Synthesis, Crystal Structure, and Reactivity of (μ-H)Os₃(CO)₁₀(μ₃-CPh)[1]

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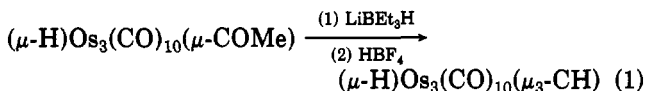
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The complex (μ-H)Os₃(CO)₁₀(μ₃-CPh) (1) has been prepared by treatment of (μ-H)Os₃(CO)₁₀(μ-COMe) sequentially with PhLi and MeOSO₂CF₃. Compound 1 has been characterized by IR, ¹H and ¹³C NMR, and mass spectroscopies together with a single-crystal X-ray diffraction study. Treatment of 1 with H₂ at 150 °C in decane solution produces (μ-H)₃Os₃(CO)₉(μ₃-CPh) (2) quantitatively. Pyrolysis of solid 1 in vacuo generates the ortho-metalated product (μ-H)Os₃(CO)₉(μ₃-η³-CHC₆H₄) (3) in high yield. The complex 1 crystallizes in the centrosymmetric monoclinic space group P2₁/m (C²₂ₕ; No. 11) with a = 8.1205 (11) Å, b = 14.2658 (26) Å, c = 8.9165 (18) Å, β = 98.701 (14)°, V = 1021.1 (3) Å³, and D(calcd) = 3.06 g cm⁻³ for mol wt 940.8 and Z = 2. The molecule possesses crystallographically imposed Cₛ(m) symmetry. Final discrepancy indices are R_F = 2.5% and R_wF = 2.7% for all 1286 independent data [R_F = 2.2% and R_wF = 2.7% for those 1192 data with |F_o| > 3.0σ(|F_o|)]. The molecule contains a triangular arrangement of osmium atoms in which Os(1)–Os(2) = Os(1)–Os(2′) = 2.845 Å and Os(2)–Os(2′) = 2.860 Å. The unique Os(1) is linked to four terminal carbonyl ligands while Os(2) and Os(2′) are each linked to three terminal carbonyls. The Os(2)–Os(2′) linkage is bridged by a hydride ligand [Os(2)–H(B) = Os(2′)–H(B) = 1.82 (5) Å; ∠Os(2)–H(B)–Os(2′) = 103.7 (31)°] and by a bridging benzylidyne ligand [Os(2)–C(1) = Os(2′)–C(1) = 2.035 (8) Å; ∠Os(2)–C(1)–Os(2′) = 89.26 (35)°]. This latter ligand lies over the triosmium triangle and interacts significantly with the third osmium atom [Os(1)...C(1) = 2.586 (10) Å].

Introduction

Recently, the transformation of (μ-H)Os₃(CO)₁₀(μ-COMe) into (μ-H)Os₃(CO)₁₀(μ₃-CH) (eq 1) was described.[3]

$$(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-COMe}) \xrightarrow[\text{(2) HBF}_4]{\text{(1) LiBEt}_3\text{H}}$$
$$(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH}) \quad (1)$$

The molecular structure determined for (μ-H)Os₃(CO)₁₀(μ₃-CH) showed that the methylidyne ligand adopted a unique "semi-triply bridging" configuration in which the third osmium atom acted as an electron pair donor to the electrophilic carbon center.[3] In order to probe the generality of this structure, we have sought to prepare and characterize related compounds of the formula HOs₃(CO)₁₀(C-R), where R ≠ H. In this paper we report information concerning the synthesis, structure, and reactivity of the benzylidyne complex (μ-H)Os₃(CO)₁₀(μ₃-CPh) (1). A molecule of this same type, (μ-H)Os₃(CO)₁₀(μ₃-CCH₂CHMe₂), but prepared quite differently, has been reported very recently by Green and co-workers.[4]

Experimental Section

(μ-H)Os₃(CO)₁₀(μ-COMe) was prepared by Keister's method.[5] (μ-D)Os₃(CO)₁₀(μ-COMe) was prepared in the same way, except that D₂O replaced H₂O in the first step. ¹³CO-enriched Os₃(CO)₁₂ (ca. 50% enriched) was prepared by heating a solution of Os₃(CO)₁₂ in dry decalin at 110 °C for 48 h under 12 equiv of ¹³CO (90% ¹³CO, Mound Laboratories) in a pressure bottle. Phenyllithium (Alfa, 1.4 M in ether/benzene), methyl trifluoromethanesulfonate (Aldrich), and CP grade hydrogen gas were used directly as received. Diethyl ether was distilled from sodium benzophenone ketyl, and decane was distilled from sodium immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from Silica Gel G (Type 60, E. Merck). Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. Melting points were determined in sealed capillaries. ¹H NMR spectra were obtained on either a Varian EM-390 spectrometer (90 MHz) or a Nicolet NT-360 spectrometer (360 MHz). ¹³C NMR spectra were obtained with the latter spectrometer at 90.56 MHz. IR spectra were taken on a Perkin-Elmer 281 B spectrometer and were calibrated with polystyrene film and cyclohexane (2138.5 cm⁻¹). 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 (μ-H)Os₃(CO)₁₀(μ₃-CPh) from (μ-H)Os₃(CO)₁₀(μ-COMe). An oven-dried, 100-mL three-necked round-bottomed flask was equipped with a magnetic stir bar, a glass stopcock, a rubber serum stopper, and a nitrogen inlet. The stopper was briefly removed, and (μ-H)Os₃(CO)₁₀(μ-COMe) (180 mg, 0.20 mmol) was added against a nitrogen flow. Freshly distilled diethyl ether (50 mL) was then introduced by means of a cannula through the serum stopper. After the solution was cooled to 0 °C with an ice bath, phenyllithium (350 μL, 0.476 mmol) was added via a syringe over a period of 30 min. Methyl trifluoromethanesulfonate (500 μL, 4.4 mmol) was then added to the resulting orange-red solution via a syringe. The solution was concentrated to ca. 25 mL under vacuum at 0 °C, then placed under nitrogen, and stirred at 25 °C for 60 h. n-Pentane (25 mL) and water (10 mL) were added to the flask, and the mixture was stirred for 5 min. The bottom, aqueous layer was removed with a pipet. The organic solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness on a rotary evaporator. The oily red residue was subjected to TLC, eluting with n-pentane. Crystallization of the material forming the first, orange-red band from acetone produced air-stable, red crystals of (μ-H)Os₃(CO)₁₀(μ₃-CPh) (1) (95 mg, 0.106 mmol, 50%): mp 144–146 °C; mass spectrum, m/z 946 (M⁺, ¹⁹²Os); IR (C₆H₁₂) ν(CO) 2107 (w), 2063 (s), 2023 (s), 2000 (m), 1995 (m) cm⁻¹; ¹H NMR (CCl₄, 25

