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Trinuclear Osmium Clusters as Models for Intermediates in Carbon Monoxide Reduction Chemistry. 1. Stepwise Reduction of CO to a μ-CH$_2$ Ligand on an Os$_3$ Cluster Face

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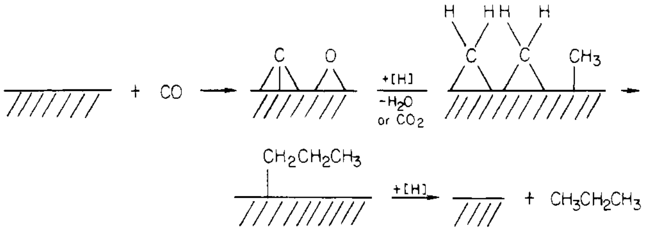
Abstract: Treatment of $Os_3(CO)_{12}$ in tetrahydrofuran (THF) with K[BH(O-*i*-Pr)$_3$] at 0 °C gives an unstable formyl complex $K[Os_3(CO)_{11}(CHO)]$ (**1**). Acidification of THF solutions of **1** with aqueous 20% H_3PO_4 yields the new cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$ which has been spectroscopically characterized. Attempted alkylation of **1** with $[(CH_3)_3O]BF_4$ also gave $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Methane is produced when $Os_3(CO)_{11}(\mu\text{-}CH_2)$ is heated under an H_2 atmosphere, but when the mixture is heated in the absence of H_2, CO loss occurs to yield $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$, which has been spectroscopically characterized. The mechanism of the $[Os_3(CO)_{11}(CHO)]^-$ to $Os_3(CO)_{11}(\mu\text{-}CH_2)$ transformation is discussed as well as the possible relevance of these results to CO reduction on metal surfaces.

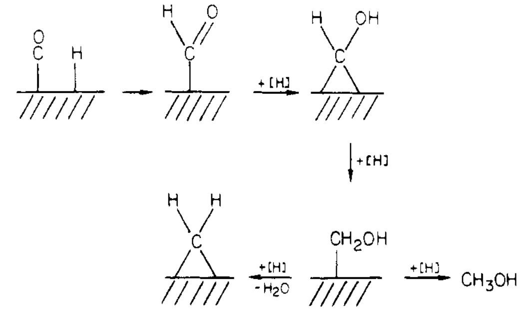
Numerous mechanistic schemes have been proposed for the metal-surface-catalyzed reduction of carbon monoxide.[1-6] Several of these invoke migration of hydrogen to CO to give formyl intermediates which are subsequently transformed into reduced products.[3,4] However, more recent work has tended to discount the intermediacy of formyls, and the CO-dissociative route[1,6] now appears most popular. According to this mechanism (Scheme I) CO is assumed to dissociate upon adsorption to give surface-bound carbon species which are subsequently hydrogenated to produce surface methylene and methyl fragments. These can then oligomerize and add hydrogen to give hydrocarbon products. Although this mechanism has been called into question by some authors,[7] it is supported by detailed surface-science measurements and pulse-reactor studies over the metals Co, Ru, and Ni.[6,8,9] Also taken as support for this mechanism are experiments which apparently generate surface-bound methylenes from decomposition of CH_2N_2, and these react with H_2 to give product distributions similar to Fischer–Tropsch distributions over the same metals.[10] Earlier experiments with CH_2CO led Blyholder and Emmett[11] to conclude that ketene dissociates to yield surface methylenes which initiate CO-propagated chain growth during Fischer–Tropsch catalysis. It is generally assumed that such surface methylenes derive from hydrogenation of surface carbon generated via CO dissociation.

However, we wish to point out that surface methylenes could also arise from formyl intermediates as outlined in Scheme II. Addition of hydrogen to the oxygen atom of a surface formyl would produce a hydroxymethylene which can be further hydrogenated to give a hydroxymethyl species. Cleavage of the carbon–oxygen bond of this intermediate by hydrogen would then yield a surface-bound methylene. A mechanism of this type could explain the production of hydrocarbons over metals such as Pd and Pt for which experimental data do not support a CO-dissociative mechanism.[9,12] The mechanism of Scheme II could also explain the production of methanol observed over Pd, Pt, Ir, and Rh[13] since addition of hydrogen across the surface–carbon bond of the hydroxymethyl group gives this product directly.

Scheme I



Scheme II



We have attempted to model these various transformations by the use of cluster compounds. We have previously communicated results which show the organometallic feasibility of the formation of methylene ligands via reactions which model Scheme II[14] and also the methylene + CO reaction to give a cluster-bound ketene ligand.[15] Herein we report full details of the first of these studies in which a CO ligand of $Os_3(CO)_{12}$ is transformed into a μ-CH$_2$ ligand in $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (eq 1).

Experimental Section

General. $Os_3(CO)_{12}$[16] and $Os_3(CO)_{12-x}(PR_3)_x$[17] where $x = 1\text{-}3$ and $PR_3 = PMe_2Ph$ and $P(OPh)_3$ were prepared according to literature procedures. K[BH(O-*i*-Pr)$_3$] and Li[BDEt$_3$] (Aldrich Chemical Corp.) and PMe$_2$Ph and P(OPh)$_3$ (Strem Chemical Co.) were purchased and

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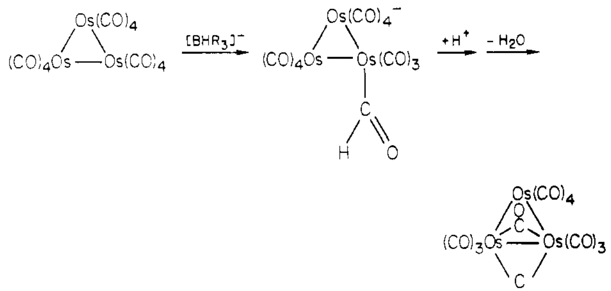

(1)

used as received. Solvents were dried by standard methods and all reactions were conducted under a prepurified N_2 atmosphere with use of standard Schlenk techniques.[18] IR spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer with use of 0.5-mm NaCl solution IR cells. These were sealed with Luer-lock fittings and purged with N_2 to record spectra of air-sensitive solutions. Electron impact (EI) mass spectra were obtained with an AEI-MS9 mass spectrometer with a source voltage of 70 eV and probe temperature in the 100–200 °C range. NMR spectra were recorded on Bruker WP 200, Bruker WM 360, an JEOL PFT-100 NMR spectrometers, and $Cr(acac)_3$ (1.0 mol %) was added to ^{13}C NMR samples as a shiftless relaxation agent.[19] Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY.

