Hydrogenation of Trimetallic Clusters of the Iron Triad Containing Bridging Carbyne Ligands. Reductive Cleavage of a Triply Bridging Carbyne

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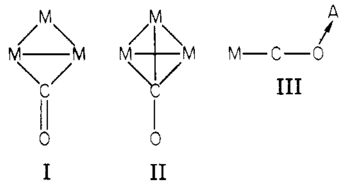
The clusters $HM_3(\mu\text{-COMe})(CO)_{10}$ (1) (**a**, M = Fe; **b**, M = Ru; **c**, M = Os), prepared by methylation of the corresponding $HM_3(\mu\text{-CO})(CO)_{10}$ monoanion, react with hydrogen to give $H_3M_3(\mu_3\text{-COMe})(CO)_9$ (2). This process may be reversed under carbon monoxide. For these and other related carbyne-containing clusters the relative stabilities of $HM_3(\mu\text{-CX})(CO)_{10-n}L_n$ and $H_3M_3(\mu_3\text{-CX})(CO_{9-n}L_n$ are found to depend upon (i) the metal, (ii) the carbyne substituent X, and (iii) the ligands L. Thus, although **2a** is unstable under ambient conditions, reverting nearly quantitatively to **1a**, the substituted derivative $H_3Fe_3(\mu_3\text{-COMe})(CO)_7(SbPh_3)_2$ (**5a**) can be isolated in fair yield by hydrogenation of **1a** in the presence of triphenylantimony. Similarly, although $HRu_3(\mu\text{-CN(Me)CH}_2\text{Ph})(CO)_{10}$ (4) does not react with hydrogen to give a stable product, in the presence of 4 equiv of triphenylantimony $H_3Ru_3(\mu_3\text{-CN(Me)CH}_2\text{Ph})(CO)_6(SbPh_3)_3$ (6) can be prepared in good yield. These observations are rationalized in terms of the relative importance of M_3–CX and C–X π-bonding interactions and the relative metal–carbonyl and metal–hydrogen bond strengths. Under more severe conditions reductive cleavage of the carbyne ligand as CH_3X can be achieved. At 130 °C and 3.5 MPa of 1:1 carbon monoxide–hydrogen, **2b** decomposes to dimethyl ether and $Ru_3(CO)_{12}$. This process represents overall reduction of a carbonyl ligand by molecular hydrogen and is made possible by the activation of this carbonyl by methylation. The trends observed for cluster hydrogenation may have implications for potential Lewis acid activation of cluster-bound carbonyl ligands.

Catalytic reduction of metal-coordinated carbon monoxide by hydrogen is presently the object of intensive research because of the importance of carbon monoxide–hydrogen gas mixtures as basic petrochemical feedstocks. Two of the strategies that have been suggested for activation of carbon monoxide toward reduction are (1) reduction of the C–O bond order through formation of η^1-μ- or η^1-μ_3-bridging carbonyls (schematic I or II, respectively) and (2) reduction of the C–O bond order by coordination of a Lewis acid to the oxygen of a metal-bound carbonyl ligand (III) in order to activate the carbonyl carbon toward nucleophilic attack by hydride.[1,2] We have sought to exploit both strategies by examining the reduction behavior of metal cluster-bound carbonyl ligands that are simultaneously O-complexed to a Lewis acid. A number of complexes having this feature have been reported.[3-12] Of particular interest to us were two systems based upon trimetallic clusters, Lewis acid adducts of the $HFe_3(\mu\text{-CO})(CO)_{10}$ and $Co_3(\mu_3\text{-CO})(CO)_9$ monoanions.



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Complexes of the $HFe_3(\mu\text{-CO})(CO)_{10}$ anion with Lewis acids $HNEt_3^+$, BF_3, and Na^+ have been characterized by infrared and ^{13}C NMR spectroscopy by Todd and Wilkinson, who concluded that for each adduct the Lewis acid is coordinated to the oxygen of the bridging carbonyl.[4] Later Shriver and co-workers showed that the carbonyl oxygen of this anion is sufficiently nucleophilic to be methylated with methyl fluorosulfonate to give $HFe_3(\mu\text{-COMe})(CO)_{10}$; further work by the same group showed that protonation of the anion initially produces highly unstable $HFe_3(\mu\text{-COH})(CO)_{10}$.[8]

The $Co_3(\mu_3\text{-CO})(CO)_9$ anion[9] also displays high nucleophilicity for the triply bridging carbony.[5,10] The O-methylated derivative $Co_3(\mu_3\text{-COMe})(CO)_9$ has been prepared.[11] Recently the syntheses and structures of adducts with UCp_3[5] and $TiClCp_2$[6] have been described. Protonation of this anion gives $Co_3(\mu_3\text{-COH})(CO)_9$.[12]

We set out to examine the hydrogenation behavior of Lewis acid complexes of the type described above. However, due to the expected difficulty in maintaining the M–C–O→A structure in solution, we have begun our work by studying the reactions of the O-methylated complexes $HFe_3(\mu\text{-COMe})(CO)_{10}$ and $Co_3(\mu_3\text{-COMe})(CO)_9$, believing that these species would give more tractable products because of their high stability to heat and to air, high solubility, and relatively inert O–Me bond. Recognizing

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the greater stabilities of clusters of the second- and third-row metals, we also have examined the hydrogenation reactions of the analogous $HM_3(\mu\text{-}COMe)(CO)_{10}$ clusters for M = Ru and Os. To the extent that these complexes can be considered as acid–base adducts between cluster-bound carbonyls and the strongly acidic methyl cation, their reactivity should represent the tendencies of adducts of weaker Lewis acids.

We describe here the hydrogenation of $HM_3(\mu\text{-}COMe)(CO)_{10}$, M = Fe, Ru, and Os, to give the corresponding $H_3M_3(\mu_3\text{-}COMe)(CO)_9$, the first functionalized methylidyne clusters of the iron triad, and the further reaction of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ with carbon monoxide to give dimethyl ether and $Ru_3(CO)_{12}$.[13] This chemistry demonstrates the facile interconversion of the μ- and the μ_3-CO·A ligands. The nature of the μ-CX (X = O^-, OR, and NR_2) ligand and its effect in the reactivities of these clusters are also discussed.