(1) Structural Studies on Polynuclear Osmium Carbonyl Hydrides. Part 30. For previous parts, see ref 2.

(2) (a) Part 25. Samkoff, D. E.; Shapley, J. R.; Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1984**, *23*, 397. (b) Part 26. Churchill, M. R.; Missert, J. R. *J. Organomet. Chem.* **1983**, *256*, 349. (c) Part 27. Churchill, M. R.; Bueno, C. *J. Organomet. Chem.* **1983**, *256*, 357. (d.) Part 28. Churchill, M. R.; Bueno, C.; Partk, J. T.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 1017. (e) Part 29. Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1984**, *23*, 4476.

(3) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(4) Green, M.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 37.

(5) Keister, J. B. *J. Chem. Soc., Chem. Commun.* **1979**, 214.

(6) (a) Strickland, D. S. Ph.D. Thesis, University of Illinois, 1983. The method of preparation was analogous to that used for H₃Ru₃(CO)₉(μ₃-CPh).⁶ᵇ (b) Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304.

°C) δ 7.8–7.6 (m, 2 H), 7.2–7.4 (m, 3 H), –16.6 (s, 1 H); ^{13}C NMR (CD$_2$Cl$_2$, 17 °C) δ 314.2 (s, 1 C, CPh), 175.9 (s, 2 C), 175.0 (s, 4 C), 174.0 (d, 2 C, J_{CH} = 11 Hz), 169.8 (s, 2 C); see Figure 2. Anal. Calcd for Os$_3$C$_{17}$H$_6$O$_{10}$: C, 21.70; H, 0.64; Os, 60.6. Found: C, 21.60; H, 0.51; Os, 59.6. The above procedure is optimized for the production of complex 1. Other products formed in the reaction, the relative amounts of which vary with conditions, are still under investigation. [**Note Added in Proof**: The second major product (ca. 30%) formed under these conditions has been identified spectroscopically and by X-ray crystallography as Os$_3$(CO)$_9$(μ$_3$-CPh)(μ$_3$-COMe).]

The crystal of (μ-H)Os$_3$(CO)$_{10}$(μ$_3$-CPh) found suitable for X-ray analysis was grown from acetone/dichloromethane at room temperature.

Preparation of (μ-D)Os$_3$(CO)$_{10}$(μ$_3$-CPh) from (μ-D)Os$_3$-(CO)$_{10}$(μ-COMe). (μ-D)Os$_3$(CO)$_{10}$(μ$_3$-CPh) was prepared by the same method as described above. It was characterized by its IR and ^{1}H NMR spectra, which are identical with those for (μ-H)-Os$_3$(CO)$_{10}$(μ$_3$-CPh), except for the missing NMR signal at δ –16.6. The level of deuteration for both (μ-D)Os$_3$(CO)$_{10}$(μ-COMe) and (μ-D)Os$_3$(CO)$_{10}$(μ$_3$-CPh) was >95%, and no loss of the label after TLC was observed in either case.

Hydrogenation of (μ-H)Os$_3$(CO)$_{10}$(μ$_3$-CPh). An oven-dried 100-mL three-necked round-bottomed flask was equipped with a magnetic stir bar. One neck was stoppered, and one had a reflux condenser topped with a stopcock connected to an oil bubbler, and the third neck had an inlet tube for introduction of hydrogen gas into the solution. A solution of (μ-H)Os$_3$(CO)(μ$_3$-CPh) (30 mg, 0.0317 mmol) in decane (50 mL) was transferred into the flask and saturated with hydrogen gas. With hydrogen bubbling through the solution, it was heated at 150 °C for 20 min, at which point the color was pale yellow. The solvent was then removed by vacuum into a dry ice–2-propanol trap. Crystallization of the residue from dichloromethane–methanol produced pale yellow crystals of (μ-H)$_3$Os$_3$(CO)$_9$(μ$_3$-CPh) (2) (27 mg, 0.30 mmol, 95%). The complex was identified by comparison of IR and ^{1}H NMR data with an authentic sample:[6a] IR (C$_6$H$_{12}$) ν(CO) 2080 (vs), 2073 (sh), 2022 (s), 2017 (s), 2007 (sh), 1980 (vw); ^{1}H NMR (CDCl$_3$, 25 °C) δ 7.8–6.8 (m, 5 H), –18.7 (s, 3 H).

The reaction was complete also at a bath temperature of 110 °C in 90 min.