Reaction of $Os_3(CO)_{12}$ with K[BH(O-*i*-Pr)$_3$]. A tetrahydrofuran (THF) solution of K[BH(O-*i*-Pr)$_3$] (0.260 mL of a 1 M solution) was added via syringe to a THF suspension of $Os_3(CO)_{12}$ (0.2032 g, 0.224 mmol) maintained at 0 °C by an ice–water bath. The pale yellow suspension turned light orange upon addition of K[BH(O-*i*-Pr)$_3$], and this color deepened as the $Os_3(CO)_{12}$ dissolved over the course of 0.75–1.0 h. At this point the clear orange solution showed IR bands at 2032 m, 2018 m, 1998 vs, 1960m, 1610 vw, and 1577 cm^{-1} and a formyl resonance at δ 16.0 s in its ^1H NMR spectrum, indicating the formation of K[$Os_3(CO)_{11}(CHO)$]. Upon warm-up to 22 °C, this solution turned dark orange and the 1577-cm^{-1} formyl vibration decreased in intensity as new bands grew in at 2082 w, 1704 w, and 1660 m cm^{-1}. This transformation was complete in 3–5 h. Addition of [$(Ph_3P)_2N$]Cl in CH_2Cl_2 to this solution, followed by slow solvent concentration, gave a microcrystalline yellow precipitate of [$(Ph_3P)_2N$][$HOs_3(CO)_{11}$] (75.6% yield) identified by comparison of its IR spectrum (ν_{CO}, CH_2Cl_2: 2032 w, 2020 s, 1993 s, 1955 m, and 1675 w cm^{-1}) to published data.[20]

Preparation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Excess 20% H_3PO_4 (~10–20 mL) was added dropwise to a K[$Os_3(CO)_{11}(CHO)$] solution prepared exactly as described above when the 1577-cm^{-1} IR band was at its maximum intensity. The solution immediately turned dark red. The reaction mixture was extracted in air with 50-mL portions of CH_2Cl_2 until the extracts were colorless. These were combined, dried over $MgSO_4$, and filtered. The CH_2Cl_2 solvent was evaporated, and the resultant orange solid was dissolved in a minimum amount of hexane. Chromatography on SiO_2 with hexane eluant gave a faint yellow fraction of $Os_3(CO)_{12}$ followed by an orange fraction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Solvent evaporation gave deep red microcrystalline $Os_3(CO)_{11}(\mu\text{-}CH_2)$ in 37% yield (0.0731 g, 0.0744 mmol). Anal. Calcd for $C_{12}H_2O_{11}Os_3$: C, 15.92; H, 0.45. Found: C, 16.14; H, 0.23. IR (hexane) 2116 w, 2063, s, 2031 s, 2031 s, 2010 m, 1995 m, 1920 vw, 1869 vw cm^{-1}. *m/z*: 894 (M^+) + fragment ions corresponding to loss of 11 CO's and 2 H's. $^{13}C\{^1H\}$ (CD_2Cl_2): δ 193.4, 184.0, 180.9, 174.3, 173.9, 172.6, 171.9, 62.5.

In a separate experiment the [$Os_3(CO)_{11}(CHO)$]$^-$ solution was carefully filtered at 0 °C to remove unreacted $Os_3(CO)_{12}$. This solution was acidified with H_3PO_4 as above, and the organometallic products were extracted into CH_2Cl_2. The CH_2Cl_2 was evaporated and the resultant solid washed with several portions of hexane to extract all the $Os_3(CO)_{11}(\mu\text{-}CH_2)$. What remained was essentially pure $Os_3(CO)_{12}$ (38.0 mg, 41.9 mmol). Evaporation of solvent from the $Os_3(CO)_{11}(\mu\text{-}CH_2)$ solution gave 44.7 mg (50.1 mmol) of this product.

Acidification of [$Os_3(CO)_{11}CHO$]$^-$ with CF_3COOD. Treatment of $Os_3(CO)_{12}$ (0.1014 g, 0.112 mmol) in 30 mL of THF with a 1 M THF solution of K[BH(O-*i*-Pr)$_3$] (0.150 mL, 0.150 mmol) at 0 °C resulted in an intense orange solution of K[$Os_3(CO)_{11}CHO$] similar to that described above. After 45 min this reaction mixture was acidified dropwise with excess 20% CF_3CO_2D/D_2O (~20 mL). Following workup as described above, red microcrystalline $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was isolated in 23.5% yield (0.0236 g, 0.0264 mmol). The ^1H NMR and mass spectra of this sample were identical with those of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ prepared as above.

Acidification of [$Os_3(CO)_{11}CDO$]$^-$ with H_3PO_4. Treatment of $Os_3(CO)_{12}$ (0.2539 g, 280 mmol) in 30 mL of THF with a 1 M THF solution of Li[$BDEt_3$] (0.280 mL, 0.280 mmol) at 0 °C immediately gave an intense orange colored solution. After 10 min, this reaction mixture was acidified dropwise with excess 20% H_3PO_4/H_2O (~20 mL). Following workup as described above, microcrystalline $Os_3(CO)_{11}(\mu\text{-}CD_2)$ was isolated in 17.4% yield (0.0437 g, 0.0488 mmol). *m/e*: 896 (M^+) + fragment ions corresponding to loss of 11 CO's and two D's. ^1H NMR (acetone-d_6): no observable signals. ^2H NMR (acetone): δ 7.7 (s, br), 6.6 (s, br).

Reaction of [$Os_3(CO)_{11}(CHO)$]$^-$ with [$(CH_3)_3O$]BF_4. A THF (10 mL) solution of [$Os_3(CO)_{11}(CHO)$]$^-$ was prepared as described above from 0.152 g of $Os_3(CO)_{12}$. To this was added a suspension of [$(CH_3)_3O$]BF_4 in THF (30 mL) at 0 °C. Over the course of 0.5 h, the solution changed color from yellow-orange to dark red. This solution was extracted with CH_2Cl_2, the CH_2Cl_2 evaporated, and the red-orange residue dissolved in acetone-d_6. The ^1H NMR spectrum of this solution showed only the characteristic doublets of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ at δ 7.75 and 6.47.

