

Preliminary communication

REARRANGEMENT OF O-PROTONATED METAL CARBONYL CLUSTERS. CONVERSION OF $\text{HRu}_3(\text{COH})(\text{CO})_{10}$ TO $\text{H}_2\text{Ru}_3(\text{CO})_{11}$

J.B. KEISTER*

*Corporate Research-Science Laboratories, Exxon Research and Engineering Co., Linden,
New Jersey 07036 (U.S.A.)*

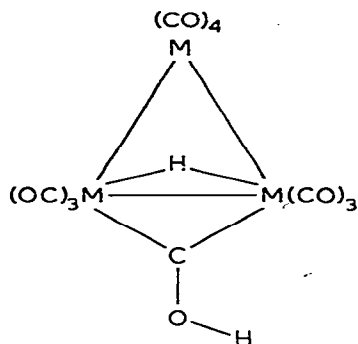
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Summary

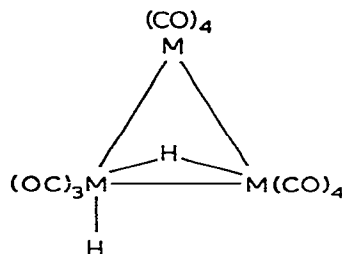
Protonation of the $\text{HRu}_3(\text{CO})_{11}$ anion at -60°C gives $\text{HRu}_3(\text{COH})(\text{CO})_{10}$ as the initial product, but at higher temperatures rearrangement to $\text{H}_2\text{Ru}_3(\text{CO})_{11}$ is observed. The latter product is proposed to contain one bridging and one terminal hydride ligand. At 25°C $\text{H}_2\text{Ru}_3(\text{CO})_{11}$ decomposes rapidly to $\text{Ru}_3(\text{CO})_{12}$.

Recently, protonation of the $\text{HFe}_3(\mu_2\text{-CO})(\text{CO})_{10}$ anion under anhydrous conditions was shown to give an *O*-protonated product $\text{HFe}_3(\mu_2\text{-COH})(\text{CO})_{10}$ at low temperatures [1]. On the other hand, protonation of the $\text{HOs}_3(\mu_2\text{-CO})(\text{CO})_{10}$ anion at room temperature has been reported to give the moderately stable $\text{H}_2\text{Os}_3(\text{CO})_{11}$ with both hydrogens bound to metal atoms [2]. As part of a study of the reactivity of cluster-bound carbonyl ligands *O*-complexed with Lewis acids, we have examined the protonation of the analogous $\text{HRu}_3(\mu_2\text{-CO})(\text{CO})_{10}$ anion. Our preliminary results indicate that, while the initial product of the low-temperature protonation is $\text{HRu}_3(\text{COH})(\text{CO})_{10}$, analogous to the iron product, at slightly higher temperatures this species rearranges to $\text{H}_2\text{Ru}_3(\text{CO})_{11}$, analogous to the osmium cluster. Furthermore, at 25°C $\text{H}_2\text{Ru}_3(\text{CO})_{11}$ decomposes to predominantly $\text{Ru}_3(\text{CO})_{12}$.

Recent work by Shriver and co-workers has demonstrated the nucleophilicity of oxygen lone pairs of polynuclear metal carbonyl anions [1,3]. For example, attack at the bridging carbonyl oxygen of $\text{HFe}_3(\mu_2\text{-CO})(\text{CO})_{10}^-$ by methyl fluoro-sulfonate yields the *O*-methylated cluster $\text{HFe}_3(\mu_2\text{-COCH}_3)(\text{CO})_{10}$ [4]. Even more interestingly at -90°C the anion can be protonated to give $\text{HFe}_3(\mu_2\text{-COH})(\text{CO})_{10}$ [1]. The ^1H NMR spectrum of this product consists of a sharp singlet at τ 28.4 assigned to a bridging hydride ligand and a broad singlet at τ -5.0 assigned to an oxygen-bound proton. The ^{13}C spectrum of this species suggests that the structure is analogous to that of the *O*-methylated cluster $\text{HFe}_3(\mu_2\text{-COCH}_3)(\text{CO})_{10}$, for which the crystal structure has been determined (structure I). At temperatures above -30°C , $\text{HFe}_3(\mu_2\text{-COH})(\text{CO})_{10}$ decomposes to $\text{Fe}_3(\text{CO})_{12}$.