Pyrolysis of Solid (μ-H)Os$_3$(CO)$_{10}$(μ$_3$-CPh) in Vacuo. (μ-H)Os$_3$(CO)$_{10}$(μ$_3$-CPh) (1) (35 mg, 0.037 mmol) was sealed in glass tubing under vacuum (0.1 mm Hg), and the tube was placed in a silicon oil bath at 170 °C. During the first minute of pyrolysis, vigorous bubbling of gas was observed. After 25 min, the tube was removed from the bath, cooled to room temperature, and opened in air. The brown residue was dissolved in dichloromethane, applied to a preparative TLC plate, and eluted with n-pentane–dichloromethane (9:1, v/v). The first, yellow band was extracted with dichloromethane. After the dichloromethane was removed on a rotary evaporator, an air-stable orange-red solid, characterized as (μ-H)Os$_3$(CO)$_9$(μ$_3$-η^3-CHC$_6$H$_4$) (3), was obtained (28 mg, 0.031 mmol, 83%): mass spectrum, m/z 918 (M$^+$, ^{192}Os); IR (C$_6$H$_{12}$) ν(CO) 2097 (m), 2069 (s), 2049 (s), 2033 (vw), 2018 (s), 2007 (s), 2000 (s), 1994 (m), 1988 (sh) cm^{-1}; ^{1}H NMR ((CD$_3$)$_2$CO, 25 °C) δ 10.08 (s, 1 H), 8.30–8.12 (m, 1 H), 8.10–8.01 (m, 1 H), 7.92–7.83 (m, 2 H), –18.91 (s, 1 H). Anal. Calcd for Os$_3$C$_{16}$H$_6$O$_9$: C, 21.04; H, 0.66; Os, 62.52. Found: C, 21.08; H, 0.70; Os, 63.7.

Pyrolysis of Solid (μ-D)Os$_3$(CO)$_{10}$(μ$_3$-CPh) in Vacuo. This reaction was carried out and worked up in a fashion identical with that above. The product showed the same IR spectrum and differed only in that the ^{1}H NMR spectrum showed 0.5 H at both δ 10.08 and –18.91.

Collection of X-ray Diffraction Data. A deep red crystal of approximate dimensions 0.30 × 0.27 × 0.20 mm^3 was selected for the structural analysis. It was glued onto a thin glass fiber which was fixed (with beeswax) into an aluminum pin mounted in a eucentric goniometer on a Syntex P2$_1$ automated four-circle diffractometer. Crystal alignment, determination of unit cell parameters (along with orientation matrix) and data collection were carried out as described previously.[7] Details appear in Table I.

(7) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, *16*, 265.

Table I. Experimental Data for the X-ray Diffraction Study of (μ-H)Os$_3$(CO)$_{10}$(μ$_3$-CPh)

(A) Crystallographic Parameters

cryst system: monoclinic   space group: $P2_1/m$
(C^2_{2h}; No. 11)

a = 8.1205 (11) Å	formula: C$_{17}$H$_6$O$_{10}$Os$_3$
b = 14.2658 (26) Å	mol wt: 940.8
c = 8.9165 (18) Å	Z = 2
β = 98.701 (14)°	D(calcd) = 3.06 g cm^{-3}
V = 1021.1 (3) Å^3	T = 23 °C (296 K)

(B) Data Collection

diffractometer: Syntex P2$_1$
radiation: Mo Kᾱ ($\bar{λ}$ = 0.710730 Å)
monochromator: highly oriented graphite, equatorial geometry, 2θ$_m$ = 12.2°, assumed 50% perfect
reflctns measd: entire shell (4 equiv forms) for 2θ = 4.0–45.0°
scan type: coupled θ (crystal)–2θ (counter)
scan width: symmetrical, [2.0 + Δ(α$_2$ – α$_1$)]°
scan speed: 2.0 deg/min (in 2θ)
bkgd measd: stationary-crystal, stationary-counter at beginning and end of 2θ scan; each for half of total scan time
std reflctns: 3 check reflctns remeasd after each 97 reflctns; no decay was obsd
reflctns collectd: 5454 total; merged to 1286 unique data [OSFR file name]
μ(Mo Kα): 197.8 cm^{-1}; empirical correction applied

The observed systematic absences (0k0 for k = 2n + 1 only) are consistent with two possible monoclinic space groups—the noncentrosymmetric space group P2$_1$ (No. 4) and the centrosymmetric space group P2$_1$/m (No. 11). With Z = 2 either is possible, and the asymmetric unit is one entire molecule in P2$_1$ or one half-molecule (imposed C$_s$ molecular symmetry or disorder) in P2$_1$/m. We decided to collect all four possible data forms (i.e., ±h, ±k, ±l). The successful solution of the structure indicated the correct space group was P2$_1$/m.

All data were corrected for Lorentz and polarization factors and for the effects of absorption (via interpolation both in 2θ and φ between a series of ψ scans of close-to-axial reflections). The "R factors" for averaging the four equivalent sets of reflections were R(I) = 1.94% and R$_w$(I) = 1.69%. Data were placed on an approximately absolute scale by means of a Wilson plot.

Solution of the Crystal Structure. All computations were performed by use of the Syntex XTL system (Nova 1200 computer, Diablo disk, and the XTL interactive crystallographic program package as modified at SUNY—Buffalo). The analytical atomic scattering factors for neutral Os, O, C, and H were corrected for both the real (Δf′) and imaginary (Δf″) components of anomalous dispersion. The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = \{[\sigma(|F_o|)]^2 + 0.01|F_o|^2\}^{-1}$.

The positions of the heavy atoms were quickly and unambiguously determined from a Patterson map which indicated that the space group was probably P2$_1$/m. All non-hydrogen atoms were located from a difference-Fourier map. The bridging hydride ligand was located directly from a "cut-down" difference-Fourier synthesis (using only data with (sin θ)/λ < 0.3). Hydrogen atoms of the phenyl ring were included in calculated positions (sp^2 geometry and d(C–H) = 0.95 Å) with B = 6.0 Å^2. Full-matrix least-squares refinement of positional parameters (for all except phenyl hydrogens), anisotropic thermal parameters for non-hydrogen atoms, and the isotropic thermal parameter for the bridging hydrogen atom H(B) led to convergence with R$_F$ = 2.5%, R$_{wF}$ = 2.7%, and GOF = 0.98 for all 1286 independent data [R$_F$ = 2.2%, R$_{wF}$ = 2.7%, and GOF = 1.00 for those 1192 data with |F$_o$| > 3.0σ(|F$_o$|)].