Reaction of $Os(CO)_{12-x}(PMe_2Ph)_x$ (x = 1–3) with K[BH(O-*i*-Pr)$_3$]. Treatment of $Os_3(CO)_{11}PMe_2Ph$ (0.0641 g, 0.0545 mmol) in THF with K[BH(O-*i*-Pr)$_3$] (0.075 mL, 0.075 mmol) at 0 °C gave an orange, air-sensitive solution. The IR spectrum of this solution showed bands at 2105 vw, 2067 w, 2048 m, 2035 m, 2000 s, 1970 vs, 1935 s, and 1570 w cm^{-1} with the latter band suggesting the formation of [$Os_3(CO)_{10}(PMe_2Ph)(CHO)$]$^-$. Warm-up of this solution to 22 °C resulted in disappearance of the 1570-cm^{-1} band, but the products were not characterized. $Os_3(CO)_{10}(PMe_2Ph)_2$ and $Os_3(CO)_9(PMe_2Ph)_3$ did not react with K[BH(O-*i*-Pr)$_3$] under identical conditions. Excess deoxygenated 20% H_3PO_4 was added dropwise to a solution of the presumed [$Os_3(CO)_{10}(PMe_2Ph)(CHO)$]$^-$ when this species' 1570-cm^{-1} band was at its maximum intensity (~45 min at 0 °C after addition of K[BH(O-*i*-Pr)$_3$]). The solution immediately turned dark red and then slowly bright yellow. The solution was extracted with 50-mL aliquots of CH_2Cl_2 until the aliquots were colorless. These were combined, dried over anhydrous $MgSO_4$, and filtered. Evaporation of the solvent gave a yellow powder identified as $Os_3(CO)_{11}PMe_2Ph$ by its IR[17] and mass spectra. IR (hexane): 2108 w, 2054 s, 2034 s, 2021 s, 2021 vw, 2002 m, 1990 m, 1973 m, and 1954 w cm^{-1}. *m/z*: 1018 (M^+) + fragment ions corresponding to loss of 11 CO's.

Reaction of $Os_3(CO)_{11}P(OPh)_3$ and $Os_3(CO)_{10}(P(OPh)_3)_2$ with K[BH(O-*i*-Pr)$_3$]. Treatment of $Os_3(CO)_{11}P(OPh)_3$ (0.2630 g, 0.221 mmol) in THF at 0 °C with K[BH(O-*i*-Pr)$_3$] (0.260 mL, 0.26 mmol) gave an orange, air-sensitive solution which showed carbonyl bands in its IR spectrum at 2112 w, 2076 w, 2061 m, 2042 m, 2000 s, 1970 vw, 1935 s, and 1571 w cm^{-1}. The IR band at 1571 cm^{-1} suggested the presence of [$Os_3(CO)_{10}(P(OPh)_3)(CHO)$]$^-$. Warm-up of this solution to room temperature resulted in decomposition of the formyl, but the decomposition products were not characterized. No reaction of $Os_3(CO)_{10}(P(OPh)_3)_2$ with K[BH(O-*i*-Pr)$_3$] occurred under identical conditions. Excess deoxygenated 20% H_3PO_4 was added to a solution of the presumed [$Os_3(CO)_{10}(P(OPh)_3)(CHO)$]$^-$ complex when the 1571-cm^{-1} IR band was at its maximum intensity (~45 min after addition of K[BH(O-*i*-Pr)$_3$]). The solution immediately turned dark red. Extraction of the reaction mixture as described above with CH_2Cl_2 gave an orange solution which was dried over anhydrous $MgSO_4$ and filtered and the solvent evaporated to give a yellow-orange solid. The solid was dissolved in a minimum amount of 20% CH_2Cl_2:80% hexane and chromatographed on SiO_2 with use of 20% CH_2Cl_2:80% hexane eluant. This gave a yellow band of $Os_3(CO)_{11}(P(OPh)_3)$ overlapping with an orange band of $Os(CO)_{10}(P(OPh)_3)(\mu\text{-}CH_2)$, tentatively characterized by its ^1H NMR and mass spectra. The two bands did not separate well, and the isolated $Os_3(CO)_{11}P(OPh)_3$ and $Os_3(CO)_{10}(P(OPh)_3)(\mu\text{-}CH_2)$ could not be obtained in pure form. Removal of the solvent from the largely $Os_3(CO)_{10}(P(OPh)_3)(\mu\text{-}CH_2)$ fraction gave a red solid with the following spectral characteristics: *m/z* 1148 ($M - CO^+$) + fragment ions corresponding to loss of 9 CO's and 2 H's. ^1H NMR (acetone-d_6): δ 7.4 (m), 6.51 (dd, $J_{^1H-^{31}P}$ = 16.5 Hz, $J_{^1H-^1H}$ = 7.3 Hz), 6.39 (d, $J_{^1H-^1H}$ = 6.7 Hz).

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with H_2. $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (7.3 mg) in 5 mL of benzene was placed in a 25-mL Carius tube under 1 atm of H_2 and heated to 70–80 °C for 2 days. The gases above the sample were analyzed by connecting the Carius tube to the direct inlet port of a mass spectrometer. The mass spectrum showed only the presence of CH_4 and H_2. Thermolysis of $Os_3(CO)_{11}(\mu\text{-}CD_2)$ under an H_2 atmosphere under similar conditions resulted in the formation of only CD_2H_2. Thermolyses of both $Os_3(CO)_{11}(\mu\text{-}CD_2)$ and $Os_3(CO)_{11}(\mu\text{-}CH_2)$ under an N_2 atmo-

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sphere gave no methane formation. In a quantitative experiment, a benzene solution (5 mL) of $Os_3(CO)_{11}(\mu\text{-}CD_2)$ (prepared from $Os_3(CO)_{12}$ and $Li[BDEt_3]$; 0.0237 g, 0.0265 mmol) was placed in a 25-mL Carius tube under 1 atm of H_2 and heated at 70–80 °C for 1 week. All noncondensable gases above the reactant solution were collected with a Toepler pump. Benzene vapor was separated from these gases by distillation through an acetone–dry ice slush bath. GC analysis showed CH_2D_2 to account for ~95% of the residual gas and Toepler pump analysis showed that 0.0053 mmol of CH_2D_2 was formed, corresponding to a yield of 20.1%. Chromatography and mass spectral analysis of the organometallic residues from these reactions showed the formation of small amounts of $Os_3(CO)_{12}$ (~10%) and a trace of $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$.[21] Most of the residue remained at the top of the column and would not elute.

Thermolysis of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ to yield $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$. An orange toluene (20 mL) solution of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (0.0644 g, 0.0721 mmol) was placed in a 25-mL Carius tube under reduced N_2 pressure and heated at 75 °C for 3 days. The solution changed color to light yellow and deposited a yellow precipitate of $Os_3(CO)_{12}$. The $Os_3(CO)_{12}$ was removed by filtration, and the filtrate was evaporated to give $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$[21] as a pale yellow solid in 72% yield (0.045 g, 0.052 mmol). IR (hexane): ν_{CO} 2121 w, 2086 s, 2064 vs, 2055 vs, 2034 w, 2006 m, 1994 m, 1984 m cm^{-1}. *m/z* 866 (M^+) + fragment ions corresponding to loss of 10 CO's and 2 H's. ^1H NMR (benzene-d_6, 22 °C): δ −20.1 s. ^1H NMR monitoring showed the $Os_3(CO)_{11}(\mu\text{-}CH_2)$ to $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ conversion to be complete within 1–2 h without buildup of detectable intermediates.