Results

Syntheses of $HM_3(\mu\text{-}COMe)(CO)_{10}$ (1b, M = Ru; 1c, M = Os). The O-methylated carbonyl cluster $HFe_3(\mu\text{-}COMe)(CO)_{10}$ (**1a**) was prepared by Shriver and co-workers by reaction of $[NEt_4][HFe_3(\mu\text{-}CO)(CO)_{10}]$ with methyl fluorosulfonate.[7a] Because of the higher stabilities of ruthenium and osmium clusters, we considered it more desirable to study hydrogenation reactions of $HM_3(\mu\text{-}COMe)(CO)_{10}$ (**1b**, M = Ru; **1c**, M = Os), which had not been reported at the time we began this work. At that time $[NMe_4][HOs(\mu\text{-}CO)(CO)_{10}]$ had been prepared by reduction of $Os_3(CO)_{12}$ with potassium hydroxide in methanol,[14] but the ruthenium anion was poorly characterized, having been prepared by Knight and Mays through reduction of $Ru_3(CO)_{12}$ with the $Mn(CO)_5$ anion.[15] Thus, we wanted to develop a convenient and general synthesis for these trimetallic anions from the corresponding $M_3(CO)_{12}$, which could be coupled with a methylation step to give the desired clusters. Using a modification of the synthesis of $[NHEt_3][HFe_3(\mu\text{-}CO)(CO)_{10}]$,[16] we were able to prepare $[NHEt_3][HM_3(\mu\text{-}CO)(CO)_{10}]$ in essentially quantitative yield by reacting $M_3(CO)_{12}$ with triethylamine and water in tetrahydrofuran at 60 °C:

$$M_3(CO)_{12} + H_2O + NEt_3 \rightarrow [NHEt_3][HM_3(\mu\text{-}CO)(CO)_{10}] + CO_2$$

This preparation is particularly convenient for the subsequent methylation because the only nonvolatile components of the product solution are the metal species. Thus, the synthesis of $HM_3(\mu\text{-}COMe)(CO)_{10}$ can be carried out in one pot without isolation of the air-sensitive $HM_3(\mu\text{-}CO)(CO)_{10}$ monoanions:

$$[NHEt_3][HM_3(\mu\text{-}CO)(CO)_{10}] + MeSO_3F \rightarrow HM_3(\mu\text{-}COMe)(CO)_{10} + [NHEt_3][SO_3F]$$

Shortly after we prepared these clusters, Lewis, Johnson, and co-workers[17] and Ford and co-workers[18] independently reported syntheses of the $HRu_3(\mu\text{-}CO)(CO)_{10}$ monoanion, and reports also appeared describing syntheses similar to ours for **1b**[19] and **1c**.[20] Details of the characterizations of these compounds have been reported. X-ray diffraction studies of **1b**[19,21] have confirmed that the structure is very similar to that found for **1a**[7a] (Figure 1).

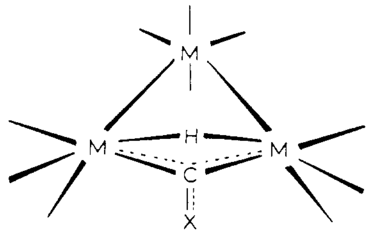
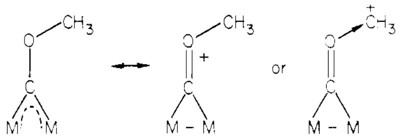


Figure 1. Structure of $HM_3(\mu\text{-}CX)(CO)_{10}$ (**1a**, M = Fe, X = OMe; **1b**, M = Ru, X = OMe; **1c**, M = Os, X = OMe; **3**, M = Ru, X = $NHCH_2Ph$; **4**, M = Ru, X = $N(Me)CH_2Ph$).

The bonding within the μ-COMe ligand can be described as arising primarily from two contributing resonance structures, IV and V. Structure IV represents the COMe



IV V

ligand as a bridging carbyne, while structure V expresses the multiple character of the C–OMe bond. In the most general case of a bridging carbonyl complexed to a Lewis acid, the relative importance of structure IV increases as the acid strength increases. The μ-COMe ligand is revealed by infrared and ^{13}C NMR spectroscopy and by the crystal structures of **1a** and **1b** to be best described as a bridging carbyne. The stretching frequency attributed to the C–OMe bond is ca. 250 cm^{-1} lower than the bridging carbonyl stretch of the anionic precursor (**1a**,[7b] 1452, **1b**,[19] 1415, and **1c**, 1456 cm^{-1} vs. $[NR_4][HM_3(\mu\text{-}CO)(CO)_{10}]$, M = Fe,[4] 1718, Ru,[17] 1691, and Os,[14] 1667 cm^{-1}) and is consistent with a C–OMe bond order between 1 and 2. The ^{13}C NMR signal for the bridging carbon of **1** is shifted far downfield from the chemical shift of the bridging carbonyl of the corresponding $HM_3(\mu\text{-}CO)(CO)_{10}$ anion (**1a**, 356.5,[7b] **1b**, 366.5,[19] and **1c**, 352.2[20] ppm vs. $[NR_4][HM_3(\mu\text{-}CO)(CO)_{10}]$, M = Fe, 285.7,[4] Ru, 286.2,[17] 281.8[18] ppm) to a value similar to those found for mononuclear metal carbenes and carbynes.[22] Furthermore, the C–OMe bond length of 1.30 Å[7a,19,21] is intermediate between the values expected for single (1.40-Å) and double (1.20-Å) C–O bonds. The planar nature of the $M_2(\mu\text{-}COC)$ group and the restricted rotation about the μ-CO bond (13.5 kcal for Os,[20] ca. 10 kcal for Ru[19]) indicate that some multiple-bond character remains.

(Alkylamino)- and (dialkylamino)carbyne derivatives can also be prepared. The cluster $HRu_3(\mu\text{-}CNMe_2)(CO)_{10}$ has been prepared by reaction of $Ru_3(CO)_{12}$ with $Sn(CH_2NMe_2)Me_3$.[23] The osmium analogues $HOs_3(\mu\text{-}CNHR)(CO)_{10}$ have been prepared by reaction of $H_2Os_3(CO)_{10}$ with isocyanides CNR (R = CH_2Ph, Me, CMe_3); methylation of these compounds at nitrogen gives the corresponding $HOs_3(\mu\text{-}CN(Me)R)(CO)_{10}$.[24] The clusters

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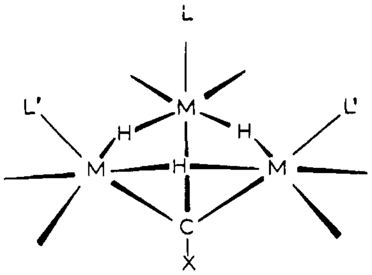

Figure 2. Structure of $H_3M_3(\mu_3\text{-}CX)(CO)_{9-n}L_n$ (**2a**, M = Fe, X = OMe, L = L' = CO; **2b**, M = Ru, X = OMe, L = L' = CO; **2c**, M = Os, X = OMe, L = L' = CO; **5a**, M = Fe, X = OMe, L = CO, L' = $SbPh_3$; **6**, M = Ru, X = $N(Me)CH_2Ph$, L = L' = $SbPh_3$).