A final difference-Fourier synthesis showed no significant features (the highest peak, of height 0.71 e/Å^3, being close to the position of an osmium atom); the structure is therefore correct and complete. Final positional parameters are collected in Table II; anisotropic thermal parameters are deposited in Table II-S.

Data were corrected for secondary extinction by using the

Table II. Atomic Coordinates for $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)^a$

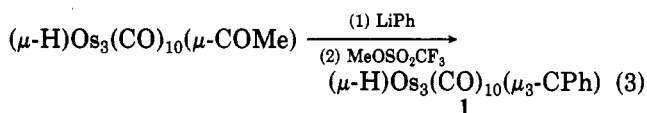| atom	x	y	z	B_{iso}, A^2
Os(1)	0.95037 (5)	0.25000 (0)	0.20255 (5)	
Os(2)	1.23381 (3)	0.35023 (2)	0.34629 (3)	
O(11)	0.72781 (78)	0.07712 (56)	0.14496 (77)	
O(12)	0.8757 (10)	0.25000 (0)	0.5299 (11)	
O(13)	0.9886 (11)	0.25000 (0)	-0.1368 (11)	
O(21)	1.10002 (81)	0.43613 (55)	0.62302 (82)	
O(22)	1.59400 (73)	0.40342 (56)	0.45000 (89)	
O(23)	1.15485 (93)	0.52430 (57)	0.1519 (10)	
C(1)	1.2666 (12)	0.25000 (0)	0.1911 (14)	
C(2)	1.3369 (12)	0.25000 (0)	0.0502 (13)	
C(3)	1.3785 (12)	0.33299 (72)	-0.0184 (12)	
C(4)	1.4557 (14)	0.33460 (85)	-0.1463 (13)	
C(5)	1.4983 (16)	0.25000 (0)	-0.2066 (17)	
C(11)	0.8109 (10)	0.14047 (64)	0.16310 (93)	
C(12)	0.9099 (12)	0.25000 (0)	0.4104 (13)	
C(13)	0.9828 (12)	0.25000 (0)	-0.0112 (15)	
C(21)	1.14812 (93)	0.40664 (66)	0.5202 (10)	
C(22)	1.4566 (10)	0.38408 (62)	0.4128 (10)	
C(23)	1.1873 (10)	0.45793 (71)	0.2211 (11)	
H(B)	1.2247 (86)	0.25000 (0)	0.4708 (93)	0.8 (15)
H(3)	1.3524	0.3909	0.0248	6.0
H(4)	1.4791	0.3923	-0.1917	6.0
H(5)	1.5576	0.2500	-0.2906	6.0

^{a} The molecule lies on a crystallographic mirror plane at $y = {}^1/_4$. Atoms in the "other half" of the molecule are labeled with a prime (') and are related to the basic asymmetric unit by the transformation $(x', y', z') = (x, {}^1/_2 - y, z)$.

simplified Zachariasen formula[8] shown in eq 2. The value determined for g was 0.105×10^{-6}.

$$|F_{o,corr}| = |F_{o,uncorr}|(1.0 + gI_o) \qquad (2)$$

Results and Discussion

Synthesis. A two-step procedure effects substitution of the methoxy group in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ by a phenyl group (eq 3), leading to the benzylidyne product

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe) \xrightarrow[\text{(2) MeOSO}_2\text{CF}_3]{\text{(1) LiPh}}$$
$$\underset{\mathbf{1}}{(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)} \qquad (3)$$

1 in up to 50% yield. This procedure is analogous to that used previously in the synthesis of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$[3] (see eq 1). However, whereas hydride attack occurs cleanly at the carbyne center to give $[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHOMe)^-]$, which can be isolated and thoroughly characterized, no analogous alkylidene intermediate is seen during the reaction with phenyllithium. Instead, our preliminary studies show that Ph^- attack occurs at a carbonyl ligand and that a complicated sequence of rearrangements occurs in the presence of the methylating agent to form finally the benzylidyne product. Thus, the H^-/H^+:Ph^-/Me^+ analogy is synthetically useful but not mechanistically parallel. Further investigation of the reaction pathway and of the coproducts is ongoing.

Crystal Structure. Crystals of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$ contain an ordered array of discrete monomeric molecular units which are mutually separated by normal van der Waals' distances. There are no abnormally short intermolecular contacts. (The shortest such contact is O-(12)···O(13) $[x,y,1 + z] = 2.974$ (14) Å.) The labeling of atoms within the molecule is shown in Figure 1. Interatomic distances are given in Table III, while intramolecular
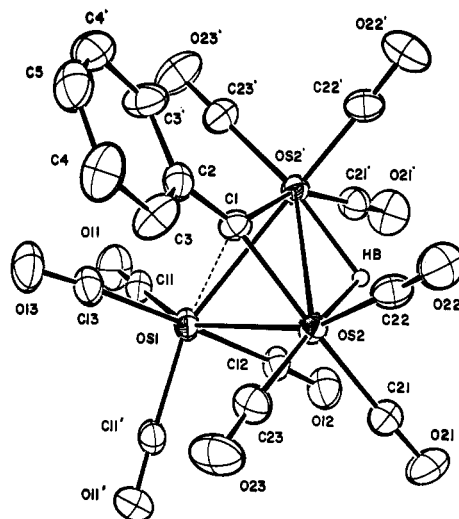
(8) Zachariasen, W. H. *Acta Crystallogr.* **1963**, *16*, 1139. See also: Stout, G. H.; Jensen, L. H. "X-Ray Structure Determination", McMillan: London, 1900; pp 411-412, especially, eq 17.16.

