

SYNTHESIS AND REACTIVITY OF METAL CLUSTERS
CONTAINING A Ru_3 OR Os_3 TRIANGLE

by

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SUMMARY

The rapid development of metal cluster chemistry has proven to be a source of new and interesting reactions. Many new bonding modes of organic ligands have been observed in trinuclear compounds. In particular, the ligand often donates more electrons to the metal core in these complexes than is observed in mononuclear species. Thus, an isocyanide ligand in $\text{Ru}_5(\text{CO})_{14}(\text{CNBu}^t)_2$ contributes six electrons, whilst in mononuclear complexes two electron addition is the observed bonding mode. This obviously implies a potentially different chemistry for the trinuclear complexes from that established for mononuclear systems, and emphasises the necessity for an extensive comparative study of the chemistry of trinuclear systems. The natural extension of such investigations to heteronuclear complexes offers a further variation in chemical reactivity, particularly if this involves the use of metals such as platinum and gold, which often form stable derivatives with 14e or 16e configurations.

Chapter One outlines a study of the substitution chemistry (with respect to Group VB ligands) of $\text{Ru}_3(\text{CO})_{12}$. The following three objectives formed the impetus for this work:

- i) to synthesize specifically substituted derivatives, $\text{Ru}_3(\text{CO})_{12-n}\text{L}_n$ ($n = 1-4$) in high yield, with a view to forming mixed ligand derivatives of the form $\text{Ru}_3(\text{CO})_9\text{L}^1\text{L}^2\text{L}^3$.
- ii) to investigate the reactivity of some of these substituted derivatives toward unsaturated organic ligands. For example, the reactivity of $\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3$ with cyclopentadiene and azulene was investigated.
- iii) to investigate the structural and spectroscopic relationships between various mono-, di-, tri-, or tetra-substituted derivatives of $\text{Ru}_3(\text{CO})_{12}$.

In describing this work, reference is made to current bonding theories of metal clusters, kinetic investigations of substitution processes, and relevant electrochemical studies.

Chapter Two focuses on a fourth objective:

iv) the synthesis of heterometallic clusters incorporating both ruthenium and platinum.

The reactivity of $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ towards suitable zerovalent platinum reagents was investigated, leading to the synthesis of a highly unstable intermediate. On the basis of subsequent reactivity with two-electron donor ligands, this intermediate was postulated to be $\text{RuPt}_2(\text{CO})_4(\text{PPh}_3)_3$, containing a Pt=Pt bond.

The early work of Nyholm and Lewis showed that stable gold-osmium clusters could be obtained by oxidative-addition of $\text{AuX}(\text{PR}_3)$ ($\text{X} = \text{halide}$) to osmium carbonyl clusters. An interesting extension of this work is the use of Group IB acetylides (as their tertiary phosphine complexes), whereby mixed metal-osmium clusters containing potentially reactive acetylide functions would be obtained. It was first necessary to develop efficient high yield syntheses of $\text{Au}(\text{C}_2\text{R})\text{PR}_3$ compounds. Chapter Three outlines these synthetic studies, and extends them to copper and silver complexes.

Chapter Four then outlines the reactivity of Group IB phosphine acetylide complexes with $\text{H}_2\text{Os}_3(\text{CO})_{10}$. For example, $\text{Au}(\text{C}_2\text{C}_6\text{F}_5)(\text{PPh}_3)$ reacts with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ to give $\text{AuOs}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CHCHC}_6\text{F}_5)(\text{PPh}_3)$ in quantitative yield. The subsequent reactivity of such clusters was investigated. For instance, initial pyrolysis of $\text{AuOs}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-CHCHC}_6\text{F}_5)(\text{PPh}_3)$ gave $\text{HAuOs}_3(\text{CO})_8(\mu\text{-}\eta^2\text{-CHCHC}_6\text{F}_5)(\text{PPh}_3)$ in good yield. The reactivity of Group IB phosphine acetylide complexes

toward $\text{Ru}_3(\text{CO})_{12}$ was also investigated. For instance, when $\text{Cu}(\text{C}_2\text{Ph})(\text{PPh}_3)$ reacts with $\text{Ru}_3(\text{CO})_{12}$ a host of products are produced, from which $\text{HCuRu}_3(\text{CO})_{10}(\text{PPh}_3)$, $\text{CuRu}_3(\text{CO})_9(\text{C}_2\text{Ph})(\text{PPh}_3)$ and $\text{Cu}_2\text{Ru}_3(\text{CO})_7(\text{C}_2\text{Ph})_2(\text{PPh}_3)_2$ can be isolated.