(I)

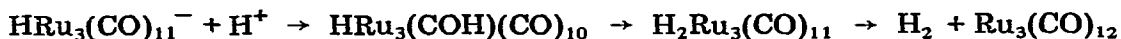


(II)

On the other hand, protonation of the $\text{HOs}_3(\mu_2\text{-CO})(\text{CO})_{10}$ anion at room temperature has been reported to give the well-characterized $\text{H}_2\text{Os}_3(\text{CO})_{11}$ [2]. The latter cluster has been shown by X-ray crystallography and spectroscopic techniques to possess one terminal hydride ligand and one bridging hydride ligand (structure II) [5]. The ^1H NMR resonances for these two hydrides appear at τ 20.25 and 29.96, respectively.

The structure of the $\text{HRu}_3(\mu_2\text{-CO})(\text{CO})_{10}$ anion has been established by X-ray crystallography to be analogous to that of the iron cluster anion [6] and its spectroscopic properties are similar to those of the osmium cluster [2]. When one equivalent of HSO_3CF_3 is added to a deuterodichloromethane solution of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{HRu}_3(\mu_2\text{-CO})(\text{CO})_{10}]$ at -60°C , the hydride resonance of the anion at τ 22.80 disappears and two pairs of singlets arise. The more intense pair consists of a sharp singlet at τ 24.60, in the region expected for a bridging hydride ligand, and a broad signal at τ -6.11, similar to the chemical shift of the *O*-bonded proton of $\text{HFe}_3(\mu_2\text{-COH})(\text{CO})_{10}$. The second pair of resonances consists of singlets of equal intensities at τ 21.98 and 28.74, similar to the chemical shifts of the terminal and bridging hydrides, respectively, of $\text{H}_2\text{Os}_3(\text{CO})_{11}$. The intensity of the former pair of resonances, tentatively assigned to $\text{HRu}_3(\text{COH})(\text{CO})_{10}$, is maximized by maintaining the temperature of the NMR tube as low as possible during the addition of the acid; if the temperature of the solution is raised above ca. -30°C the signals at τ 24.60 and -6.11 completely disappear and the second pair of resonances, assigned to the previously unobserved $\text{H}_2\text{Ru}_3(\text{CO})_{11}$, increases in intensity such that the total integral remains constant. Cooling the sample again to -60°C does not regenerate the resonances assigned to $\text{HRu}_3(\text{COH})(\text{CO})_{10}$. The dihydride cluster, presumably isostructural with $\text{H}_2\text{Os}_3(\text{CO})_{11}$, is stable in solution below -30°C , but upon warming to 25°C the solution evolves gas and $\text{Ru}_3(\text{CO})_{12}$ is isolated after 15 minutes in 90% yield. Small quantities of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ are also formed. This in contrast to the recently reported protonation of $\text{HRu}_3(\mu_2\text{-CO})(\text{CO})_{10}^-$ with concentrated sulfuric acid (presumably at room temperature), which yields $\text{HRu}_6(\text{CO})_{18}^-$ [7].

The reaction sequence suggested for protonation of the $\text{HRu}_3(\mu_2\text{-CO})(\text{CO})_{10}$ anion is:



This sequence is also likely for the iron and osmium analogs but $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ must be too unstable to be observed*. It is expected that protonation of the $\text{HOs}_3(\text{CO})_{11}$ anion at low temperatures will yield $\text{HOs}_3(\text{COH})(\text{CO})_{10}$. Further characterizations of these species are in progress.

Acknowledgment

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*A related rearrangement of $\text{Co}_3(\mu_3\text{-COH})(\text{CO})_9$ to $\text{HCo}(\text{CO})_4$ and $\text{Co}_4(\text{CO})_{12}$ has recently been reported [8].