Figure 1. Geometry and atomic labeling scheme for $(\mu\text{-}H)Os_3$-$(CO)_{10}(\mu_3\text{-}CPh)$—ORTEP-II diagram with 30% probability ellipsoids. Note that there exists a crystallographically imposed mirror plane passing through Os(1), C(1), C(2), C(5), C(12), O(12), C(13), O(13), and H(B).

Table III. Interatomic Distances (A) for $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$

(A) Metal-Metal Distances

Os(1)-Os(2)	2.845 (0.4)	Os(2)-Os(2')	2.860 (0.4)
		Os(1)···Os(mdpt)^a	2.459 (···)

(B) Osmium-(Bridging Ligand) Distances

Os(2)-C(1)	2.035 (8)	Os(2)-H(B)	1.82 (5)
Os(1)-C(1)	2.586 (10)		

(C) Osmium-Carbonyl Distances

Os(1)-C(11)	1.931 (9)	C(11)-O(11)	1.125 (11)
Os(1)-C(12)	1.931 (11)	C(12)-O(12)	1.141 (15)
Os(1)-C(13)	1.963 (13)	C(13)-O(13)	1.128 (16)
Os(2)-C(21)	1.965 (9)	C(21)-O(21)	1.131 (11)
Os(2)-C(22)	1.880 (8)	C(22)-O(22)	1.149 (11)
Os(2)-C(23)	1.903 (10)	C(23)-O(23)	1.139 (13)

(D) Distances within the CPh System

C(1)-C(2)	1.456 (16)	C(3)-C(4)	1.383 (15)
C(2)-C(3)	1.397 (12)	C(4)-C(5)	1.386 (14)

^{a} Os(mdpt) is the midpoint of the Os(2)-Os(2') linkage and has the coordinates 1.23381, ${}^1/_4$, 0.34629.

angles are collected in Table IV. Important molecular planes and dihedral angles are collected in Table V-S.

The molecule is based upon a triangular array of osmium atoms in which the dibridged Os(2)-Os(2') distance of 2.860 Å is slightly, but significantly, longer than the other two intermetallic distances (i.e., Os(1)-Os(2) = Os(1)-Os(2') = 2.845 Å). A rather greater difference was found in the parent complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$,[3] where the dibridged Os-Os distance of 2.910 (1) Å is ~0.066 Å longer than the other two Os-Os distances (2.842 (1) and 2.845 (1) Å). However, the difference is less pronounced and less regular in $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CCH_2CHMe_2)$, i.e., 2.870 (2) Å vs. 2.861 (2) and 2.827 (2) Å.[4] For comparison, we note that the unperturbed Os-Os distances in $Os_3(CO)_{12}$ average 2.8771 [27] Å.[9,10]

The most interesting feature of the structure of $(\mu\text{-}H)$-$Os_3(CO)_{10}(\mu_3\text{-}CPh)$ is that the bridging benzylidyne ligand lies *over* the triosmium plane rather than external to it. This is analogous to the situation observed for $(\mu\text{-}H)Os_3$-$(CO)_{10}(\mu_3\text{-}CH)$[3] and $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CCH_2CHMe_2)$,[4] but

(9) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(10) Esd's of average values are shown in *square* brackets.

Table IV. Interatomic Angles (deg) for $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$

(A) Angles within Metal Cluster

Os(2)-Os(1)-Os(2')	60.35 (1)	Os(1)-Os(2')-Os(2)	59.82 (1)

(B) Angles Involving Bridging Atoms

Os(2)-C(1)-Os(2')	89.26 (35)	Os(2)-H(B)-Os(2')	103.7 (31)
Os(2')-Os(2)-C(1)	45.37 (25)	Os(2')-Os(2)-H(B)	38.2 (20)
Os(1)-C(1)-Os(2)	74.94 (28)		

(C) OC-Os-CO Angles

C(11)-Os(1)-C(11')	108.06 (35)	C(21)-Os(2)-C(22)	94.87 (37)
C(11)-Os(1)-C(12)	89.69 (36)	C(21)-Os(2)-C(23)	94.00 (38)
C(11)-Os(1)-C(13)	89.11 (37)	C(22)-Os(2)-C(23)	94.23 (39)
C(12)-Os(1)-C(13)	177.94 (38)		

(D) Os-C-O Angles

Os(1)-C(11)-O(11)	177.6 (8)	Os(2)-C(21)-O(21)	177.5 (8)
		Os(2)-C(22)-O(22)	178.1 (8)
Os(1)-C(12)-O(12)	175.8 (8)	Os(2)-C(23)-O(23)	176.3 (9)
Os(1)-C(13)-O(13)	174.7 (9)		

(E) Other Angles about the Osmium Atoms

Os(2)-Os(1)-C(11)	154.3 (3)	Os(1)-Os(2)-C(21)	101.7 (3)
Os(2)-Os(1)-C(11')	95.0 (3)	Os(1)-Os(2)-C(22)	161.0 (3)
Os(2)-Os(1)-C(12)	79.1 (3)	Os(1)-Os(2)-C(23)	93.8 (3)
Os(2)-Os(1)-C(13)	102.7 (3)	Os(2')-Os(2)-C(21)	114.2 (3)
C(1)-Os(1)-C(11)	123.5 (3)	Os(2')-Os(2)-C(22)	104.9 (3)
		Os(2')-Os(2)-C(23)	143.8 (3)
C(1)-Os(1)-C(12)	110.6 (3)	C(1)-Os(2)-C(21)	157.3 (3)
C(1)-Os(1)-C(13)	71.4 (3)	C(1)-Os(2)-C(22)	100.1 (4)
C(1)-Os(2)-H(B)	83.4 (20)	C(1)-Os(2)-C(23)	101.7 (4)