$HOs_3(\mu\text{-}CNMeR)(CO)_{10}$ (R = Me, CH_2Ph) have also been prepared from $Os_3(CO)_{12}$ with trimethyl- or benzyldimethylamine at high temperatures.[25] Iron analogues have been prepared by several methods,[26] but a general synthesis from $HFe_3(\mu\text{-}CO)(CO)_{11}^-$ and isocyanides CNR, followed by methylation, has recently appeared.[27]

Using the method of Howell and Mathur,[27] we have prepared $HRu_3(\mu\text{-}CNHCH_2Ph)(CO)_{10}$ (**3**) and $HRu_3(\mu\text{-}CN(Me)CH_2Ph)(CO)_{10}$ (**4**). Direct reaction of $[NHEt_3][HRu_3(\mu\text{-}CO)(CO)_{10}]$ with benzyl isocyanide in dichloromethane gives **3** in up to 77% yield. The N-methylated derivative **4** is obtained in 90% yield from **3** by reaction with sodium methoxide and methyl iodide in methanol. Characterizations of **3** and **4** are straightforward. The mass spectrum of each displays the molecular ion and usual fragmentation pattern. The infrared and ^1H NMR spectra of **3** and **4** are very similar to those of their osmium analogues.[24,25] The substantial double-bond character for the μ-C–N bond results in restricted rotation and the methylene protons for each compound are diastereotopic, giving rise to an AB pattern in the ^1H NMR spectrum. For **3** the ^1H NMR spectrum consists of signals at τ 1.4 (br, 1 H_A), 2.67 (m, 5 H), 5.02 (dd, 1 H_B), 5.15 (dd, 1 H_C), and 24.70 (d, 1 H_D) with J_{AB} = 1.5 Hz, J_{AC} = 3.4 Hz, J_{BC} = 14.7 Hz, and J_{AD} = 1.4 Hz; these signals are respectively assigned to the NH proton, the protons on the phenyl ring, the two diastereotopic methylene protons, and the bridging hydride ligand. The spectrum of **4** is as expected for the N-methylated analogue: τ 2.7 (m, 5 H), 4.61 (d, 1 H_A), 4.96 (d, 1 H_B), 6.43 (s, 3 H), and 24.74 (s, 1 H) with J_{AB} = 14.7 Hz, assigned respectively to the phenyl protons, the two diastereotopic methylene protons, the methyl group, and the hydride ligand.

Cluster Hydrogenation. With the methylated clusters in hand we examined their reactions with hydrogen. When hydrogen is bubbled through a solution of **1b** in refluxing hexane, the infrared absorptions due to the starting material gradually diminish and are replaced with bands at 2106 (vw), 2078 (s), 2075 (s), 2036 (vs), 2028 (m), 2018 (s), 2014 (m), and 2000 (w) cm^{-1}. After 2 h a single, orange, crystalline product, characterized as $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ (**2b**), is isolated in 90% yield after recrystallization from methanol.

The methylidyne cluster **2b** (Figure 2) is proposed to be isostructural with $H_3Ru_3(\mu_3\text{-}CX)(CO)_9$ (X = Me,[28] CH_2CMe_3,[29] and Cl[30]) for which the structures have been established by X-ray crystallography. The ^1H NMR spectrum of **2b** consists of two singlets of equal intensities at τ 6.23 and 27.53, which are assigned to the methyl protons and three equivalent bridging hydrides, respectively. The electron-impact mass spectrum displays the molecular ion (*m/e* 608 ($^{104}Ru_3$)), followed by ions resulting from stepwise loss of nine carbonyls and the COMe unit; Ru_3C^+ ions are also observed. The compound is mildly air-sensitive, particularly in solution, decomposing to a dark red, sparingly soluble material that has not been characterized.

Similarly, **1c** reacts with hydrogen at 1 atm and 120 °C in decane to give $H_3Os_3(\mu_3\text{-}COMe)(CO)_9$ (**2c**) in 75% yield after 1 h. The infrared spectrum of this product in cyclohexane solution consists of only terminal carbonyl absorptions: 2107 (w), 2077 (s), 2074 (s), 2022 (vs), 2013 (m), 2008 (m), and 1995 (w) cm^{-1}. The ^1H NMR spectrum in deuteriochloroform consists of two singlets of equal intensities at τ 6.20 and 28.58.[31] As for **2b**, the electron-impact mass spectrum displays the molecular ion (*m/e* 900 ($^{192}Os_3$)) and ions resulting from sequential loss of nine carbonyls and the COMe moiety, down to the bare Os_3^+ ion; intense, doubly charged trinuclear ions are also observed.

Additional evidence for the proposed structure is obtained from the proton-decoupled ^{13}C NMR spectrum of **2c**. In deuteriochloroform (0.2 M chromium(III) acetylacetonate) this consists of resonances at 69.3 (1 C), 166.4 (3 C), 167.0 (6 C), and 205.2 (1 C) ppm downfield from Me_4Si. These signals are assigned to the methyl carbon, three equivalent axial carbonyls, the six equivalent radical carbonyls, and the methylidyne carbon,[34] respectively. The ^{13}C resonances for the carbonyls of $H_3Ru_3(\mu_3\text{-}CMe)(CO)_9$ have been reported to occur at 190.1 (6 C) and 189.3 (3C) ppm; the methylidyne carbon resonance was not observed.[39]

While the iron analogue **1a** does react with hydrogen (1 atm) at 60 °C to give a new species, as evidenced by infrared spectroscopy, this product is unstable under ambient conditions, reverting nearly quantitatively to the starting cluster. The instability of the new species seems to be related to both temperature and hydrogen pressure, and factors affecting its stability are currently under investigation. Strictly on the basis of the similarity of the

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(31) ^1H NMR spectrum of $H_3Os_3(\mu_3\text{-}CMe)(CO)_9$, isostructural with the ruthenium analogue,[32] consists of equally intense singlets at τ 5.55 and 28.58.[33]

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(34) Previously, the only reports of chemical shifts for methylidyne carbons bridging three metal atoms were 118.4 ppm for $H_3Os_3(\mu_3\text{-}CH)(CO)_9$[35] and 255–310 ppm for $Co_3(\mu_3\text{-}CR)(CO)_9$.[36] More recently values of 303.2 ppm for $[Rh_3(\mu_3\text{-}CH)(CO)_2Cp_3]^+$[37] and 295.8 ppm for $Mo_3O(\mu_3\text{-}CCH_3)(OAc)_6(H_2O)_3$[38] have been reported.

