

SYNTHETIC ASPECTS AND THE CHEMISTRY OF SOME NOVEL CLUSTER COMPLEXES

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The telluro cluster $\text{Fe}_3\text{Te}_2(\text{CO})_9$ has been used as a starting block for the synthesis of a number of mixed metal complexes of the general form $\text{Fe}_3\text{MTe}_2(\text{CO})_9(\text{PPh}_3)_i$, $M = \text{Pt, Pd, Ni}$, as well as a novel higher nuclearity telluro ruthenium cluster. The mechanism in a majority of the reactions of $\text{Fe}_3\text{Te}_2(\text{CO})_9$ involves the formation of the adduct $\text{Fe}_3\text{Te}_2(\text{CO})_9L$, $L = \text{CO, PPh}_3$. The adduct readily undergoes substitution of the $\text{Fe}(\text{CO})_3L$ fragment by incoming, new metal fragments. The reactive dinuclear molecule, $\text{Fe}_2\text{Te}_2(\text{CO})_6$ readily adds coordinatively unsaturated triosmium or triruthenium fragments to give the novel clusters, $\text{Fe}_2\text{Os}_3\text{Te}_2(\text{CO})_{17}$ and $\text{Fe}_2\text{Ru}_3\text{Te}_2(\text{CO})_{17}$. The activation of carbene ligands on $\text{Fe}_3\text{Te}_2(\text{CO})_9$ has been studied and the new bis methylidene complex, $\text{Fe}_2\text{Te}_2(\text{CO})_6(\text{CH}_2)_2$ has been prepared.

Key Words : Mixed Metal; Clusters; tellurium; Synthesis

INTRODUCTION

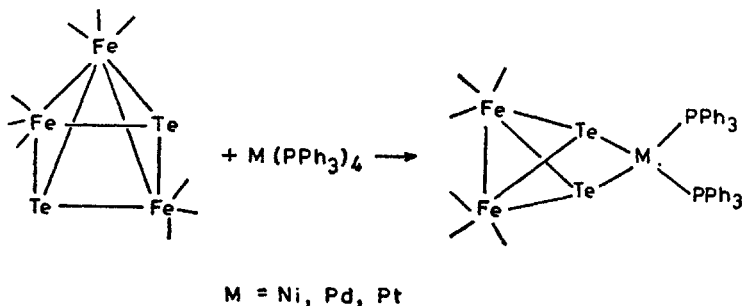
DUE to their potential as a novel breed of catalysts, transition metal clusters continue to attract much attention.^{1,2} However, only recently have systematic synthetic strategies for obtaining clusters of somewhat predictable electronic and structural properties started to appear in the literature.³⁻⁵ A well-tested and convenient method for building metal clusters has been the use of single atom ligands derived from certain main group elements of the Periodic Table as coupling sites.⁶ Numerous sulphido clusters have been prepared using this approach, and it has been shown that the sulphido ligands act as initial points of contact for incoming metal carbonyl units as a first step in the cluster growth reactions.⁷ Often the bridging ligands influence ligand elimination leading to new metal-metal bond formation. Apart from sulphur as a ligand, several examples exist where the selenium ligand has been used for the cluster build-up reactions.⁸ In spite of the recognised utility of the chalcogen ligands in cluster chemistry, the use of tellurium as a ligand in clusters has so far been restricted to far fewer examples than sulphur or selenium. The few examples of tellurium containing complexes that do exist display properties which suggest that the chemistry of tellurium as a ligand will in fact be quite different from that of sulphur and selenium due to its considerably larger size and its relative Lewis acidity. Here, we wish to discuss the use of $\text{Fe}_3\text{Te}_2(\text{CO})_9$ as a starting material for the synthesis of a number of novel telluro complexes.

EXPERIMENTAL

All reactions were routinely performed on millimolar scales using standard Schlenk techniques under pure Ar atmosphere. The solvents were purified and dried prior to use. In a typical reaction, the reactants were dissolved in the degassed solvent in a Schlenk tube and the reaction monitored by infrared spectroscopy and tlc. On completion of the reaction, the solvent was removed *in vacuo* and the residue chromatographed on analytical grade silica gel plates using varying proportions of hexane and dichloromethane. The products were recrystallised from hexane/dichloromethane mixtures at -25 .

