound carbene complexes.[2b,27]

Structural Features of the μ-Acyl Group. The distance C-(34)–O(34) of 1.29 (2) Å is much closer to that of a carbon-oxygen double bond (see above) than is the C(25)–O(27) distance in the carbene group. The Os(3)–C(34) distance of 2.04 (2) Å, on the other hand, is just below that expected for an Os–C single bond.[28] Thus, there is very little carbene character to the bridging

(17) (a) We omit the conventional vector between metal atoms of the doubly bridged edge of the metal triangle because we believe that this representation better reflects the octahedral coordination around the metal atoms in question, see: Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243–260. (b) The single bond between the metal atoms is established by orbital overlaps through the bridging groups, cf. (i) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl, L. F.; *J. Organomet. Chem.* **1974**, *70*, 413. (ii) Mason, R.; Mingos, D. M. P. *Ibid.* **1973**, *50*, 53. (iii) Kostic, N. M.; Fenske, R. F. *Inorg. Chem.* **1983**, *22*, 666.

(18) Churchill, M. R.; De Boer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(19) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–1930.

(20) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176–183.

(21) Cf. Bruce, M. I. In "Comprehensive Organometallic Chemistry: Index of Structures Determined by Diffraction Methods"; Wilkinson, G., Stone, F. G. A., Abel, E. W.; Eds.; Pergamon Press: New York, 1982, Vol. 9, pp 1392–1395 and 1446–1447.

(22) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, 656–660.

(23) (a) Ferraris G.; Gervasio, G. *J. Chem. Soc., Dalton Trans.* **1974**, 1813–1817. (b) Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636–639. (c) Henrick, K.; McPartlin, M.; Deeming, A. J.; Hasso, S.; Manning, P. *J. Chem. Soc., Dalton Trans.* **1982**, 899–906.

(24) *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*.

(25) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1–32. (b) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1978**, *50*, 857.

(26) (a) Fischer, E. O.; Offhaus, E.; Müller, J.; Nöthe, D. *Chem. Ber.* **1972**, *105*, 3027–3059. (b) Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Marten, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053–3059. (c) Fischer, E. O.; Rustmeyer, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 627–630.

(27) (a) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1279–1281. (b) Calvert, R. B.; Shapley, J. R. *Ibid.* **1977**, *99*, 5225–5226. See also: *Ibid.* **1978**, *100*, 6544. (c) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *Ibid.* **1981**, *103*, 6975–6977.

(28) (a) Typical values of Os–C(sp^2) are found in the range 2.06–2.18 Å; see ref 23a–c. (b) If we take half of the single Os–Os bond (1.446 Å) and add the radius of C(sp^2) of 0.667 Å,[24] we obtain 2.113 Å for the expected Os–C(sp^2) separation.

acyl group (resonance form B) as also observed in $(OC)_3Fe\{O=CPh\}_2Fe)CO_3$,[29a] $(\eta^5\text{-}C_5H_5)Ir\{\mu\text{-}O=CMe;\mu\text{-}O=CPh;\mu\text{-}PPh_2\}\text{-}Mn(CO)_3$,[29b] or **11**.[22]
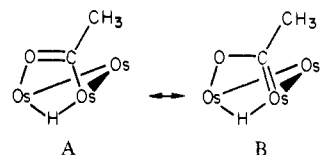
Experimental Section

The following were purchased[30a] and, except for specific instances described below, used as received; triosmium dodecacarbonyl and bis-(triphenylphosphine)nitrogen(1+) chloride ([PPN][Cl]), (Strem); phenyllithium (2.4 M in cyclohexane/diethyl ether, 70/30), trifluoromethanesulfonic acid, silver trifluoromethanesulfonate, ethyl iodide, methyl trifluoromethanesulfonate (methyl triflate), triethyl phosphite, and methyl-d_3 iodide (Aldrich); methyllithium (1.6 M in diethyl ether, low halide, Alfa). Methyl-d_3 triflate and ethyl triflate were prepared by the reaction of silver triflate with the corresponding alkyliodide.[30b] Tetrahydrofuran was dried by reflux over potassium benzophenone ketyl and freshly distilled under nitrogen. Chloroform was distilled from phosphorus pentoxide under nitrogen atmosphere immediately before use. All reactions were conducted under a nitrogen atmosphere by using standard Schlenk techniques.[31] Petroleum ether, boiling range 35–60 °C, and methylene chloride (Mallinckrodt) were used without further purification in chromatographic separations. All separations were carried out on a 20 × 2 cm column of 60-mesh silica gel (EM Reagents).