(F) Angles within CPh System

Os(1)-C(1)-C(2)	123.7 (6)	C(3')-C(2)-C(3)	115.8 (8)
Os(2)-C(1)-C(2)	134.1 (7)	C(2)-C(3)-C(4)	123.0 (10)
Os(2')-C(1)-C(2)	134.1 (7)	C(3)-C(4)-C(5)	118.5 (10)
C(1)-C(2)-C(3)	122.0 (8)	C(4)-C(5)-C(4')	121.1 (11)

(G) Angles Involving Os(mdpt)

Os(mdpt)-Os(1)-C(11)	124.89	Os(mdpt)-Os(1)-C(1)	33.25
		Os(mdpt)-C(1)-Os(1)	68.58
Os(mdpt)-Os(1)-C(12)	77.38	C(1)-Os(mdpt)-Os(1)	78.17
Os(mdpt)-Os(1)-C(13)	104.68	C(1)-Os(mdpt)-H(B)	173.25

in contradistinction to that observed for all other $(\mu\text{-H})$-$\text{Os}_3(\text{CO})_{10}(\mu\text{-L})$ (L = μ-bridging ligand) complexes.[11]

There are various measures of the unusual location for the benzylidyne ligand: (1) The Os(1)···C(1) distances of 2.586 (10) Å (0.551 Å longer than the Os(2)-C(1) and Os(2')-C(1) distances of 2.035 (8) Å) is indicative of some direct interaction. Although the formal bond order is small, it is sufficient to characterize this bonding mode as "semi-triply bridging".[12] The analogous Os···C distance is shorter in $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH})$ (2.353 (10) Å)[3] but longer in $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CCH}_2\text{CHMe}_2)$ (2.640 (26) Å).[4] The latter effect may be due to a more pronounced steric interaction with the Os(CO)₄ unit for a conical sp³-hybridized substituent attached to the bridging carbon than for a relatively flat sp²-hybridized group (vide infra).

(2) The angle between the Os(2)-C(1)-Os(2') system and the Os(2)-Os(1)-Os(2') ring is acute (78.17°). [Tracking the order of Os···C distances, the analogous acute dihedral angles are 69.7° and 82.1° for $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CH})$[3] and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CCH}_2\text{CHMe}_2)$,[4] respectively.] In contrast to this, the angle between the Os(2)-H(B)-Os(2') and

Os(2)-Os(1)-Os(2') systems is obtuse (108.58°). The bridging Os(2)-C(1)-Os(2') and Os(2)-H(B)-Os(2') systems are thus close to being coplanar. (The dihedral angle is 173.25°.)

(3) The semi-triply bridging mode of binding the benzylidyne ligand to the triosmium framework causes severe repulsions between the phenyl group and the Os(CO)₄ system centered on Os(1). Thus, the phenyl group is not coplanar with the Os(2)-C(1)-Os(2') system but is bent away from the triosmium plane such that the dihedral angle between Os(2)-C(1)-Os(2') and phenyl rings is 163.25°. [Note that this angle is a "flap" or "splay" angle. The molecular mirror plane through Os(1)···C(1)-C(2)···C(5) prevents there being any torsional component about the C(1)-C(2) axis.] The axial carbonyl ligand C(13)-O(13) is repulsed by the phenyl group in such a way that the entire Os(CO)₄ group is rotated about its Os(1) center. This causes the Os(mdpt)···Os(1)-C(13) angle of 104.68° to be some 27.3° larger than that involving the other axial ligand (i.e., Os(mdpt)···Os(1)-C(12) = 77.38°). The two axial ligands are still close to colinear, with ∠C(12)-Os-(1)-C(13) = 177.94 (38)°. This phenyl ↔ Os(CO)₄ repulsion also causes the equatorial ligands on Os(1) to drop below the triosmium plane (deviations from planarity are −0.258 (8) Å for C(11) and C(11') and −0.456 (7) Å for O(11) and O(11')).

The principal osmium–benzylidyne bonds (Os(2)-C(1) = Os(2')-C(1) = 2.035 (8) Å) are similar in length to the principal osmium–methylidyne bonds in $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}$-$(\mu_3\text{-CH})$ (2.003 (11) and 2.011 (12) Å)[3] and osmium–al-

(11) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2905. (See, also, all references associated with Table VII of this paper.)

(12) In considerations of "semibridging" carbonyl groups, it is customary to calculate the α value, defined as $(d_2 - d_1)/d_1$ (where d_1 and d_2 are the shorter and longer M-CO distances). Values with $0.1 < \alpha < 0.6$ are considered "semibridging". Comparison of Os(2)-C(1) and Os(1)··· C(1) distances in the present molecule yields an equivalent α value of 0.271 (i.e., (2.586 − 2.035)/2.035).

(13) Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096. See footnote 13 on p 2098.
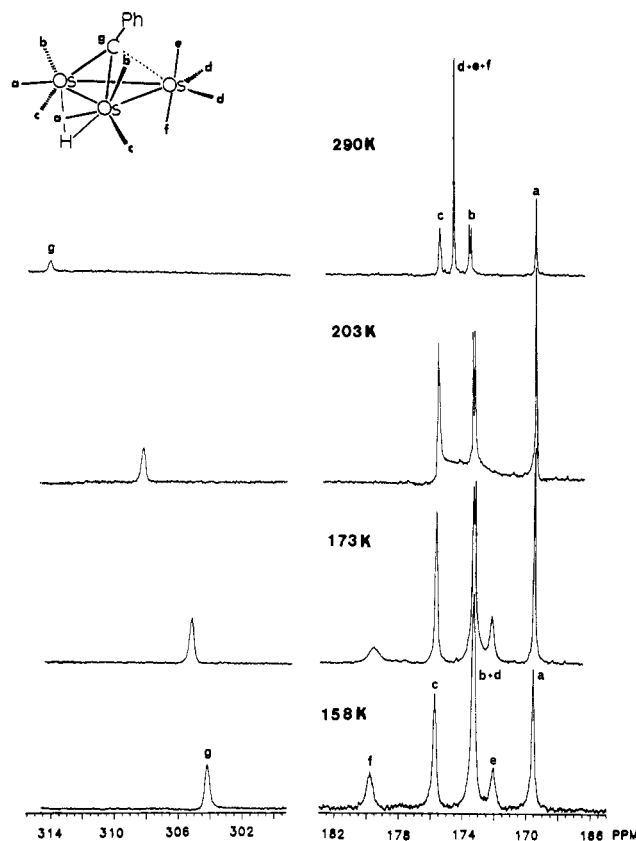
Figure 2. Variable-temperature 90-MHz ^{13}C NMR spectra for $(\mu\text{-}H)Os_3(*CO)_{10}(\mu_3\text{-}*CPh)$.