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new bands in the infrared spectrum of the product solution to the spectra of **2b** and **2c**, the unstable iron product is proposed to be $H_3Fe_3(\mu_3\text{-COMe})(CO)_9$ (**2a**). From subtraction of the absorptions due to **1a** (2096 (m), 2049 (s), 2038 (vs), 2018 (s), 2008 (sh), 1992 (m), 1980 (m) cm^{-1}) the infrared spectrum of **2a** displays terminal carbonyl absorptions at 2060 (s), 2023 (s), and 2004 (m) cm^{-1}; other bands may be masked by those of **1a**. Very recently a *stable* iron methylidyne cluster $H_3Fe_3(\mu_3\text{-CMe})(CO)_9$ has been isolated and characterized by X-ray crystallography.[40]

The stability of the hydrogenated cluster product can be increased by substituting group 5 donor ligands for carbonyls. Hydrogenation of **1a** at 1 atm and 60–70 °C in the presence of 3 equiv of triphenylantimony gives a dark brown, crystalline product, characterized as $H_3Fe_3(\mu_3\text{-COMe})(CO)_7(SbPh_3)_2$ (**5a**; Figure 2), in 22% yield after chromatography. The infrared spectrum of this compound displays only terminal carbonyl stretches; the ^1H NMR spectrum in deteriochloroform consists of resonances at τ 2.83 (m, 30 H), 5.49 (s, 3 H), 31.15 (t, 1 H), and 32.02 (d, 2 H, J 5.3 Hz), assigned respectively to the aryl protons of the $SbPh_3$ ligands, the methyl group, the hydride bridging the $(Ph_3Sb)(OC)_3FeFe(CO)_3(SbPh_3)$ vector, and the two hydrides bridging to the $Fe(CO)_3$ moiety. Both spectra of **5a** are very similar to those of $H_3Ru_3(\mu_3COMe)(CO)_7(SbPh_3)_2$ (**5b**), which can be prepared by direct substitution on **2b**.

The NMR spectra in the hydride region for the substituted products $H_3M_3(\mu_3\text{-CX})(CO)_{9-n}L_n$ are particularly useful for characterization. The monosubstituted derivatives display a triplet (1 H) close to the chemical shift of the unsubstituted parent cluster and a doublet (2 H) about 0.5 ppm to lower field with a coupling constant of 3–5 Hz; the disubstituted derivatives display a triplet (1 H) about 0.5 ppm downfield from a doublet (2 H, J = ca. 3 Hz), both of which are downfield from the signals due to the monosubstituted derivative; the trisubstituted clusters display a singlet hydride resonance, which is slightly downfield from the lowest field hydride resonance of the disubstituted derivative. Thus, the ^1H NMR spectra of $H_3Ru_3(\mu_3\text{-COMe})(CO)_{9-n}(SbPh_3)_n$ in deuteriochloroform are as follows: $n = 3$, τ 25.78 (s, 3 H); $n = 2$, 26.15 (t, 1 H), 26.74 (d, 2 H, J = 3.4 Hz); $n = 1$, 26.91 (d, 2 H), 27.58 (t, 1 H, J = 3.4 Hz); $n = 0$, 27.50 (s, 3 H). Resonances due to hydrides bridging to metal atoms substituted with a group 5 ligand are shifted downfield relative to hydrides bridging to unsubstituted metal atoms. The spectra of the mono- and disubstituted derivatives are consistent with either axial coordination of the group 5 donor ligand, which would make two of the hydrides chemically equivalent, or with radial coordination and fluxional exchange of the group 5 ligand between the two radial sites on the metal atom. The isoelectronic $Co_3(\mu_3\text{-CMe})(CO)_6(P(Me)_3)_3$ was shown to have radially coordinated phosphite ligands.[41] However, very recently $H_3Os_3(\mu_3\text{-CMe})(CO)_8(PPh_3Et)$ was shown by ^{13}C NMR spectroscopy to have an axially coordinated phosphine ligand;[42] the similarity between the ^1H NMR spectra of this compound and $H_3Ru_3(\mu_3\text{-COMe})(CO)_8L$ implies that the group 5 donor ligands in all these complexes are axially coordinated as well.

Although **4** does not react with hydrogen to form the analogous $H_3Ru_3(\mu_3\text{-CN(Me)CH}_2\text{Ph})(CO)_9$ up to the temperature of decomposition, in the presence of 4 equiv of triphenylantimony and at 60–70 °C for 8 h under 1 atm of hydrogen red-orange $H_3Ru_3(\mu_3\text{-CN(Me)CH}_2\text{Ph})(CO)_6(SbPh_3)_3$ **6** can be isolated after recrystallization from methanol in good yield. This product is isostructural (Figure 2) with $H_3Ru_3(\mu_3\text{-CX})(CO)_6L_3$ (X = Cl, Ph, OMe; L = $AsPh_3$, $SbPh_3$) that can be prepared by direct reaction of the corresponding $H_3Ru_3(\mu_3\text{-CX})(CO)_9$ with L,[43] and its infrared spectrum is very similar to those of the latter molecules. The ^1H NMR spectrum of **6** consists of a singlet hydride resonance at τ 25.58 (3 H) and signals due to the carbyne ligand at τ 5.25 (s, 2 H) and 6.82 (s, 3 H), in addition to resonances due to phenyl protons.

Reductive Elimination of Dimethyl Ether. The objective of our study was the ultimate reduction of a cluster-bound carbonyl ligand. Conversion of $HM_3(\mu\text{-COMe})(CO)_{10}$ to $H_3M_3(\mu_3\text{-COMe})(CO)_9$ results in a small reduction in the $C-OCH_3$ bond order, as shown by the lowering of the $C-OCH_3$ stretching frequency from ca. 1450 to 1170 cm^{-1}. Perhaps more importantly the reaction also introduces into the cluster the two hydrogen atoms needed to complete the reduction of the bridging CO unit. Under more severe conditions reductive elimination of dimethyl ether can be induced. When **2b** was heated in toluene at 130 °C under carbon monoxide and hydrogen (1:1, 3.5 MPa) for 23 h, mass spectroscopic analysis of the portion of the gas phase that could be trapped out by venting the autoclave slowly through a U trap at −196 °C showed a significant quantity of dimethyl ether. The predominant metal-containing product was $Ru_3(CO)_{12}$ (89% isolated yield). However, traces of $Ru(CO)_5$ collected in the trap along with the volatile products. A more careful analysis of the gases was performed after the reaction was repeated by using parafin oil as solvent; mass spectrometric analysis of the condensable gases showed traces of 1,2-dimethoxyethane and methyl formate, in addition to a considerable amount (ca. 10% yield) of dimethyl ether. Quantitative analysis was not attempted under these conditions because of the difficulty of recovering dimethyl ether quantitatively at this pressure. Hydrogen is required in this reaction because of the equilibrium between **1b** and **2b**.