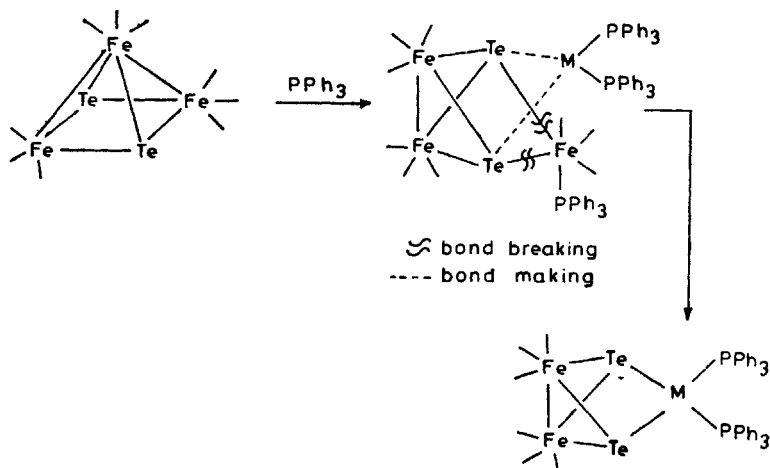
RESULTS AND DISCUSSION

Stirring of a benzene solution containing $\text{Fe}_3\text{Te}_2(\text{CO})_9$ and $M(\text{PPh}_3)_4$, $M = \text{Pt}, \text{Pd}, \text{Ni}$, leads to formation of the mixed metal complexes, $\text{Fe}_2\text{Te}_2(\text{CO})_6 M(\text{PPh}_3)_2$, as well as some $\text{Fe}_3\text{Te}_2(\text{CO})_7(\text{PPh}_3)_2$, (Scheme 1). The Pt and the Pd containing complexes are stable in solution as well as solid states. However, the Ni analogue, though isolable, slowly disproportionates in solution to give $\text{Fe}_3\text{Te}_2(\text{CO})_8(\text{PPh}_3)$. The $M(\text{PPh}_3)_4$ complexes are known to be useful sources of $M(\text{PPh}_3)_2$ and $M(\text{PPh}_3)_3$ species.



SCHEME 1

The former may also be obtained from $M(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$. However, attempts to use the latter complex as a source of the coordinatively unsaturated species have been unfruitful for the synthesis of $\text{Fe}_2\text{Te}_2(\text{CO})_6 M(\text{PPh}_3)_2$, thus indicating that the free triphenylphosphine liberated in solution by $M(\text{PPh}_3)_4$ plays a significant role in the formation of the telluro mixed metal complexes. The reaction of triphenylphosphine with $\text{Fe}_3\text{Te}_2(\text{CO})_9$ leads to the formation in good yield of the adduct, $\text{Fe}_3\text{Te}_2(\text{CO})_9(\text{PPh}_3)$, which when treated with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ gives the complex $\text{Fe}_2\text{Te}_2(\text{CO})_6 \text{Pt}(\text{PPh}_3)_2$ in good yield (Scheme 2). The mechanism of formation of the diironplatinum telluro complex therefore must involve the initial formation of the triphenylphosphine adduct followed by the replacement of the $\text{Fe}(\text{CO})_3\text{PPh}_3$ group by the $M(\text{PPh}_3)_2$ unit.



SCHEME 2

The reactions of $\text{Fe}_3\text{Te}_2(\text{CO})_9$ are in marked contrast to those of the related $\text{Os}_3\text{S}_2(\text{CO})_9$. Thus, whereas $\text{Os}_3\text{S}_2(\text{CO})_9$ readily reacts with $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ to form the mixed metal clusters $\text{Os}_3\text{S}_2(\text{CO})_9\text{Pt}(\text{PPh}_3)_L$, $L = \text{CO}, \text{PPh}_3$, the assembly of which involves the formation of new Os-Pt bonds,⁷ the larger size of tellurium prevents the formation of any new metal-metal interaction and there is a tendency for the formation of the new mixed metal complexes by substitution of a metal fragment in the original molecule. The size of the hetero metal atom also has a significant role in dictating the overall stability, or lack of it, in the mixed metal complex. For instance, the larger sizes of Pt (1.30Å) and Pd (1.28Å) as compared to that of Ni (1.15Å) would imply an opening of the cluster framework during substitution of the Fe (1.17Å) fragment during the formation of the complexes $\text{Fe}_2\text{Te}_2(\text{CO})_6\text{M}(\text{PPh}_3)_2$. The relatively greater stabilities and the higher yields of the Pt and Pd containing mixed metal complexes prepared suggest that there is indeed some reduction of strain in the cluster framework when Pt or Pd, rather than Ni substitutes the Fe fragment.