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with PPh_3 and PMe_2Ph. $Os_3(CO)_{11}(\mu\text{-}CH_2)$ rapidly reacts with PPh_3 and PMe_2Ph in THF solution at 22 °C to give an orange to yellow color change. Chromatography of the PPh_3 reaction mixture on SiO_2 using 30:70 CH_2Cl_2/hexane as eluant gave four fractions which were analyzed by mass spectrometry and IR. In the order of elution they are a red band containing a small amount of unreacted $Os_3(CO)_{11}(\mu\text{-}CH_2)$, a pale orange band containing a trace of $Os_3(CO)_{12}$ and another unidentified compound, an orange band containing $Os_3(CO)_{12}$, $Os_3(CO)_{11}(PPh_3)$ (*m/z* 1142 (M^+)), and a compound identified as $Os_3(CO)_{10}(\mu\text{-}CH_2)(PPh_3)$ (*m/z* 1100 (M^+ − CO) + fragment ions corresponding to loss of 9 CO's), and a brilliant orange-yellow band of $Os_3(CO)_{10}(PPh_3)_2$. The mass spectrum of the reaction mixture from $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and excess PMe_2Ph showed $Os_3(CO)_{10}(PMePh_2)_2$ as the major product with a trace of $Os_3(CO)_{11}(PMe_2Ph)$.

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with C_2H_4. A saturated $CDCl_3$ solution (2 mL) of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was placed in a 5-mm NMR tube inside a Parr Model 4564 pressure reactor. The reactor was sealed and pressurized to 1200 psi with C_2H_4 for 3 days at 22 °C. Upon depressurization, the ^1H NMR spectrum showed only $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and dissolved C_2H_4 (δ 5.28 s) to be present.

Results

Reaction of $Os_3(CO)_{12}$ with $K[BH(O\text{-}i\text{-}Pr)_3]$. A suspension of $Os_3(CO)_{12}$ in THF smoothly reacts with $K[BH(O\text{-}i\text{-}Pr)_3]$ or $Li[BHEt_3]$ at 0 °C to produce the anionic formyl complex $[Os_3(CO)_{11}(CHO)]^-$ (eq 2). The formyl complex is not sufficiently stable to isolate as it slowly decomposes in solution to give mainly $[HOs_3(CO)_{11}]^-$ (eq 3). This known[20] cluster can be isolated as its $[(Ph_3P)_2N]^+$ salt in 75% yield following metathesis of such solutions with $[(Ph_3P)_2N]Cl$.

$$Os_3(CO)_{12} + [BHR_3]^- \xrightarrow[\text{THF}]{0\text{ °C, 1 h}} [Os_3(CO)_{11}(CHO)]^- + BR_3 \quad (2)$$

$$[Os_3(CO)_{11}(CHO)]^- \xrightarrow[\text{THF}]{22\text{ °C, 2–5 h}} CO + [HOs_3(CO)_{11}]^- \quad (3)$$

The formyl cluster $[Os_3(CO)_{11}(CHO)]^-$ was spectroscopically characterized. When prepared from $K[BH(O\text{-}i\text{-}Pr)_3]$, it shows a characteristic ^1H NMR resonance at δ 16.0 s and a ν_{CO} stretch at 1577 cm^{-1}, indicative of a formyl ligand. The ν_{CO} stretch shifts to 1557 cm^{-1} when the cluster was prepared from $Li[BHEt_3]$, indicating association of either the cation or the BR_3 Lewis acid formed in the course of the reaction with the formyl oxygen. Addition of a 6-fold excess of LiCl to a THF solution of $K[Os_3(CO)_{11}(CHO)]$, generated from $K[HB(O\text{-}i\text{-}Pr)_3]$, resulted in a shift of the formyl vibration from 1577 to 1557 cm^{-1}, implying that association of the cation with the formyl ligand is more important than association of BR_3. A similar conclusion was reached by Winter et al. for the formyl complex $[Fe(CO)_4(CHO)]^-$.[22] The $[Os_3(CO)_{11}(CHO)]^-$ cluster has also been observed by Pruett et al.,[23] and their spectroscopic data and observations of its thermal instability parallel those described here.

Protonation of $[Os_3(CO)_{11}(CHO)]^-$ To Yield $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Addition of excess 20% H_3PO_4 to solutions of $[Os_3(CO)_{11}(CHO)]^-$ immediately induces an orange to red color change. Workup of such protonated solutions yields $Os_3(CO)_{11}(\mu\text{-}CH_2)$ (eq 4). The

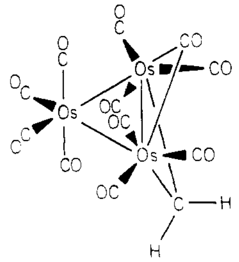
$$[Os_3(CO)_{11}(CHO)]^- + H^+ \rightarrow \rightarrow Os_3(CO)_{11}(\mu\text{-}CH_2) \quad (4)$$

yields of this product are markedly dependent upon the reaction conditions (see below). The most reliable procedure involves monitoring the IR spectrum of a solution following reaction of $Os_3(CO)_{12}$ with $[BHR_3]^-$ and adding the acid when the ν_{CO} stretch of the formyl ligand first begins to lose intensity. The yield also appears to be a sensitive function of the manner of acid addition; rapid addition of acid gives lower yields than when the acid is added in a dropwise fashion. In our hands $Os_3(CO)_{11}(\mu\text{-}CH_2)$ results in comparable yield if CF_3CO_2H is used as acid rather than H_3PO_4, although $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was not reported by Pruett et al.[23] to be a product of their reaction of $[Os_3(CO)_{11}(CHO)]^-$ with CF_3CO_2H. Since our original communication of the synthesis of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ by reaction 4, this compound has been independently synthesized by three other research groups. Both Shapley et al.[24] and Johnson, Lewis et al.[25] reported its preparation by the addition of CH_2N_2 to $Os_3(CO)_{11}(CH_3CN)$ (eq 5), and Deeming et al.[26] observed this compound to result from the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with ketene (eq 6). Its

$$Os_3(CO)_{11}(CH_3CN) + CH_2N_2 \rightarrow Os_3(CO)_{11}(\mu\text{-}CH_2) + N_2 + CH_3CN \quad (5)$$

$$Os_3(CO)_{10}(CH_3CN)_2 + CH_2CO \rightarrow Os_3(CO)_{11}(\mu\text{-}CH_2) + 2CH_3CN \quad (6)$$

characterization has thus been rather extensive, including a partial X-ray diffraction study by Churchill et al.[27] Crystals of the complex were severely disordered, but the structure indicated by the diffraction data was that which we initially deduced from its spectral properties, drawn below for illustration.



