Hydrogenation of *O*-Methylated Carbon Monoxide on Clusters of the Iron Triad

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Summary The carbyne clusters $[HM_3(\mu_2\text{-COMe})(CO)_{10}]$, M = Fe, Ru, or Os, formed by methylation of the corresponding $[HM_3(\mu_2\text{-CO})(CO)_{10}]$ anion, react under mild conditions with hydrogen to give $[H_3M_3(\mu_3\text{-COMe})(CO)_9]$; $[H_3Ru_3(\mu_3\text{-COMe})(CO)_9]$ reacts with $CO:H_2$ (1 : 1) under more vigorous conditions to form dimethyl ether and $[Ru_3(CO)_{12}]$.

ACTIVATION of metal-co-ordinated carbonyls by Lewis acids has been suggested as being important for the catalytic reduction of carbon monoxide.[1] Although many Lewis acid–base adducts of the type MCO→A are known, most of these complexes are quite unstable and studies of their reactions are difficult. The *O*-methylated carbonyl cluster $[HFe_3(\mu_2\text{-COMe})(CO)_{10}]$, synthesized by treatment of the $[HFe_3(\mu_2\text{-CO})(CO)_{10}]$ anion with $MeSO_3F$,[2] possesses spectral properties similar to those of more conventional Lewis acid adducts, such as $[HFe_3(\mu_2\text{-CO}{\cdot}BF_3)(CO)_{10}]^-$,[3] $[HFe_3(\mu_2\text{-CO}{\cdot}HNEt_3)(CO)_{10}]$,[3] and $[HFe_3(\mu_2\text{-CO}{\cdot}H)(CO)_{10}]$;[4] additionally, methylation of the $[HFe_3(\mu_2\text{-CO})(CO)_{10}]$ anion induces structural changes expected for acid co-ordination to the bridging carbonyl.[2] We have synthesized the new complexes $[HM_3(\mu_2\text{-COMe})(CO)_{10}]$, M = Ru or Os, and have examined the hydrogenation of these clusters as examples of the reactions of Lewis acid-activated metal carbonyls.

The clusters $[HM_3(\mu_2\text{-COMe})(CO)_{10}]$, M = Ru or Os, were synthesized by the reactions of the corresponding $[HM_3(\mu_2\text{-CO})(CO)_{10}]$ anions† with $MeSO_3F$. The general synthesis from $M_3(CO)_{12}$ is given by equation (1). The compounds

$$[M_3(CO)_{12}] \xrightarrow[H_2O]{NEt_3} [HM_3(\mu_2\text{-CO})(CO)_{10}]^- \xrightarrow{MeSO_3F} [HM_3(\mu_2\text{-COMe})(CO)_{10}] \qquad (1)$$

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† Syntheses and characterizations of $[HM_3(\mu_2\text{-CO})(CO)_{10}]$ anions, M = Ru (B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. Süss, submitted to *J.C.S. Dalton*) or Os (C. R. Eady, J. J. Guy, B. F. G. Johnson, J. Lewis, M. C. Malatesta, and G. M. Sheldrick, *J.C.S. Chem. Comm.*, 1976, 602) have recently been reported.

$[HM_3(\mu_2\text{-COMe})(CO)_{10}]$ have been fully characterized by their i.r., ^1H and ^{13}C n.m.r., and mass spectra; additionally, the structure of $[HRu_3(\mu_2\text{-COMe})(CO)_{10}]$ (Figure 1) has been confirmed by *X*-ray crystallography, the details of which will be published elsewhere. A variety of spectral and structural data indicates that the μ_2-COMe ligand in these complexes is best regarded as a bridging carbyne. Thus, the ^{13}C chemical shifts of the bridging carbon atoms of all three compounds (Os 346, Ru 328, and Fe 360 p.p.m.[4]) are similar to those observed for other metal–carbyne complexes, the bridging C–OMe stretching frequencies are $<1500\ cm^{-1}$, and the free energy of activation for rotation about the C–OEt bond of $[HOs_3(\mu_2\text{-COEt})(CO)_{10}]$, prepared using $EtSO_3F$, is *ca.* $13\cdot5\ kcal\ mol^{-1}$. Finally, the C–OMe bond length of $1\cdot30$ Å is intermediate between the values expected for a single and a double C–O bond.

