

Synthesis, Reactivity, Kinetics and Stereochemistry of Cluster Complexes with the Coin Metals and Mercury as Hetero Metal Atoms

The thesis describes the reactivity of the anions resulting from the deprotonation of the phosphido and sulfido bridged compounds $\text{Os}_3(\mu - \text{H})(\mu - \text{E})(\text{CO})_{10}$ ($\text{E} = \text{PPh}_2, \text{SPh}$). The anions were reacted with the coin metal complexes ClMPPH_3 ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) giving the new cluster complexes $\text{Os}_3(\mu - \text{MR})(\mu - \text{E})(\text{CO})_{10}$ ($\text{E} = \text{PPh}_2, \text{R} = \text{PPh}_3, \text{M} = \text{Cu}, \text{Ag}, \text{Au}, \text{E} = \text{SNph}, \text{R} = \text{PPh}_3, \text{M} = \text{Cu}, \text{Ag}, \text{Au}, \text{R} = \text{P}(p - \text{C}_6\text{H}_4\text{F})_3, \text{M} = \text{Ag}$) in good yields. All molecular structures were derived from single crystal X-ray analysis.

In an attempt to extend the above reaction pattern the anions were condensed with the mercury containing compounds $\text{ClHgMoCp}(\text{CO})_3$ and HgCl_2 giving the sulfur bridged cluster $\text{Os}_3(\mu - \text{HgMoCp}(\text{CO})_3)(\mu - \text{SNph})(\text{CO})_{10}$ and the spirocyclic cluster $[\text{Os}_3(\mu - \text{SR})(\text{CO})_{10}]_2(\mu_4 - \text{Hg})$ ($\text{R} = \text{Nph}, \text{Ph}$). The molecular structures of both complexes were confirmed by single crystal X-ray analysis.

Analogous experiments with the phosphido bridged anion $[\text{PPN}][\text{Os}_3(\mu - \text{PPh}_2)(\text{CO})_{10}]$ gave the new clusters $[\text{Os}_3(\mu - \text{PPh}_2)(\text{CO})_{10}](\mu_4 - \text{Hg})[\text{Os}_3(\mu - \text{PPh}_2)(\mu - \text{CO})(\text{CO})_9]$, $[\text{Os}_3(\mu - \text{PPh}_2)(\mu - \text{CO})(\text{CO})_9]_2(\mu_4 - \text{Hg})$ and $\text{Os}_6(\mu_6 - \text{Hg})(\mu - \text{PPh}_2)_2(\text{CO})_{20}$ **1**. The structures of the metal framework differ significantly from the sulfido bridged cluster mentioned above. As illustrated in Figure 1 the complex **1** shows a novel, wheel-shaped mercury centered framework.

The formation of **1** was investigated by ^{31}P -NMR and UV/vis spectroscopic measurements. From these data the thermodynamic parameters were derived, indicating an intramolecular rearrangement of the metal framework.

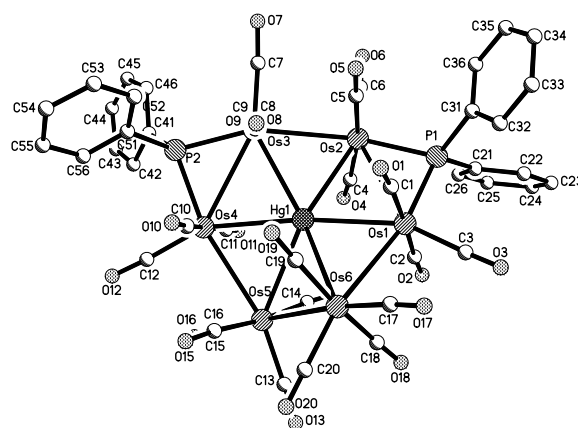


Figure 1: Molecular structure of $\text{Os}_6(\mu_6 - \text{Hg})(\mu - \text{PPh}_2)_2(\text{CO})_{20}$ **1**