The mass spectrum of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and its C, H analysis are consistent with the formulation given. Its IR spectrum shows bands in the terminal ν_{CO} region and an extremely weak band at 1869 cm^{-1} assigned to the bridging CO. This band has less than 1% of the relative intensity of the most intense ν_{CO} band, and can only be unambiguously observed in concentrated solutions or by the use of an FT/IR spectrophotometer.

The ^1H NMR spectrum of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ is shown in Figure 1. It shows two equal intensity doublets at δ 7.75 and

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[23] (a) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1979**, *182*, C57. (b) Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *Ibid.* **1981**, *206*, C43.

[24] Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975.

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[27] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 825.

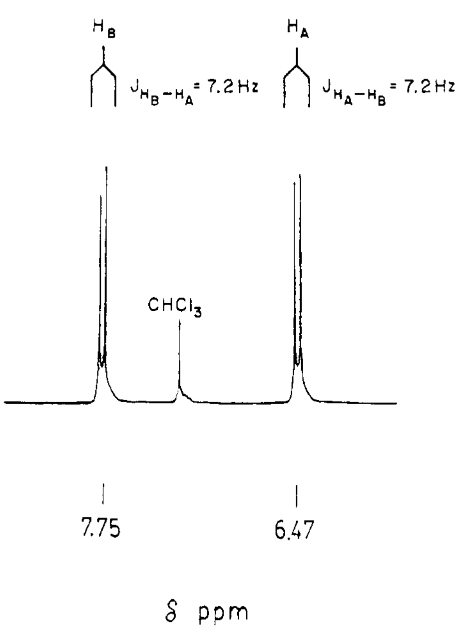

Figure 1. ^{1}H NMR spectrum of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ in $CDCl_3$ solution.

6.47 ($J_{^1H-^1H}$ = 7.2 Hz) assigned to the two nonequivalent protons of the methylene ligand. The ^{13}C NMR spectrum is shown in Figure 2. The seven resonances in the δ 171–193 region are assigned to the carbonyl ligands and show an approximate intensity ratio of 1:1:1:2:2:2:2, consistent with the structure drawn. This resonance pattern is remarkably similar to the ^{13}C NMR spectrum of $[HOs_3(CO)_{11}]^-$[20] which has a structure similar to $Os_3(CO)_{11}(\mu\text{-}CH_2)$ except with the bridging hydride ligand replacing the bridging methylene group. The ^{13}C NMR spectrum also shows a pseudo triplet at δ 62.5, but selective decoupling experiments show this to be a doublet of doublets (Figure 1). Thus, decoupling of proton H_A by irradiation of the δ 6.47 ^{1}H NMR resonance causes the ^{13}C NMR spectrum to show a doublet at δ 62.5 with $J_{^1H_B-^{13}C}$ = 147 Hz. Likewise, a doublet at δ 62.5 with $J_{^1H_A-^{13}C}$ = 144 Hz results when the H_B proton is selectively decoupled.

The $Os_3(CO)_{11}(\mu\text{-}CH_2)$ complex is quite stable. It shows no appreciable air sensitivity either in solution or in the solid state, and it is quantitatively recovered following chromatography on SiO_2. It is soluble in all common organic solvents including saturated hydrocarbons such as pentane.

Experiments To Elucidate the Mechanism of Formation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. 1. Labeling Experiments. In order to determine the source of the hydrogens in the μ-CH_2 ligand of $Os_3(CO)_{11}(\mu\text{-}CH_2)$, the two H/D labeling experiments shown in eq 7 and 8 were conducted. Thus when $Os_3(CO)_{12}$ was reacted

$$Os_3(CO)_{12} + [BH(O\text{-}i\text{-}Pr)_3]^- \rightarrow \xrightarrow{CH_3CO_2D} Os_3(CO)_{11}(\mu\text{-}CH_2) \quad (7)$$

$$Os_3(CO)_{12} + [BDEt_3]^- \rightarrow \xrightarrow{H_3PO_4} Os_3(CO)_{11}(\mu\text{-}CD_2) \quad (8)$$

with $K[BH(O\text{-}i\text{-}Pr)_3]$ followed by protonation with acetic acid-*d*, the isolated sample of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ showed a mass spectrum identical with that obtained when acidification was conducted with H_3PO_4; i.e., the most intense peak in the envelope for the parent ion was at *m/z* 894. However, when the reduction was carried out with triethylborodeuteride and then acidified with H_3PO_4 (eq 8) the product isolated showed its most intense peak in the parent ion envelope at *m/z* 896, two mass units higher than $Os_3(CO)_{11}(\mu\text{-}CH_2)$, implying the formation of $Os_3(CO)_{11}(\mu\text{-}CD_2)$. This product did not show any signals in its ^{1}H NMR spectrum, but its ^{2}H NMR spectrum showed two broad singlets at δ 7.7 and 6.6, consistent with its formulation.

2. Timing of Reagent Addition. Several experiments were conducted to determine which solution species leads to $Os_3(CO)_{11}(\mu\text{-}CH_2)$. First it was observed that no $Os_3(CO)_{11}(\mu\text{-}CH_2)$ formed if acidification of the solution was conducted after the IR spectrum indicated that all of the $[Os_3(CO)_{11}(CHO)]^-$ had decayed to $[HOs_3(CO)_{11}]^-$. Instead, $HOs_3(CO)_{10}(OH)$[16] and $H_2Os_3(CO)_{10}$[28] were the primary products identified, as had been previously found for acidification of pure samples of $[HOs_3(CO)_{11}]^-$.[20] Furthermore, little $Os_3(CO)_{11}(\mu\text{-}CH_2)$ could be isolated if the acid was added immediately after the $K[BH(O\text{-}i\text{-}Pr)_3]$ addition and before the IR spectrum indicated significant formation of $[Os_3(CO)_{11}(CHO)]^-$. Unreacted $Os_3(CO)_{12}$ was the major product from such reaction. In our numerous syntheses of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ we have found that the best yields result when acidification is carried out when the IR spectrum indicates $[Os_3(CO)_{11}CHO)]^-$ to be present at its maximum concentration. These several experiments strongly implicate $[Os_3(CO)_{11}(CHO)]^-$ as the species which is protonated and which leads to $Os_3(CO)_{11}(\mu\text{-}CH_2)$.