Hydrogenation of (methylidyne)tricobalt clusters has been investigated under photolytic conditions by Geoffroy and Epstein.[44] Photolysis of $Co_3(\mu_3\text{-CH})(CO)_9$ under a carbon monoxide–hydrogen atmosphere yielded methane and $Co_2(CO)_8$. We had independently observed that $Co_3(\mu_3\text{-CCO}_2\text{CH}_3)(CO)_9$ reacted with hydrogen (1 atm) in refluxing toluene to give methyl acetate and metallic cobalt, but we observed no new cluster products or intermediates by infrared spectroscopy. Geoffroy and Epstein have proposed homolytic cleavage of Co–Co bonds upon photolysis as a possible mechanism leading to activation of hydrogen, although photolysis also leads to carbon monoxide dissociation. Our experiments were performed at temperatures sufficiently high for either carbon monoxide dissociation or metal–metal bond cleavage to be occurring. In considering the origin of the trace of 1,2-dimethoxyethane observed in thermolysis of **2b**, it is interesting to note that thermolysis of $Co_3(\mu_3\text{-CC}_6\text{H}_5)(CO)_9$ in the absence of hydrogen has been reported to give small amounts of diphenylacetylene.[45] Very recently Fachinetti has reported that reaction of $Co_3(\mu_3\text{-COMe})(CO)_9$ with carbon monoxide and hydrogen yields $MeOCH_2CH_2OH$ (60%), Me_2O (10%), and $MeOCH_2CH_2CHO$ (10%).[46]

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Discussion

Our original objective was to determine the reactivity of O-alkylated carbonyl ligands toward reducing agents, primarily molecular hydrogen. The reaction sequence (Scheme I) for conversion of carbon monoxide on $Ru_3(CO)_{12}$ to dimethyl ether (eq 1–4) effects the reduction of a carbonyl ligand by hydrogen under mild conditions due to the activation of the carbonyl by "coordination" of the strongly acidic methyl cation. This type of activation is, of course, impractical for catalytic reduction of carbon monoxide since the "acid" stoichiometrically reacts with the reduced carbonyl product. However, activation might also be achieved by using an acid that could be recovered economically. Therefore, it may be useful to consider the role of the methyl group in facilitating carbonyl reduction.

Scheme I

$$Ru_3(CO)_{12} + H_2O + NEt_3 \rightarrow [NHEt_3][HRu_3(\mu\text{-}CO)(CO)_{10}] + CO_2 \quad (1)$$

$$[NHEt_3][HRu_3(\mu\text{-}CO)(CO)_{10}] + MeSO_3F \rightarrow HRu_3(\mu\text{-}COMe)(CO)_{10} + [NHEt_3][SO_3F] \quad (2)$$

$$HRu_3(\mu\text{-}COMe)(CO)_{10} + H_2 \rightarrow H_3Ru_3(\mu_3\text{-}COMe)(CO)_9 + CO \quad (3)$$

$$H_3Ru_3(\mu_3\text{-}COMe)(CO)_9 + 3CO \rightarrow Ru_3(CO)_{12} + CH_3OMe \quad (4)$$

Methylation of the bridging carbonyl of the $HM_3(\mu\text{-}CO)(CO)_{10}$ anion, as previously discussed, effectively reduces the C–O bond order from ca. 2 to 1.5. In comparing the C–O stretching frequencies and ^{13}C chemical shifts for the bridging carbonyl of the $HFe_3(\mu\text{-}CO)(CO)_{10}$ anion in the presence of Lewis acids, Wilkinson and Todd noted that, as the acid strength increased, the C–O stretching frequency lowered and the ^{13}C resonance shifted downfield.[4] Thus, the values for the μ-CO stretching frequency and μ-^{13}C NMR signal for the anion with noncoordinating cations (NEt_4^+, 1709 cm^{-1}; $(Ph_3P)_2N^+$, 285.7 ppm) are shifted with the hydrogen-bonding triethylammonium cation (1639 cm^{-1}, 301.3 ppm), and in the presence of boron trifluoride the ^{13}C chemical shift (355.1 ppm) is nearly as far downfield as for $HFe_3(\mu\text{-}COMe)(CO)_{10}$ (356.5 ppm).[7] Shriver[47] has attributed the trend of decreasing C–O stretching frequency with increasing acid strength to decreasing C–O bond order because of increasing delocalization of electrons from metal d orbitals to the carbonyl π^* orbital.

The first step in the reduction of the activated carbonyl is oxidative addition of molecular hydrogen to give $H_3M_3(\mu_3\text{-}COMe)(CO)_9$ (**2**), a reaction which, in addition to introducing the two remaining hydrogen atoms needed to complete reduction of the COMe ligand, also reduces the C–OMe bond order still further.[48] Although several examples of additions of molecular hydrogen by clusters are known,[49] neither mechanistic nor systematic studies of cluster hydrogenations have been reported. In this work we have established three factors which influence hydrogenation of $HM_3(\mu\text{-}CX)(CO)_{10-n}L_n$: (i) the identity of the metal, (ii) the nature of the CX moiety, and (iii) the nature of the other ligands on the cluster.

Only limited data are available at this time concerning the influence of the metal upon cluster hydrogenation. In our series, **1a** does hydrogenate to **2a**, but **2a** is unstable at ambient temperatures and reverts to **1a**; on the other hand, elevated temperatures are required to carbonylate **2b** and **2c** back to **1b** and **1c**. In this case it would appear that the relative stability of $H_3M_3(\mu_3\text{-}COMe)(CO)_9$, rather than the reactivity of $HM_3(\mu_3\text{-}COMe)(CO)_{10}$, is responsible for this difference. For different carbyne groups CX coordinated to the same metal framework, the trend of increasing ease of hydrogenation is $X = O^- < NR_2 < OR$. On the other hand, for X = Cl, Br, H, Ph, alkyl, and CO_2R, the analogues $HM_3(\mu\text{-}CX)(CO)_{10}$ cannot be prepared by carbonylation of the known $H_3M_3(\mu_3\text{-}CX)(CO)_9$.[50] Here again, the relative stabilities of $HM_3(\mu\text{-}CX)(CO)_{10}$ and $H_3M_3(\mu_3\text{-}CX)(CO)_9$ may be responsible. Demethylation of $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ by reaction with amines even at room temperature does not give the expected $H_3Ru_3(\mu_3\text{-}CO)(CO)_9^-$ but only $HRu_3(\mu\text{-}CO)(CO)_{10}^-$ and $H_3Ru_4(CO)_{12}^-$. Replacing carbonyl ligands with group 5 ligands stabilizes the hydrogenated product. Thus, both **5a** and **6** are stable under ambient conditions, even though neither of the parent carbonyls can be isolated.