IR spectra were recorded on a Nicolet MX-1 FT-IR spectrometer. NMR spectra were recorded on Bruker 200 MHz and JEOL FX-90 FT NMR spectrometers. Gas chromatographic (GC) measurements were performed on a Hewlett-Packard 5880A GC using a flame ionization detector and a 10-m OV-101 column. GC/MS was performed on a Kratos MS-25 spectrometer.

Attempted Alkylation of [Li][Os$_3$\{η^1-C(O)CH$_3$\}(CO)$_{11}$], [Li][2]. Formation of Os$_3$(THF)(CO)$_{11}$, 3. A solution of 0.50 g (0.55 mmol) of Os$_3$(CO)$_{12}$, **1**, in 500 mL of THF is titrated with a 1.6 M diethyl ether solution of LiCH$_3$ at 0 °C to the disappearance of the IR absorptions of **1**. The solution is warmed to 25 °C and treated with methyl triflate (0.125 mL, 1.10 mmol). Monitoring the reaction by GC, a product of short retention time is observed in increasing amounts over a 2-h period. This product is identified as acetaldehyde by its retention time and GC/MS: m/e (relative intensity) 44 (100), 43 (55), 42 (16), 29 (62). Calibration with a standard solution of acetaldehyde in THF indicates a stoichiometric amount of the acetaldehyde is present after 2 h of reaction. The solvent is then removed under vacuum and the residue extracted with 0.4 mL of benzene-d_6; 115 mg of **1** remain undissolved. For complex **3** in benzene-d_6, ^{1}H NMR (ppm): 3.43 (t, J = 5.1 Hz, CH$_2$OCH$_2$), 1.77 (q, J = 3.0 Hz, CH$_2$CH$_2$). These resonances, due to coordinated THF, are shifted from free THF added to the solution: ^{1}H NMR (ppm) 3.65 (t, J = 6.6 Hz, CH$_2$OCH$_2$), 1.50 (q, J = 3.3 Hz, CH$_2$CH$_2$).

Protonation of [Li][2]. Formation of 3. A solution of 0.10 g (0.11 mmol) of **1** in 100 mL of THF is titrated with a 1.6 M diethyl ether solution of LiCH$_3$ at 0 °C to the disappearance of the IR absorptions of **1**. The solution is warmed to 25 °C and treated with 10 µL (11 mmol) of trifluoromethanesulfonic acid. GC analysis of the solution shows quantitative production of acetaldehyde. The solvent is removed under vacuum and **3** is extracted from the residue with 0.4 mL of benzene-d_6; 28 mg of **1** remain undissolved.

Reaction of 3 with P(OMe)$_3$. Treatment of a THF solution of **3** with 2 equiv of P(OMe)$_3$ at 25 °C gives rise to its instantaneous quantitative conversion to Os$_3$(CO)$_{11}$P(OMe)$_3$; IR spectrum is identical with that of a sample prepared by the method of Johnson, Lewis, and Pippard:[32] ν_{CO} (cm^{-1}, cyclohexane solution) 2111 (w), 2057 (s), 2039 (m), 2021 (vs), 2003 (w), 1992 (m), 1981 (w), 1970 (vw).

Reaction of Li[2] with Methyl Triflate. To a Schlenk flask containing 1.00 g (1.10 mol) of **1** is added 1 L of THF previously dried over potassium benzophenone and redistilled from lithium aluminum hydride. The resulting solution is titrated at 0 °C with a 1.6 M diethyl ether solution of LiCH$_3$ to the disappearance of the IR absorptions of **1**. The solution is then warmed to 25 °C, and methyl triflate (0.125 mL, 1.10 mmol, freshly distilled from P$_2$O$_5$) is added. Monitoring by IR, no reaction is seen until the mixture has become a viscous syrup owing to polymerization of the THF (14 h).

Reaction of PPN[2] with Methyl Triflate. A solution of Li[2] (1.10 mmol in 1 L of THF) is prepared as in the preceding paragraph. [PPN][Cl] (700 mg, 1.22 mmol) in 1 mL of methanol is then added and the temperature raised to 25 °C. At this point methyl triflate (0.125 mL, 1.10 mmol, freshly distilled from P$_2$O$_5$) is added. Monitoring by IR, no reaction is seen before the solution becomes a viscous syrup (14 h).