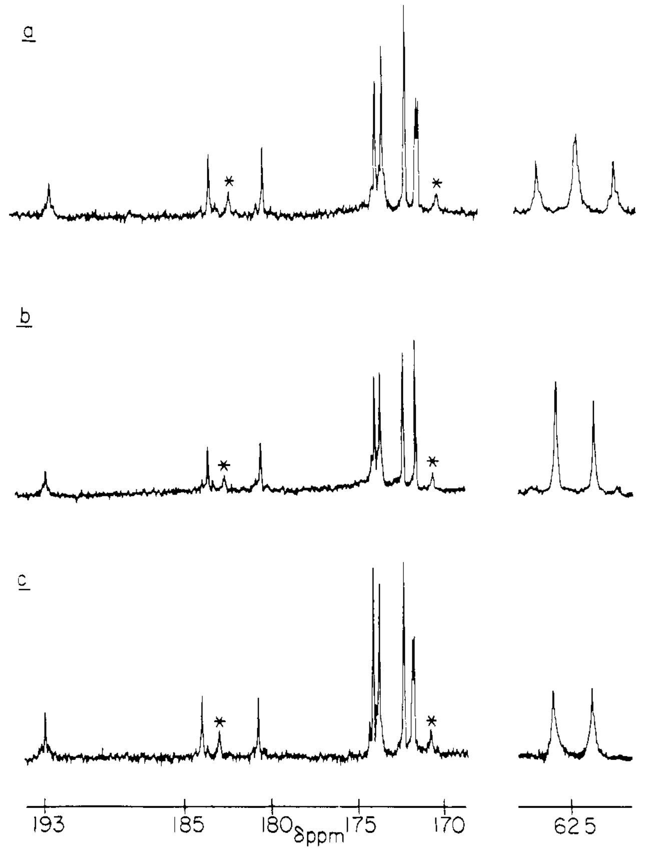

Figure 2. ^{13}C NMR spectra of $Os_3(CO)_{11}CH_2$ in CD_2Cl_2: (a) fully ^{1}H coupled; (b) $^{13}C\{^1H_A\}$; and (c) $^{13}C\{^1H_B\}$. Resonances at 171 and 183 ppm marked with an asterisk are due to $Os_3(CO)_{12}$ impurity.

3. Observations. The presence of excess $K[BH(O\text{-}i\text{-}Pr)_3]$ was found not to increase the yield of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ isolated; only the rate of formation of $[Os_3(CO)_{11}(CHO)]^-$ was enhanced. This suggests that $K[BH(O\text{-}i\text{-}Pr)_3]$ is not involved in the reaction to produce $Os_3(CO)_{11}(\mu\text{-}CH_2)$ any further than forming the initial formyl precursor complex. Excess borohydride is likely to be immediately destroyed upon initial addition of acid.

It was observed that $Os_3(CO)_{12}$ always forms when the acid is added, even though the IR spectrum of the solution prior to acidification shows none to be present. In a careful quantitative experiment, 0.84 equiv of $Os_3(CO)_{12}$ was isolated compared to the amount of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ formed, suggesting that the reactions following acidification of $[Os_3(CO)_{11}(CHO)]^-$ produce an equivalent of $Os_3(CO)_{12}$ for each equivalent of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ produced.

The methylene-bridged cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$ also formed when solutions of $[Os_3(CO)_{11}(CHO)]^-$ were allowed to react with $[(CH_3)_3O]BF_4$ instead of H_3PO_4. This observation is consistent

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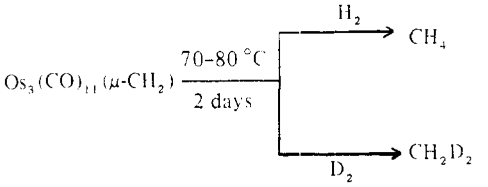
with the mechanism to be discussed shortly in which the function of the acid is to protonate the formyl oxygen and remove it as H_2O. A similar transformation with CH_3^+ can occur to methylate the formyl oxygen and subsequently transform it into dimethyl ether.

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with H_2 and D_2. $Os_3(CO)_{11}(\mu\text{-}CH_2)$ reacts with H_2 and D_2 to yield significant quantities of CH_4 and CH_2D_2, respectively (eq 9). Likewise, CD_4 and CH_2D_2 result from the reaction of $Os_3(CO)_{11}(\mu\text{-}CD_2)$ with D_2 and H_2, respectively. A quantitative experiment showed that the amount of CH_2D_2 formed from the reaction of H_2 with $Os_3(CO)_{11}(\mu\text{-}CD_2)$ was 20.1% of that expected on the basis of the quantity of $Os_3(CO)_{11}(\mu\text{-}CD_2)$ consumed. Mass spectral and chromatographic analyses of the organometallic residues from these reactions showed the presence of a small amount of $Os_3(CO)_{12}$ and $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$[21] (see below). A large quantity of material would not elute from the SiO_2 chromatography column and thus was not identified.

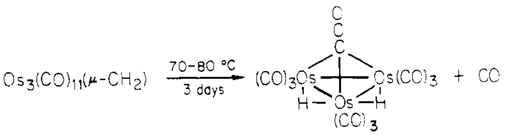


(9)

In separate experiments it was observed that if $Os_3(CO)_{11}(\mu\text{-}CH_2)$ was left under H_2 pressure (1500 psi) at room temperature, a slow reaction occurred to yield not only CH_4 but also CH_3CHO (eq 10). The acetaldehyde product of this reaction likely forms from hydrogenation of a ketene-substituted cluster which we have shown derives from $Os_3(CO)_{11}(\mu\text{-}CH_2)$ by CO insertion.[15] This species, $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$, reacts with H_2 to form CH_3CHO.[29]

$$Os_3(CO)_{11}(\mu\text{-}CH_2) \xrightarrow[20-22\ °C]{H_2\ (1500\ psi)} CH_4 + CH_3CHO + Os_x \text{ products} \quad (10)$$

Thermolysis of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. Although $Os_3(CO)_{11}(\mu\text{-}CH_2)$ is quite stable at ambient temperatures, it does slowly transform when heated to 70–80 °C under N_2 for several hours. The product isolated in 72% yield from such a reaction is $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ (eq 11). This species was also obtained by Shapley and co-workers[21a] from the identical thermolysis and has been fully characterized by the Churchill group by an X-ray diffraction study.[21b] The latter showed the structure given in eq 11 with two bridging hydrides and the μ_3-CCO ligand standing upright, perpendicular to the Os_3 plane. The spectral data are consistent with this structure. The complex shows no methylene protons in its ^1H NMR spectrum but instead equivalent hydrides at δ −20.1 s. In order to determine if this species is an intermediate in the reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with H_2 to give CH_4, in which it was obtained in small quantity, this complex was allowed to react with H_2 under conditions identical with those of eq 9. However, no reaction was observed, and $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$ was recovered unchanged.