Upon hydrogenation of $HM_3(\mu\text{-}CX)(CO)_{10-n}L_n$ to $H_3M_3(\mu_3\text{-}CX)(CO)_{9-n}L_n$ the changes in bonding are (a) replacement of one carbonyl ligand with two hydride ligands, (b) an increase in the degree of metal-to-CX bonding upon conversion from a μ- to μ_3-carbyne, and (c) a decrease in the C–X bond order. The trends observed undoubtedly are the cumulative result of all of these factors. The relative metal–hydride bond energies may account substantially for the influence of the metal and ligands L. Metal–hydride bond strengths increase in the order Fe < Ru < Os,[49] and, thus, the relative stabilities of the $H_3M_3(\mu_3\text{-}CX)(CO)_{9-n}L_n$ clusters might be expected to follow the same order. There is also evidence that metal–hydride bond strengths are increased by replacement of carbonyl ligands with ligands having lower ionization potentials.[51] However, it is difficult to account for the effect of the carbyne ligand in terms of relative metal–hydride bond strengths.

A major factor influencing the relative stabilities of $HM_3(\mu\text{-}CX)(CO)_{10-n}L_n$ and $H_3M_3(\mu_3\text{-}CX)(CO)_{9-n}L_n$ may be the relative importance of M–CX and C–X π bonding. The μ-C-X bond order is expected to decrease as X changes from O^- to NR_2 to OMe as the electronegativity of X increases. Indeed, there is substantial support for this in the C-X stretching frequencies,[17,19,20] C-X bond lengths,[17,19,23] and free energies of activation for rotation about the C–X bond.[19,20] Since conversion from a μ- to μ_3-carbyne increases the metal-to-carbyne bonding at the expense of C–X π bonding, substituents X that favor a strong C–X π bond (such as O^- and NR_2) might understandably make hydrogenation more difficult than substituents that do not. Since O coordination of Lewis acids to the μ-CO ligand lowers the C–O bond order for $HM_3(\mu\text{-}CO)(CO)_{10}^-$, the Lewis acid also should facilitate cluster hydrogenation. In this light, it is interesting that at low temperature, *protonation* at the $HFe_3(\mu\text{-}CO)(CO)_{10}$ monoanion forms $HFe_3(\mu\text{-}COH)(CO)_{10}$, which, on the basis of the extremely low-field ^{13}C NMR signal for the μ-carbon (359 ppm), is very similar in structure to **1a**.[8] Similar results are observed for the $HRu_3(\mu\text{-}CO)(CO)_{10}$ monoanion.[52] However, hydrogenation of $HM_3(\mu\text{-}COH)(CO)_{10}$ to $H_3M_3(\mu_3\text{-}COH)(CO)_9$ has not been possible because of the

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(48) This may be demonstrated by comparison of the C–OMe stretching frequencies for **1c** (1460 cm^{-1}) and **2c** (1195, 1140 cm^{-1}).

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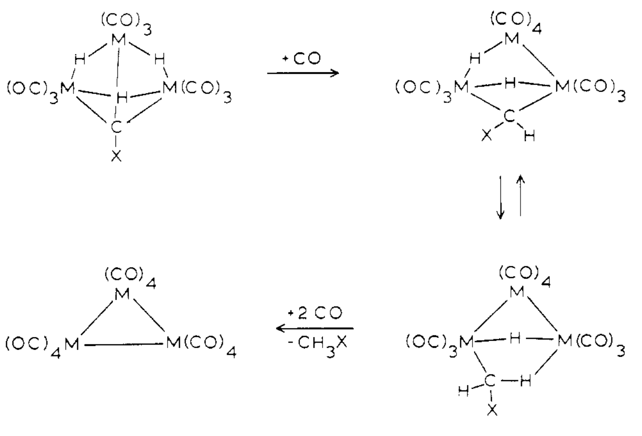

Figure 3. Proposed mechanism for elimination of CH_3X (X = OMe, H, CO_2Me) from $H_3M_3(\mu_3\text{-}CX)(CO)_9$.

very rapid rearrangement of these species to the corresponding $H_2M_3(CO)_{11}$ at temperatures above ca. −40 °C. Thus, effective acid cocatalysts for carbon monoxide reduction via the chemistry described here must be strong acids (BF_3, H^+, CH_3^+) to facilitate hydrogenation to $H_3M_3(\mu_3\text{-}CO{\cdot}A)(CO)_9$ but must not react with the product irreversibly and must not provide alternative decomposition pathways. Recently, the isoelectronic $Co_3(\mu_3\text{-}COH)(CO)_9$ has been isolated and characterized by X-ray crystallography.[12c]

The final step of reduction of the COMe ligand (eq 4) is reductive elimination of three M–C σ bonds and three M–H–M bonds to give dimethyl ether and either $M_3(CO)_{12}$ or $M(CO)_5$. We favor the mechanism shown in Figure 3, on the basis of the reverse sequence found by Calvert and Shapley[35] for conversion of $HOs_3(CH_3)(CO)_{10}$ to $H_3Os_3(\mu_3\text{-}CH)(CO)_9$, that is, sequential C–H bond formation without metal–metal bond cleavage. Since, under the conditions used for cleavage of dimethyl ether from **2b**, $Ru_3(CO)_{12}$ and $Ru(CO)_5$ are in equilibrium,[53] no conclusion can be reached at this time about the importance of metal–metal bond cleavage in this instance. Mechanistic studies of both hydrogenation and reductive cleavage steps and quantitative evaluations of the influence of the metal, carbyne ligand, and other ligands upon these processes are in progress.

Experimental Section

Chemicals. $Ru_3(CO)_{12}$ was prepared according to literature procedures.[54] $Os_3(CO)_{12}$ was purchased from Strem Chemical. Methyl fluorosulfonate was purchased from Chemical Dynamics Corp. and ethyl fluorosulfonate from Aldrich. $HFe_3(\mu\text{-}COMe)(CO)_{10}$ was prepared by the procedure of Shriver.[7]

Characterizations. The ^1H NMR spectra were recorded on Varian CFT-80, EM-360, EM-390, or XL-100 spectrometers. ^{13}C NMR spectra were recorded on Varian CFT-80 or XL-100 spectrometers with 0.02 M chromium(III) acetylacetonate as a relaxation agent. Mass spectra were obtained by Allen Clauss at the University of Illinois Mass Spectrometry Laboratory on a Varian CH-5 instrument at 70 eV and a solid probe temperature of 25–150 °C. Infrared spectra were generally run on cyclohexane solutions by using a Perkin-Elmer 467 or Beckman 4250 spectrophotometer and were calibrated with the 2138.5-cm^1 absorption of cyclohexane or with polystyrene. Analyses were performed by Galbraith Laboratories.

$HRu_3(\mu\text{-}COMe)(CO)_{10}$ (1b). Warning! Due to the extreme toxicity of methyl and ethyl fluorosulfonate, all operations involving these compounds should be carried out in an efficient hood. Excess reagent may be destroyed with a slurry of potassium carbonate in methanol.