Preparation of [PPN][Os$_3$\{1,2-μ-O=C(Me)\}(CO)$_{10}$], [PPN][4]. A solution of [PPN][2] (1.10 mmol in 1 L of THF) is prepared as in the preceding paragraph and brought to 25 °C. The solution is stirred for 24 h during which time the absorption of the η^1-acyl group at 1602 cm^{-1} is seen to diminish while bands corresponding to terminal CO absorptions of the μ-acyl complex make their appearance. The volume of the THF is reduced to 50 mL resulting in the precipitation of LiCl; this is removed by filtration. The remaining THF is removed under vacuum, and 50 mL of chloroform is added. At this time the η^1- and μ-acyl anionic complexes are present in a ratio of approximately 30/70 as determined by ^{1}H NMR. Conversion of the η^1-acyl complex is brought to completion by several additional cycles of solvent removal and replacement. During each removal of solvent under vacuum, small amounts of **1** precipitate from the solution when it has been reduced to 5 mL or less; this is removed by centrifugation before the remaining solvent is evaporated. In all, a total of 9.4 mg of **1** is recovered. The main product is an orange powder whose ^{1}H NMR spectrum shows only [PPN][4]; yield 87% (1.37 g).

Preparation of Os$_3$\{C(O)CH$_3$\}\{1,2-μ-O=C(Me)\}(CO)$_9$, 5, and Its Disproportionation to 7a and 8 (and 6a) during Chromatography on Silica Gel. A solution of **4** (250 mg, 182 µmol) in 100 mL of chloroform is treated at 25 °C with 0.0206 mL (182 µmol) of methyl triflate. Alkylation is complete after 2 h, giving rise to the highly reactive (bis(acyl) derivative **5**: see Tables I and II for spectroscopic characterization. The chloroform is removed by vacuum, the residue taken up in 5 mL of petroleum ether and placed on a column of silica gel. Eluting first with petroleum ether gives rise to a faint yellow band: Os$_3$\{1,2-μ-Cl;1,2-μ-O=C(Me)\}(CO)$_{10}$, **6a**, 9 mg (5% yield). This product arises from residual LiCl not completely removed in previous steps. Elution next with CH$_2$Cl$_2$ gives two fractions: a rapidly moving orange-yellow band, Os$_3$\{1-η^1-C(OMe)Me\}\{1,2-μ-H;1,2-μ-O=C(Me)\}(CO)$_9$, **7a**, 64 mg (38% yield), and a slower moving yellow-green band, Os$_3$\{1,2-μ-OH;1,2-μ-O=C(Me)\}(CO)$_{10}$, **8**, 41% yield (68 mg).

Preparation of Os$_3$\{C(O)CD$_3$\}\{(1,2-μ-O=C(Me)\}(CO)$_9$, 5-d_3. A 5-mm NMR tube is charged with a solution of **4** (100 mg, 70 µmol) in 0.2 ml of chloroform. CD$_3$OSO$_3$CF$_3$ (0.0079 mL, 70 µmol) is added and the tube sealed under nitrogen. After 2 h at 25 °C only a single resonance is observed in the ^{2}H NMR, 2.11 ppm (relative to CDCl$_3$). The spectrum remains unchanged after the sample is allowed to stand a week.

Reaction of 5-d_3 with Water. Disproportionation to Os$_3$\{1-η^1-C-(OCD$_3$)CD$_3$\}\{1,2-μ-H;1,2-μ-O=C(Me)\}(CO)$_9$, 7a-d_6 and 8 (and 6c). The NMR tube containing the chloroform solution of **5-d_3** prepared as above is opened and a drop of water added. The solvent is removed under vacuum, and the residue is extracted with 5 mL of petroleum ether. The volume is reduced to 0.4 mL, a drop of CDCl$_3$ is added, and the ^{2}D NMR spectrum is obtained: 4.33 (s, OCD$_3$) and 2.56 ppm (s, CD$_3$). These resonances match those of the \{1-C(OCH$_3$)CH$_3$\} group in the ^{1}H NMR spectrum of **7a**. Two additional constituents are present in this mixture (product mixture A) as ascertained by column chromatography, described next.

Chromatography of Product Mixture A. H/D Exchange in 7a-d_6. The petroleum ether solution of product mixture A is placed on a column of silica gel. Elution with petroleum ether gives rise to a minor amount of Os$_3$\{1,2-μ-I;1,2-μ-O=C(Me)\}(CO)$_{10}$, **6c**, 6 mg (8% yield). Elution with CH$_2$Cl$_2$ gives rise to two major products characterized by a combination of ^{1}H NMR and ^{2}H NMR. The first band is Os$_3$\{1-C(OCD$_3$)CH$_3$\}\{1,2-μ-H;1,2-μ-O=C(Me)\}(CO)$_9$, **7a-d_3**, 23 mg, 35% yield, followed by **8**, 22 mg, 33% yield. For **7a-d_3**: ^{1}H NMR (in CDCl$_3$, ppm) 2.56 (s, 3 H, carbene methyl), 2.33 (s, 3 H, μ-acyl methyl), and −15.20 (s, 1 H, cluster); ^{2}H NMR (in CHCl$_3$, ppm)) 4.33 (s, 3 D, carbene-OCD$_3$).