kylidyne bonds in $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CCH_2CHMe_2)$ 2.020 (24) and 1.966 (22) Å.[4] These values indicate some multiple-bond character throughout the Os(2)–C(1)–Os(2') systems. For comparison one may cite the established saturated Os–C distances in a variety of species, viz., 2.155 [7] Å in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH=NEt_2)$,[14] 2.161 [18] Å in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$,[15] and 2.174 [20] Å in $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)$.[16] In keeping with these data, we note that principal Os–C–Os angles in the *al-kylidyne* complexes are close to right angles (92.90 (44)° in $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$,[3] 92.2 (8)° in $(\mu\text{-}H)Os_3(CO)_{10}\text{-}(\mu_3\text{-}CCH_2CHMe_2)$,[4] and Os(2)–C(1)–Os(2') = 89.26 (35)° in the present $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh))$, whereas the Os–C–Os angles in *alkylidene* complexes are distinctly acute (80.6 (9)° in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH=NEt_2)$,[14] 80.8 (3)° in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$,[15] and 79.0 (5)° in $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)^{16})$.
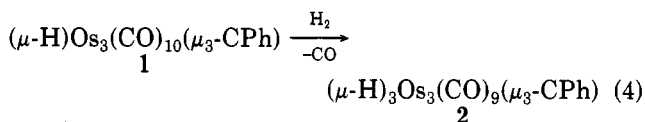
Stereodynamics in Solution. Variable-temperature ^{13}C NMR spectra for $(\mu\text{-}H)Os_3(*CO)_{10}(\mu_3\text{-}*CPh)$ (each enriched site ca. 50% ^{13}C) are shown in Figure 2. The spectrum at 17 °C shows the benzylidyne carbon at δ 314.2 and the carbonyl carbons in a 2:4:2:2 pattern in the usual range of δ 170–178. The 4 C signal is revealed as arising from the Os(*CO)$_4$ unit, since it collapses at –70 °C and splits into a 1:2:1 pattern below –100 °C. By comparing the spectra observed at –115 and at –70 °C, the signals can be assigned on the basis of the following arguments. (i) The 1 C resonance at δ 179.7 is in a normal position for

a carbonyl perpendicular to the the Os$_3$ plane ("axial" for Os$_3$(CO)$_{12}$), whereas the other 1 C signal is displaced significantly to higher field (δ 172.0). This effect is attributed to the distortions induced in the Os(CO)$_4$ group, and, presumably, the signal most affected is that due to the carbonyl on the same side of the triangle as the benzylidyne group. The same effect is seen in the limiting low-temperature spectrum for $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$,[3] except that the unique 1 C signal appears even further upfield. Even when site exchange no longer contributes, the line widths of the signals due to the pseudoaxial carbonyls (e, f) are broader than the other signals. This is attributed to relatively large (but unresolved) trans ^{13}C–^{13}C coupling, which in other cases has been measured as ca. 35 Hz.[3] (ii) The signal due to the two "equatorial" carbonyls (d) on the Os(CO)$_4$ unit is superimposed on another 2 C signal at δ 173.2 in the limiting spectrum at –115 °C. The average position calculated from the low-temperature data (δ 174.6) agrees well with that observed at ambient conditions (δ 175.0). (iii) The 2 C signal that is buried at –115 °C appears as a doublet ($J(^{13}C\text{-}^1H)$ = 11 Hz) at higher temperatures and is assigned to the carbonyls (b) trans to the bridging hydride. (iv) The 2 C signal at δ 176 is significantly broader than the 2 C signal at δ 170 at all temperatures. The broadening is apparently due to coupling to the benzylidyne carbon, which is enriched to the same level. Therefore, the former signal is assigned to the two carbonyls (c) trans to the benzylidyne carbon, and the latter signal is assigned to the remaining two carbonyls (a), which are trans to the Os–Os bonds.

The distinct carbonyls in the Os(CO)$_4$ unit of $(\mu\text{-}H)\text{-}Os_3(CO)_{10}(\mu\text{-}COMe)$ are observed to equilibrate by two separate threefold rotations involving the two pseudoequatorial carbonyls with one or the other pseudoaxial carbonyl.[17] Similar processes are probably operating for $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh)$, since one pseudoaxial carbonyl signal (at δ 180) broadens slightly faster than the other (at δ 172); however, the rate difference is small. From the coalescence point at ca. –70 °C, an approximate value of $\Delta G^{\ddagger}$ = 8.8 kcal/mole for the axial–equatorial carbonyl exchange can be estimated. This value is considerably less than the value ($\Delta G^{\ddagger}$ = 17 kcal/mol) determined for $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)^{17}$ but comparable with the value ($\Delta G^{\ddagger}$ = 9 kcal/mol) found for $(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CH)$.[3] Both of the lower values involve osmium centers which are pseudo-seven-coordinate due to interaction with the carbyne carbon.