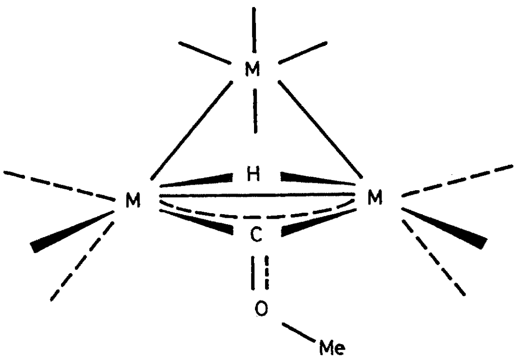

Figure 1. Structure of $[HM_3(\mu_2\text{-COMe})(CO)_{10}]$, M = Fe, Ru, or Os.

The carbyne clusters $[HM_3(\mu_2\text{-COMe})(CO)_{10}]$ react readily with hydrogen under mild conditions (M = Ru or Fe: 60 °C, 1 atm; M = Os: 120 °C, 1 atm) to form the corresponding $[H_3M_3(\mu_3\text{-COMe})(CO)_9]$. For M = Fe the reaction does not go to completion under 1 atm of H_2 and the product $[H_3Fe_3(\mu_3\text{-COMe})(CO)_9]$ decomposes to $[HFe_3(\mu_2\text{-COMe})(CO)_{10}]$ in the absence of hydrogen. However, the Ru and Os analogues are stable even at 70 °C under carbon monoxide. The structures proposed for $[H_3M_3(\mu_3\text{-COMe})(CO)_9]$, M = Ru or Os, (Figure 2) are based upon that established by *X*-ray crystallography for $[H_3Ru_3(\mu_3\text{-CMe})(CO)_9]$[5] and upon that proposed for $[H_3Os_3(\mu_3\text{-CH})(CO)_9]$[6] and are fully consistent with the i.r., ^1H and ^{13}C n.m.r., and mass spectra. The ^1H n.m.r. spectrum of each displays two singlets of equal intensity with appropriate chemical shifts (M = Ru, τ 4·55 and 24·85; M = Os, τ 4·59 and 26·37). The ^{13}C n.m.r. spectrum of $[H_3Os_3(\mu_3\text{-COMe})(CO)_9]$ displays two resonances at 167·0 (6C) and 166·4 p.p.m. (3C) due to the six equivalent equatorial and three equivalent axial carbonyls, respectively; the methyl signal occurs at 69·3 p.p.m. (1C), while the bridging carbon resonates at 205·2 p.p.m. The i.r. spectra for these compounds in the 2150—1900 cm^{-1} region are very similar to those reported for $[H_3Ru_3(\mu_3\text{-CMe})(CO)_9]$ and $[H_3Os_3(\mu_3\text{-CH})(CO)_9]$.

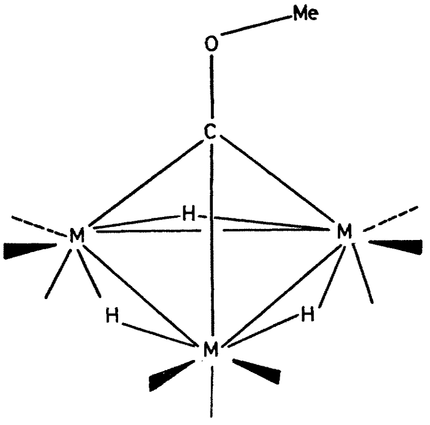

Figure 2. Proposed structure for $[H_3M_3(\mu_3\text{-COMe})(CO)_9]$, M = Fe, Ru, or Os.

The μ_2 to μ_3 transformation of the COMe ligand reduces the C–O bond order still further; reductive cleavage of the COMe group can be achieved under more vigorous conditions. When $[H_3Ru_3(\mu_3\text{-COMe})(CO)_9]$ is heated at 130 °C under $CO:H_2$ (1:1, 500 lb in^{-2}) for 24 h, dimethyl ether and $[Ru_3(CO)_{12}]$ are formed in high yield. This reaction completes the methyl promoted reduction of carbon monoxide.

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