Reaction of [PPN][4] with Methyl Triflate in THF. To a Schlenk flask containing **4** (250 mg, 182 µmol) is added 100 mL of THF previously dried over potassium benzophenone and redistilled from lithium aluminum hydride. The solution is treated at 25 °C with methyl triflate (0.0206, mL, 182 µmol). IR shows formation of some **5**, but alkylation is still not complete after 10 h. At this point workup of the reaction is

(29) (a) Fischer, E. O.; Kiener, V.; Bunbury, D. S. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *J. Chem. Soc., Chem. Commun.* **1968**, 1378–1380. (b) Blickensderfer, J. R.; Knobler, C. B.; Kaesz H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2686–2691.

(30) (a) Vendors mentioned in the Experimental Section are as follows: Strem Chemical Inc., Newburyport, MA 01950; Aldrich Chemical Co., Milwaukee, WI 53233; Alpha Division, Ventron Co., Danvers, MA 01923; Mallinckodt Inc., St. Louis, MO 63134; EM Reagents, Cincinnati, OH 45212. (b) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 4069–4079.

(31) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

(32) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407–412.

still possible before the solution becomes too viscous for handling (due to polymerization of the THF). The solvent is removed under vacuum, the resulting oil taken up in 5 mL of petroleum ether, and the solution is placed on a column of silica gel. Elution with petroleum ether gives rise to **6a** (11 mg, 6% yield). Eluting next with CH_2Cl_2 gives **7a** (23 mg, 14% yield) and **8** (28 mg, 17% yield).

Preparation of 7a from $Os_3\{1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_{10}$, **9.** The procedure of Mayr et al.)[4] was used to prepare **9**; 250 mg (279 μmol) is placed in 100 mL of dry freshly distilled diethyl ether and titrated at 0 °C with CH_3Li (1.5 M in diethyl ether) to the disappearance of the IR absorptions of **9**. Spectroscopic data of the resulting salt [Li][$Os_3\{C-(OMe)\}\{1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_9$], [Li][**10a**], are summarized in Tables I and II. To the solution of [Li][**10a**] is added methyl triflate (0.035 mL, 310 μmol) and followed by 36 h of stirring at 25 °C; **7a** is produced. The solvent is removed, the residue taken up in 5 mL of petroleum ether, and the solution placed on a column of silica gel. Elution with petroleum ether gives rise to two fractions. The first is a faint yellow-green band, $Os_3\{1,2-\mu-Br;1,2-\mu-O=C(Me)\}(CO)_{10}$, **6b** (21 mg, 8% yield, based on total starting material); the second is **9**, 24 mg, ca. 10% recovered unreacted). Eluting next with CH_2Cl_2 gives rise to **7a**, 183 mg, 71% yield. Longer reaction time leads to formation of $Os_3\{1-\eta^1-C(OEt)Me\}\{1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_9$, **7b** in increasing yields to 10% in 70 h. Attempts to separate **7a** and **7b** by silica gel column chromatography are only partially successful. Eluting solely with petroleum ether requires up to 2 L of solvent; a broad band develops whose leading edge is pure **7b**. Remaining portions of this band is a mixture of **7a** and **7b** with no pure **7a** being observed even at the trailing edge.

Preparation of 7b from 10a and $EtOSO_2CF_3$. A solution of **10a**, 0.279 mmol in 125 mL diethyl ether, is prepared as in the preceding paragraph. This is brought to 25 °C, treated with ethyl triflate (0.225 mL of a 1.27 M solution in diethyl ether), and stirred for 60 h at 25 °C. The diethyl ether is removed, the residue taken up in 5 mL of petroleum ether, and the solution placed on a silica gel column. Elution with petroleum ether gives **5b** (19 mg, 7% yield) followed by **9** (13 mg, 5% unreacted starting material). Elution with CH_2Cl_2 gives **7b** (223 mg, 85% yield).