(11)

Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with PPh_3, PMe_2Ph, and C_2H_4. The complex $Os_3(CO)_{11}(\mu\text{-}CH_2)$ rapidly reacts with both PPh_3 and PMe_2Ph in THF solution at 22 °C, but simple substituted μ-CH_2 derivatives do not form in good yield. The reaction with PPh_3 was studied in most detail. When monitored by ^1H NMR spectroscopy, the μ-CH_2 doublets at δ 7.75 and 6.47 rapidly disappeared following the addition of PPh_3, and a new singlet grew in at δ 3.58 with intensity about the same as the integrated sum of the $Os_3(CO)_{11}(\mu\text{-}CH_2)$ protons. However, we have not been able to conclusively identify this species although it may well be $Os_3(CO)_{10}(\mu\text{-}CH_2)(PPh_3)$. It does not survive chromatography which instead led to the isolation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$, $Os_3(CO)_{12}$, $Os_3(CO)_{11}(PPh_3)$, and $Os_3(CO)_{10}(PPh_3)_2$. The mass spectrum of the $Os_3(CO)_{11}(PPh_3)$ fraction showed a low intensity ion at *m/z* 1100, consistent with the presence of a small amount of $Os_3(CO)_{10}(\mu\text{-}CH_2)(PPh_3)$ if this is the (M^+ − CO) ion.

Following Norton et al.'s[30] observation of the facile reaction of $Os_2(CO)_8(\mu\text{-}CH_2)$ with C_2H_4 to give the diosmacyclopentane derivative $Os_2(CO)_8(\mu\text{-}CH_2CH_2CH_2)$, we anticipated a similar reaction with $Os_3(CO)_{11}(\mu\text{-}CH_2)$. However, $Os_3(CO)_{11}(\mu\text{-}CH_2)$ does not react with C_2H_4 even when left for 3 days under 1200 psi of this reagent.

Reaction of $Os_3(CO)_{12-x}(PR_3)_x$ (x = 1–3) Derivatives with $K[BH(O\text{-}i\text{-}Pr)_3]$. Although $Os_3(CO)_{10}(PMe_2Ph)_2$, $Os_3(CO)_9(PMe_2Ph)_3$, and $Os_3(CO)_{10}\{P(OPh)_3\}_2$ do not react with $K[BH(O\text{-}i\text{-}Pr)_3]$, $Os_3(CO)_{11}(PMe_2Ph)$ and $Os_3(CO)_{11}\{P(OPh)_3\}$ do (see Experimental Section). IR spectra of solutions of the latter complexes when treated with $[BH(O\text{-}i\text{-}Pr)_3]^-$ show formyl ν_{CO} vibrations at 1570 and 1571 cm^{-1}, respectively (eq 12. However,

$$Os_3(CO)_{11}L + [BH(O\text{-}i\text{-}Pr)_3]^- \rightarrow [Os_3(CO)_{10}(CHO)L]^- \quad (12)$$

$$L = PMe_2Ph,\ P(OPh)_3$$

no μ-CH_2 derivative could be characterized upon acidification of solutions of $[Os_3(CO)_{10}(CHO)(PMe_2Ph)]^-$; only $Os_3(CO)_{11}(PMe_2Ph)$ was isolated from such a reaction. However, protonation of solutions of $[Os_3(CO)_{10}(CHO)\{P(OPh)_3\}]^-$ gave a compound tentatively identified as $Os_3(CO)_{10}(\mu\text{-}CH_2)\{P(OPh)_3\}$. This species could not be isolated in pure form as it forms in low yield and does not separate well from $Os_3(CO)_{11}\{P(OPh)_3\}$ upon chromatography. Its mass spectrum and ^1H NMR spectrum are consistent with the indicated formulation. The latter indicates the presence of two isomers; three doublets are observed at δ 6.55, 6.47, and 6.39 with ^1H–^1H coupling constants of 7.3, 7.3, and 6.7 Hz, respectively. These all fall within the spectral range of the μ-CH_2 protons of $Os_3(CO)_{11}(\mu\text{-}CH_2)$. The two doublets at δ 6.55 and 6.47 are attributed to nonequivalent protons of one isomer of $Os_3(CO)_{10}(\mu\text{-}CH_2)\{P(OPh)_3\}$. The doublet at δ 6.39 is apparently the resonance of one proton of a second isomer with the resonance of the second proton of this isomer obscured by the phenyl resonances of the $P(OPh)_3$ ligand in the δ 7.8–7.3 region.

Discussion

The unusual aspect of this study is the formation of the methylene-bridged product $Os_3(CO)_{11}(\mu\text{-}CH_2)$ from protonation of the formyl cluster $[Os_3(CO)_{11}(CHO)]^-$. While the protonation reactions of many mononuclear formyl complexes and a few binuclear formyl compounds have been well studied,[31] this reaction represents the only example so far reported of the formation of a μ-CH_2 ligand from a formyl precursor. Protonation of mononuclear formyl complexes usually results first in the formation of hydroxymethylene intermediates which in at least one case have been isolated.[32] In most instances these either decompose to release formaldehyde[33] or react further with the formyl complex to give other derivatives.[31,34] Consequently, considerable effort was made to probe the mechanism of this unusual transformation. The mechanism shown in Scheme III is most consistent with our data and is in accord with mechanisms previously indicated for reactions of mononuclear formyl complexes.[31-34] Protonation of $[Os_3(CO)_{11}(CHO)]^-$ must occur on the formyl oxygen to give an

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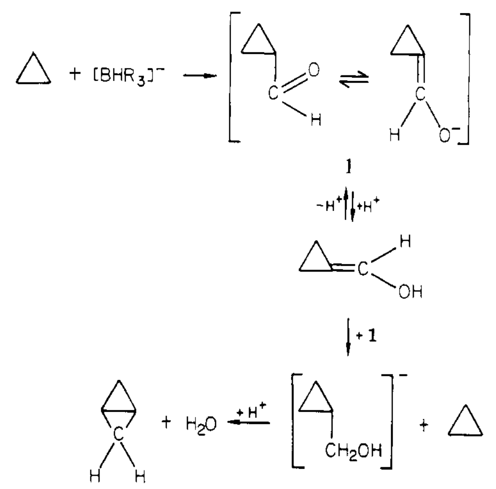
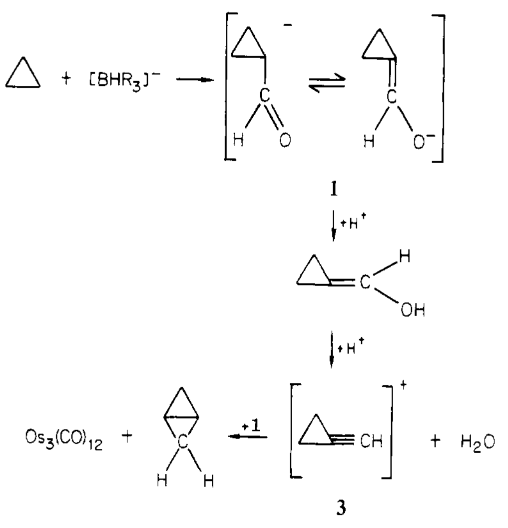
[33] Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.