To a solution of $Ru_3(CO)_{12}$ (502 mg, 0.79 mmol) in tetrahydrofuran (100 mL) in a 500-mL, three-necked, round-bottomed flask, equipped with reflux condenser, nitrogen gas inlet, pressure-equalizing dropping funnel, Vigreaux column topped with stopcock to a vacuum trap, and magnetic stir bar was added nitrogen-saturated water (50 mL) and nitrogen-saturated triethylamine (15 mL). The resulting solution was heated at 60 °C with stirring for 2 h. Then the solvent was removed by vacuum transfer until only water and a brick red precipitate remained. The water was removed with a pipet, keeping the flask under a blanket of nitrogen, and the precipitate was dried under vacuum. Then a solution of methyl fluorosulfonate (300 μL, 3.7 mmol) in dry dichloromethane (50 mL) was added from the dropping funnel, and the dark red solution was stirred overnight under nitrogen. After the reaction was complete, the solvent was vacuum transferred to a liquid nitrogen-cooled trap and the excess methyl fluorosulfonate in the trap was destroyed with a slurry of potassium carbonate in methanol. Methanol (50 mL) was added to the reaction flask, as well, and the resulting orange solution stirred for 2 h. Then the methanol was removed on a rotary evaporator, and the solid residue was purified by preparative thin-layer chromatography on silica gel eluting with cyclohexane. The product $HRu_3(\mu\text{-}COMe)(CO)_{10}$ was isolated by extraction of the highest R_f band with dichloromethane and was recrystallized from methanol to give yellow crystals: 342 mg (70%); mass spectrum, *m/e* 627 ($^{101}Ru_3$); ^1H NMR ($CDCl_3$) τ 5.44 (s, 3 H), 24.85 (s, 1 H); IR (C_6H_{12}) 2104 (w), 2064 (vs), 2054 (s), 2030 (vs), 2018 (m), 2004 (m), 1990 (w), 1968 (w) cm^{-1}. Anal. Calcd for $C_{12}H_4O_{11}Ru_3$: C, 22.95; H, 0.65; Ru, 48.35. Found: C, 22.95; H, 0.71; Ru, 48.49.

The ethyl derivative was prepared in the same manner by using ethyl fluorosulfonate: ^1H NMR ($CDCl_3$) τ 5.33 (q, 2 H, J 6.9 Hz), 8.31 (t, 3 H), 24.80 (s, 1 H); IR (C_6H_{12}) 2103 (w), 2064 (vs), 2054 (s), 2030 (vs), 2018 (m), 2006 (sh), 2002 (m), 1996 (w), 1986 (vw) cm^{-1}.

$HOs_3(\mu\text{-}COMe)(CO)_{10}$ (1c). Warning! Due to the extreme toxicity of methyl and ethyl fluorosulfonate, all operations involving these compounds should be carried out in an efficient hood. Excess reagent can be destroyed with a potassium carbonate slurry in methanol.

A solution of $Os_3(CO)_{12}$ (200 mg, 0.2 mmol), deoxygenated water (10 mL), and deoxygenated triethylamine (9 mL) in air-free tetrahydrofuran (40 mL) was heated with stirring at 60 °C for 2 h in a three-necked, 100-mL, round-bottomed flask equipped with nitrogen gas inlet, magnetic stirring bar, pressure-equalizing dropping funnel, and reflux condenser. After the solution was cooled to room temperature, tetraethylammonium bromide (150 mg, 0.7 mmol) was added and the tetrahydrofuran and triethylamine were removed by vacuum transfer. The water was then removed with a pipet, and the red precipitate remaining was washed with a air-free water (10 mL) and dried under vacuum.

Next a solution of methyl fluorosulfonate (50 μL, 0.62 mmol) in dry dichloromethane (50 mL) was added, and the resulting red solution was stirred under nitrogen for 2 h. At this point the solution was bright yellow. Excess methyl fluorosulfonate was destroyed by stirring with methanol (20 mL) for 2 h. Then the solvent was evaporated, and the residue was purified by preparative thin-layer chromatography on silica gel, eluting with cyclohexane. The product was isolated by extraction with dichloromethane of the second, yellow band, trailing a trace of purple $H_2Os_3(CO)_{10}$: yield 159 mg (81%); the sample could be recrystallized from methanol; mass spectrum, *m/e* 900 ($^{192}Os_3$); ^1H NMR ($CDCl_3$) τ 5.41 (s, 3 H), 26.39 (s, 1 H); IR (C_6H_{12}) 2109 (w), 2064 (s), 2067 (m), 2025 (s), 2012 (m), 1998 (m), 1982 (sh, vw) cm^{-1}. Anal. Calcd for $C_{12}H_4O_{11}Os_3$: C, 16.10; H, 0.45. Found: C, 16.16; H, 0.41.

The ethyl derivative was prepared in the same manner by using ethyl fluorosulfonate: ^1H NMR ($CDCl_3$) τ 5.36 (q, 2 H, J = 7.2 Hz), 8.38 (t, 3 H), and 26.31 (s, 1 H); IR (C_6H_{12}) 2105 (m), 2062 (s), 2055 (s), 2022 (s), 2007 (s), 1994 (s), 1989 (sh), 1977 (m) cm^{-1}.

$HRu_3(\mu\text{-}CNHCH_2Ph)(CO)_{10}$ (3). A solution of $Ru_3(CO)_{12}$ (99 mg, 0.15 mmol), triethylamine (5 mL), and water (5 mL) in THF (25 mL) was heated at 60–70 °C under nitrogen for 1 h. The solvent was removed under vacuum to give $[NHEt_3][HRu_3(CO)_{11}]$.

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This residue was dissolved in dichloromethane and benzyl isocyanide (25 μL) was added to the stirred solution. After about 15 min the initially bright red solution had turned orange. Then the solvent was removed under vacuum, and the residue was purified by preparative thin-layer chromatography on silica, eluting with cyclohexane. The second yellow band was extracted with dichloromethane to give the product, after evaporation of solvent, as a bright yellow solid: 84 mg (77%); IR (C_6H_{12}) 2098 (w), 2060 (vs), 2050 (s), 2025 (s), 2012 (s), 2002 (m), 1998 (s), 1986 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.4 τ (br, 1 H_A), 2.67 (br, 5 H), 5.02 (dd, 1 H_B), 5.15 (dd, 1 H_C), 24.70 (d, 1 H_D), J_{AB} = 1.5, J_{AC} = 3.4, J_{BC} = 14.7, and J_{AD} = 1.4 Hz; mass spectrum, *m/e* 702 ($^{101}Ru_3$).