The chemical shift of the carbyne carbon is quite temperature dependent, changing from δ 314.2 at 17 °C to δ 304.2 at –115 °C. A similar effect was noted for $(\mu\text{-}H)\text{-}Os_3(CO)_{10}(\mu\text{-}CCH_2CHMe_2)^4$ and was attributed to unspecified conformational equilibria in solution.

Reactivity. Hydrogenation of complex 1, with loss of a carbonyl ligand, generates the trihydrido compound $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CPh)$ (2) (eq 4). This is analogous to the

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu_3\text{-}CPh) \xrightarrow[-CO]{H_2}$$
$$\underset{1}{}$$

$$(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}CPh) \quad (4)$$
$$\underset{2}{}$$

formation of $(\mu\text{-}H)_3M_3(CO)_9(\mu_3\text{-}COMe)$ from $(\mu\text{-}H)M_3\text{-}(CO)_{10}(\mu\text{-}COMe)$ (M = Fe, Ru, Os) studied by Keister[5,18] and appears to occur with comparable facility for M = Os in both cases. Complex 2 forms air-stable pale yellow crystals with the benzylidyne ligand apparently bridging

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(15) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141. (b) Churchill, M. R.; DeBoer, B. G.; Shapley, J. R.; Keister, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 2357.

(16) (a) Churchill, M. R.; Wasserman, H. J. *J. Organomet. Chem.* **1983**, *248*, 365. (b) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975.
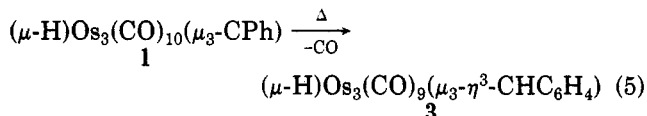
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(18) Bavaro, L. M.; Montangero, P.; Keister, J. B. *J. Am. Chem. Soc.* **1983**, *105*, 4977.

Scheme I
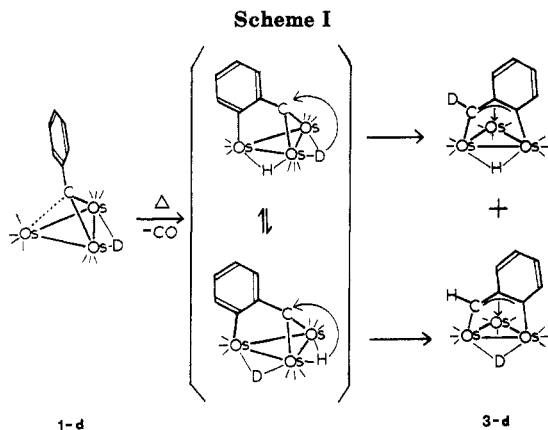
the three metal centers symmetrically. The ^{1}H NMR and IR spectra of **2** agree with those recorded by Strickland[6a] and recently reported by Shore and co-workers.[19]

Complex **1** is thermally stable in either solution or solid state to 120 °C. At higher temperatures it loses a carbonyl ligand and forms an ortho-metalated product $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-CHC}_6H_4)$ (**3**) in which a hydrogen atom has been lost from the phenyl ring and one added to the carbyne carbon (eq 5). Solid-state pyrolysis results in

$$(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-CPh}) \xrightarrow[-CO]{\Delta}$$
$$\mathbf{1}$$

$$(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-CHC}_6H_4) \quad (5)$$
$$\mathbf{3}$$

clean conversion; however, in solution (xylene, 135 °C) the product mixture is complex and only a low yield of **3** (<30%) is obtained. The IR and ^{1}H NMR spectra of **3** are in close agreement with those of $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-}CPhC_6H_4)$,[20] $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-CMeCHCH})$[21] $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-CPhCPhCH})$,[22] and $(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^3\text{-CHCHCOMe})$,[23] each of which has a face-bonded dimetallaallyl ligand. One minor difference is that the chemical shift of the allyl proton in **3** (δ 10.08) is downfield of the shifts reported for similar compounds (δ 8.7–7.4). We attribute this to the fact that in **3** this proton is con-

strained to be in the plane of the adjacent metalated phenyl ring which results in a downfield shift due to the ring current effect.

A deuterium-labeling experiment has been used to trace the origin of the allyl hydrogen in **3**. Pyrolysis of $(\mu\text{-D})$-$Os_3(CO)_{10}(\mu_3\text{-CPh})$ (**1**-*d*) yields compound **3**-*d*, in which the deuterium label is found in either the allyl or hydride position with equal probability. Since the ^{1}H NMR integrals of each signal are equal, there appears to be no direct equilibration between these two sites (for which a significant equilibrium isotope effect would be expected[24]). The distribution of label in **3**-*d* therefore occurs by a kinetically controlled process. The thermal reactivity of **1** is determined by the rate of CO loss to generate a coordinatively unsaturated species, which then can undergo oxidative addition either intermolecularly with H_2 to give **2** (see discussion in ref 18) or intramolecularly with a phenyl CH bond to give an ortho-metalated intermediate (see Scheme I). The two bridging hydrides in this intermediate apparently scramble before one H atom migrates to the benzylidyne carbon and forms **3**.

Attempts at reversing eq 5 under mild conditions (1 atm of CO, 70 °C, cyclohexane) produced no reaction. Under harsher conditions (3 atm of CO, 110 °C, toluene, 65 h), **3** was converted predominantly into $Os_3(CO)_{12}$. Hydrogenation of **3** (1 atm of H_2, 175 °C, decane) gave **2** in moderate yield and considerable decomposition. No reaction occurred below 130 °C. These reactions show that the ortho metalation can be reversed but only under forcing conditions. Keister and co-workers[25] have recently described a related H_2-induced dimetalloallyl-to-alkylidyne conversion for a triruthenium system.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table II-S), intramolcular planes (Table V-S), and observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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