Preparation of $Os_3\{1-\eta^1-C(OEt)C_6H_5\}\{1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_9$, **7c.** A quantity of **9** (250 mg, 0.279 mmol) in 100 mL of dry, freshly distilled diethyl ether is titrated at 0 °C with C_6H_5Li (Aldrich solution) to the disappearance of the IR absorptions of **9**. The resulting solution of [Li][$Os_3\{C(O)C_6H_5)\}\{1,2-\mu-H;1,2-\mu-O=C(Me)\}(CO)_9$], [Li][**10b**], is treated with 0.225 mL of 1.27 M ethyl triflate in diethyl ether (286 μmol) and stirred for 108 h. The diethyl ether is removed, the residue taken up in 5 mL of petroleum ether, and this solution placed on a silica gel column. Elution with petroleum ether gives two fractions. The first is **5b** (21 mg, 8% yield), and the second is **9** (11 mg, 4.4% unreacted starting material). Eluting with CH_2Cl_2 gives **7c** (134 mg, 48% yield).

Collection and Reduction of X-ray Data for 7a. Complex **7a** crystallizes as air and X-ray stable yellow rhombohedra by slow evaporation of a pentane solution. A crystal was mounted along the a axis on a glass fiber. Preliminary oscillation and Weissenberg (*h0l* and *h1l*) photographs taken with Cu Kα radiation indicated a monoclinic space group with systematic absences, $h + l = 2n + 1$, for all *h0l* reflections. The crystal was then centered on a Syntex P1̄ autodiffractometer equipped with a scintillation counter, graphite monochromator, and a low-temperature device.[33] Crystallographic data for the structure are summarized in Table III.

In addition to the systematic absences observed in the Weissenberg photographs, the *0k0* reflections for all $k = 2n + 1$ were observed to be

systematically absent, and the space group was determined to be $P2_1/n$. The 2θ, ϕ, ω, and χ settings of 15 reflections were determined ($2\theta = 2-21°$, Mo Kα). These values were used in a least-squares refinement of cell and orientation parameters. Intensities were measured by the $\theta-2\theta$ scan technique. Crystal and instrument stability were monitored by a set of three standard reflections $(0,1,\bar{2})$, $(3,3,3)$, and $(0,4,2)$ measured every 100 reflections; no significant variation in intensities was found. Net intensities were calculated by assuming a linear background profile between the scan limits of each reflection.

The data were reduced and processed by utilization of the program CARESS.[34] The 2728 observed reflections were corrected for Lorentz and polarization effects and converted to $|F_o|$ and $\sigma(|F_o|)$.[35]

The positions of the three osmium atoms were located from a three-dimensional Patterson synthesis. Two difference Fourier syntheses yielded the positions of all non-hydrogen atoms. Refinement was carried out by use of full-matrix least-squares procedures using atomic scattering factors compiled by Hanson et al.[36] for all non-hydrogen atoms. All non-hydrogen atoms were permitted to vary anisotropically in which treatment the carbon and oxygen atoms showed large uncertainties in the thermal parameters. One of these, the acyl carbon C(34), appeared as nonpositive definite. Examination of difference maps did not reveal any sign of disorder to account for this. A cycle of refinement was attempted omitting reflections strongly affected by secondary extinction; no appreciable change in thermal parameters was noted. In all probability, this phenomenon is not significant given the high absorption coefficient of osmium and errors in defining the shape of the crystal for absorption correction. In further refinement, an isotropic thermal parameter was assigned to C(34).

After all non-hydrogen atoms except C(34) were refined anisotropically, the metal hydride was located and refined. The final atomic positional parameters with their standard deviations are given in Table IV.

Supplementary Material Available: Tables of thermal parameters, structure factors and packing diagram (15 pages). Ordering information is given on any current masthead page.

(33) Strouse, C. E. *Rev. Sci. Instrum.* **1976**, 871.

(34) (a) CARESS is a local modification incorporating the program of the same acronym by Broach, R. W., U. of Wisconsin, and the program PROFILE by Coppens, P., Becker, P., and Blessing, R. H., SUNY—Buffalo. (b) Other programs used in this work: full-matrix least-squares and error analysis, ORFLS and ORFFE, Busing, W. R., Martin K. O., and Levy H. A. (Oak Ridge National Laboratory); absorption correction, ABSN, Coppens, P.; Least-squares planes, MGTL, Gantzel, P., and Trueblood, K. N.; thermal ellipsoid plot program, ORTEP II, Johnson, C. K. (Oak Ridge National Laboratory); structure factor table listing, PUBLIST, Hoel, E.

(35) $|F_o| = k[I/(Lp)]^{1/2}$; $\sigma(|Fo|) = (k/2)[\sigma(I)/I(Lp)]^{1/2}$ where (Lp) is the Lorentz and polarization factors.

(36) Hanson, H. P.; Herman, F.; Lea, J. D.; Skillman, S. *Acta Crystallogr.* **1964**, *17*, 1040.