[34] (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927.

Scheme III



Scheme IV



intermediate hydroxymethylene complex. Such a species would be expected to be fairly acidic, in accordance with the known acidity of the few hydroxycarbene complexes previously studied,[35] and it is likely in equilibrium with the formyl complex. In any case, the next step presumably involves reaction between the hydroxymethylene intermediate and an equivalent of the formyl complex. Mononuclear formyl complexes have been demonstrated to be potent hydride transfer reagents,[31,34a,36] and thus this reaction would yield the proposed hydroxymethyl intermediate of Scheme III. It also yields an equivalent of $Os_3(CO)_{12}$, consistent with the experimental observation of the latter cluster being produced upon protonation of the formyl complex. At this stage the anionic hydroxymethyl cluster is in solution with excess acid; protonation of the hydroxymethyl oxygen and its loss as H_2O would generate the methylene ligand, which in the final product ends up in the more stable bridging position. Note that both of the methylene hydrogens come from the borohydride reducing agent, via the intermediacy of the formyl complex, consistent with the labeling experiments discussed in the Results section. The function of the acid is then to remove the carbonyl oxygen as water.

The overall mechanism of Scheme III is similar to mechanisms proposed by Casey and Neumann[34a] for the formation of methanol upon protonation of $[Et_4N][Fe(CO)_3\{P(OPh)_3\}(CHO)]$ and Gladysz et al.[32] for the formation of $CpReNO(PPh_3)CH_3$ upon protonation of $CpReNO(PPh_3)(CHO)$. The difference in the triosmium vs. mononuclear iron and rhenium formyl chemistry is that a second metal (Os) is in close proximity when the CH_2 ligand is generated, and a stable bridging μ-CH_2 structure can be produced. Bridging methylenes are well-known to be more stable than terminal CH_2 ligands.[37] It is interesting that the results reported herein differ from those described by Pruett and co-workers.[23] These workers did acidify $[Os_3(CO)_{11}(CHO)]^-$ solutions with CF_3CO_2H and observed formation of 20–30% methanol, but no mention was made of the cluster products from their reactions nor the manner in which the methanol was characterized. In our hands, CH_3OH was not observed by gas-chromatographic techniques upon acidification with CF_3CO_2H, but $Os_3(CO)_{11}CH_2$ was produced in a yield similar to that obtained upon acidification with H_3PO_4. Also, no CH_3OH was detected when protonation was carried out with H_3PO_4.

Another mechanism that is not inconsistent with the experimental observations and cannot be excluded from consideration is that shown in Scheme IV. Excess acid could protonate the hydroxylmethyl intermediate, followed by loss of H_2O and formation of the carbyne cluster **3**. Reaction of **3** with an equivalent of **1** would yield $Os_3(CO)_{11}(\mu$-$CH_2)$ and an equivalent of $Os_3(CO)_{12}$. While we cannot rule out such a mechanism, we view it as unlikely. Casey and co-workers[38] have shown that reaction of $Cp_2Fe_2(CO)_3(\mu$-$CH_2)$ with Ph_3C^+ leads to hydride abstraction and yields the carbyne-bridged complex $[Cp_2Fe_2(CO)_3(\mu$-$CH)]^+$. Treatment of the latter with $[HBEt_3]^-$ gave regeneration of $Cp_2Fe_2(CO)_3(\mu$-$CH_2)$. If **3** were a reasonable intermediate en route to $Os_3(CO)_{11}(\mu$-$CH_2)$, it should form upon reaction of this latter complex with Ph_3C^+. Addition of $[Ph_3C]BF_4$ to a CH_2Cl_2 solution of $Os_3(CO)_{11}(\mu$-$CH_2)$ gave slow deposition of a yellow precipitate which did not yield $Os_3(CO)_{11}(\mu$-$CH_2)$ when later treated with $[BH(O$-i-$Pr)_3]^-$. Instead, a complex mixture of presently unidentified compounds was obtained. Our inability to affect the clean $Os_3(CO)_{11}(\mu$-$CH_2) \rightleftharpoons [Os_3(CO)_{11}(CH)]^+$ (**3**) conversion suggests that **3** is not a likely intermediate en route to $Os_3(CO)_{11}(\mu$-$CH_2)$.

The results described herein may be of relevance to the mechanism(s) of CO reduction on metal surfaces. While surface-bound methylene ligands have been implicated as key intermediates in hydrocarbon production from CO/H_2, they have generally been assumed to arise via the CO-dissociative path of Scheme I. However, our results show that μ-CH_2 ligands can also derive from formyl precursors and give support to the nondissociative mechanism outlined in Scheme II. While this cluster–surface chemistry analogy is not perfect, since the $CO \rightarrow CH_2$ conversion described herein requires H^-/H^+ equivalents instead of H_2 as does CO/H_2 catalysis, it does show that transformations such as those outlined in Scheme II are not unreasonable and should be considered when discussing possible CO reduction mechanisms.

Acknowledgment. This research was supported by the Department of Energy, Office of Basic Energy Sciences. G.L.G. gratefully acknowledges the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Award (1978–1983) and the John Simon Guggenheim Memorial Foundation for a fellowship (1982–1983).

Registry No. $Os_3(CO)_{12}$, 15696-40-9; $K[Os_3(CO)_{11}(CHO)]$, 89378-11-0; $[(Ph_3P)_2N][HOs_3(CO)_{11}]$, 61182-08-9; $Os_3(CO)_{11}(\mu$-$CH_2)$, 77208-32-3; $Os_3(CO)_{11}(\mu$-$CD_2)$, 89378-12-1; $Os_3(CO)_{11}PMe_2Ph$, 36885-43-5; $[Os_3(CO)_{10}(PMe_2Ph)(CHO)]^-$, 89378-13-2; $[Os_3(CO)_{10}(P(OPh)_3)(CHO)]^-$, 89378-14-3; $Os_3(CO)_{10}(P(OPh)_3)(\mu$-$CH_2)$, 89378-15-4; $H_2Os_3(CO)_9(\mu_3$-$CCO)$, 83585-34-6; $Os_3(CO)_{10}(\mu$-$CH_2)(PPh_3)$, 89378-16-5; $Os_3(CO)_{11}P(OPh)_3$, 89378-17-6; CO, 630-08-0.

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