$HRu_3(\mu$-CN(Me)CH$_2$Ph)(CO)$_{10}$ (4). **3** (84 mg, 0.12 mmol) was dissolved in methanol (25 mL) containing excess sodium methoxide under nitrogen. The solution immediately became dark orange. Then methyl iodide (200 μL, 3.2 mmol) was added with stirring. After 45 min. the solution was bright yellow. Next saturated aqueous ammonium chloride was added, and the solution was extracted with dichloromethane until no yellow color remained. The organic layer was evaporated to dryness with a rotary evaporator, and the residue was redissolved in dichloromethane and dried over magnesium sulfate. Chromatography of this material on silica eluting with 10% dichloromethane in cyclohexane gave one yellow band, which was extracted with dichloromethane to give the product (76 mg, 90%): IR (C_6H_{12}) 2096 (m), 2058 (s), 2047 (s), 2024 (s), 2010 (s), 2002 (m), 1995 (s), 1985 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 2.7 (m, 5 H), 4.61 (d, 1 H_A), 4.96 (d, 1 H_B), 6.43 (s, 3 H), 24.74 (s, 1 H), J_{AB} = 14.7; mass spectrum, *m/e* 716 ($^{101}Ru_3$).

$H_3Ru_3(\mu_3$-COMe)(CO)$_9$ (2b). A solution of **1b** (209 mg, 0.13 mmol) in hexane (100 mL) was heated at reflux with hydrogen bubbling through the solution for 2 h. The solvent was removed under vacuum, and the red-orange residue was recrystallized from methanol under nitrogen to give bright orange crystals of $H_3Ru_3(\mu_3$-COMe)(CO)$_9$. The mother liquor was evaporated to dryness, and the residue was purified by preparative thin-layer chromatography on silica gel, eluting with cyclohexane to give additional product by extraction of the second band with dichloromethane: yield 186 mg (93%); mass spectrum, *m/e* 601 ($^{101}Ru_3$); ^{1}H NMR ($CDCl_3$) τ 6.23 (s, 3 H), 27.53 (s, 3 H); IR (C_6H_{12}) 2106 (vw), 2076 (s), 2075 (s), 2036 (vs), 2028 (m), 2018 (sh), 2014 (m), 2000 (vw) cm^{-1}. Anal. Calcd for $C_{11}H_6O_{10}Ru_3$: C, 21.95; H, 1.01; Ru, 50.43. Found: C, 22.19; H, 1.11; Ru, 50.26.

$H_3Os_3(\mu_3$-COMe)(CO)$_9$ (2c). A solution of **1c** (65 mg, 0.07 mmol) in decane (50 mL) was heated at 120 °C in a 100-mL, three-necked, round-bottomed flask, equipped with reflux condenser, stir bar, and gas inlet tube, for 1 h with hydrogen bubbling through the solution. The solvent was removed under vacuum, and the residue was purified by preparative thin-layer chromatography on silica gel, eluting with cyclohexane. The major product $H_3Os_3(\mu_3$-COMe)(CO)$_9$ was isolated by extraction of the third, yellow band with dichloromethane. The compound was recrystallized from methanol: yield 44 mg (79%); mass spectrum, *m/e* 874 ($^{192}Os_3$); ^{1}H NMR ($CDCl_3$) τ 6.20 (s, 3 H), 28.53 (s, 3 H). IR (C_6H_{12}) 2107 (vw), 2077 (s), 2074 (s), 2022 (vs), 2013 (m), 2008 (m), 1995 (vw) cm^{-1}. Anal. Calcd for $C_{11}H_6O_{10}Os_3$: C, 15.20; H, 0.70: Found: C, 15.08; H, 0.67.

$H_3Fe_3(\mu_3$-COMe)(CO)$_7$(SbPh$_3$)$_2$ (5a). A hexane solution of **1a** (890 mg, 1.81 mmol) and triphenylantimony (2.292 g, 6.50 mmol) was heated at 60–70 °C for 2.5 h with hydrogen gas bubbling through the stirred solution. Then the solution was evaporated to dryness and the product mixture was separated by preparative thin-layer chromatography on silica eluting with 10% dichloromethane in cyclohexane. The product was isolated by extraction of the brown band that trailed a dark purple band: yield 451 mg (22%); IR (C_6H_{12}) 2066 (m), 2058 (m), 2018 (sh), 2008 (s), 1998 (sh), 1972 (m), 1904 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 2.83 (m, 30 H), 5.49 (s, 3 H), 31.15 (t, 1 H), 32.02 (d, 2 H, J = 5.3 Hz).

$H_3Ru_3(\mu_3$-CN(Me)CH$_2$Ph)(CO)$_6$(SbPh$_3$)$_3$ (6). A hexane solution of **4** (76 mg, 0.11 mmol) and triphenylantimony (150 mg, 0.43 mmol) was heated at 60–70 °C for 8 h with hydrogen gas bubbling through the solution. When the IR spectrum of the solution showed that complete conversion to the product had occurred, the solution was evaporated to dryness and the residue was recrystallized from dichloromethane–methanol to give red-orange crystals (112 mg, 63%). The product decomposed during chromatography but appeared to be air-stable: IR (C_6H_{12}) 2061 (vw), 2034 (vs), 2014 (s), 2007 (s), 1993 (w), 1965 (s), 1947 (vw), 1877 (vw) cm^{-1}; ^{1}H NMR ($CDCl_3$) τ 2.8 (m, 50 H), 6.80 (s, 2 H), 5.23 (s, 3 H), 25.56 (s, 3 H). Anal. Calcd for $C_{69}H_{58}NO_6Ru_3Sb_3$: C, 49.75; H, 3.51. Found: C, 48.93; H, 3.91.

Reductive Cleavage of Dimethyl Ether from 2b. A solution of **2b** (200 mg) in toluene (10 mL) was placed in the glass liner of a 75-mL Parr autoclave. The autoclave was pressurized to 500 psig with 1:1 carbon monoxide–hydrogen and was heated at 130 °C for 23 h. Then the autoclave was cooled, and the gases were vented slowly through a U-that trap was filled with glass beads and cooled with liquid nitrogen. When all the gas had been vented, the U-trap was closed off and removed. The noncondensable gases were pumped out of the U-trap, and analysis by mass spectrometry was performed on the condesable gases. Results showed a significant quantity of dimethyl ether. The toluene solution remaining in the autoclave was filtered to remove precipitated $Ru_3(CO)_{12}$ (identified by infrared spectroscopy), and the filtrate was evaporated to dryness. Additional $Ru_3(CO)_{12}$ was obtained by preparative thin-layer chromatography, on silica gel with cyclohexane. Total yield of $Ru_3(CO)_{12}$ was 188 mg (89%). Some $Ru_3(CO)_{12}$ and $Ru(CO)_5$ were noted in the U-trap.

The experiment was repeated by using parafin oil as solvent to allow for more careful analysis of the condensible gases. In these cases, in addition to dimethyl ether, traces of methyl formate and 1,2-dimethoxyethane were identified in the vapor by mass spectroscopy. The yield of dimethyl ether was estimated as 10%.

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