On refluxing equimolar amounts of $\text{Fe}_3\text{Te}_2(\text{CO})_9$ and $\text{Ru}_3(\text{CO})_{12}$ in benzene solvent for 5 hours, the tetraruthenium cluster, $\text{Ru}_4\text{Te}_2(\text{CO})_{11}$ is formed in good yield. The new ruthenium cluster has been characterised by infrared spectroscopy, mass spectrometry, and microanalysis. The infrared spectrum shows the presence of both terminal and bridging carbonyls. There is good agreement between the experimental and the computer simulated isotopic pattern for the Ru_4Te_2^+ fragment. The type of transmetallation reaction leading to the formation of $\text{Ru}_4\text{Te}_2(\text{CO})_{11}$ has precedence in $\text{Co}_4\text{Te}_2(\text{CO})_{11}$, formed from $\text{Fe}_3\text{Te}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$ ¹⁰. The related molecule $\text{Os}_4\text{S}_2(\text{CO})_{12}$ has been structurally characterised and shown to have an unusual butterfly geometry of the four metal atoms with five metal-metal bonds, i.e., one metal-metal bond more than expected for a 64 electron cluster.¹¹ Assuming tellurium to be a four electron donor, $\text{Ru}_4\text{Te}_2(\text{CO})_{11}$ is also a

62-electron cluster, and therefore is expected to have a structure based on five metal-metal bonds. The marked difference in the infrared spectra of $\text{Ru}_4\text{Te}_2(\text{CO})_{11}$ and $\text{Os}_4\text{S}_2(\text{CO})_{12}$ indicates that the two clusters adopt different geometrical shapes. The infrared spectrum of $\text{Ru}_4\text{Te}_2(\text{CO})_{11}$ in the carbonyl region is indeed very similar to the recently reported pentaruthenium sulphido cluster, $\text{Ru}_5\text{S}(\text{CO})_{15}$. If it is visualised that the sulphur and the ruthenium carbonyl fragment trans to it are replaced by tellurium, $\text{Ru}_4\text{Te}_2(\text{CO})_{12}$ would be obtained, (Fig 1).

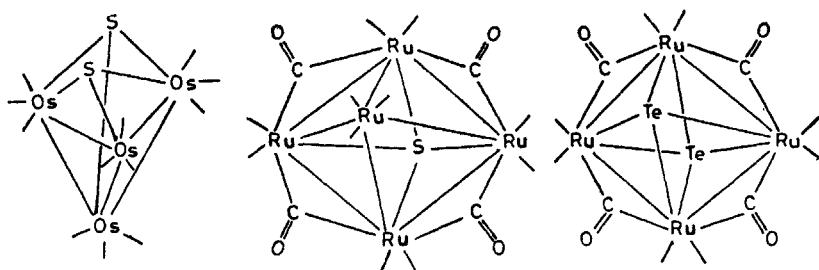


FIG 1

Polynuclear coordinatively unsaturated species have been shown to react with $\text{Fe}_2\text{Te}_2(\text{CO})_6$. The reactive complex, $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ readily reacts with $\text{Fe}_2\text{Te}_2(\text{CO})_6$ in benzene to yield a dark red coloured product, which on the basis of infrared spectroscopy, mass spectrometry, and microanalysis can be identified as the mixed metal cluster, $\text{Fe}_2\text{Os}_3\text{Te}_2(\text{CO})_{17}$. With the tellurium ligands acting as four electron donors each, $\text{Fe}_2\text{Os}_3\text{Te}_2(\text{CO})_{17}$ will be a 82-electron cluster, suggesting the presence of four metal-metal bonds on the basis of the 18 electron rule. Adams has clearly demonstrated that whenever $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$ or $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ is used as a source of reactive coordinatively unsaturated species, the trinuclearity is maintained⁷. In the preparation of the sulphido osmium cluster, $\text{Os}_7\text{S}_2(\text{CO})_{20}$ from $\text{Os}_4\text{S}_2(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ the reactive ' $\text{Os}_3(\text{CO})_{10}$ ' adds to the lone pairs on the sulphur in $\text{Os}_4\text{S}_2(\text{CO})_{12}$ by an opening of the triangular framework, i.e. by cleavage of one Os-Os bond⁹. Thus, in the formation of $\text{Fe}_2\text{Os}_3\text{Te}_2(\text{CO})_{17}$, the reactive ' $\text{Os}_3(\text{CO})_{11}$ ' probably undergoes cleavage of one Os-Os bond while adding to the tellurium-tellurium bond in $\text{Fe}_2\text{Te}_2(\text{CO})_6$. After the initial contact of osmium moiety with the tellurium ligands, even the large size of tellurium may not be sufficient to prevent an interaction between the tip osmium atoms and the two iron atoms. This may be facilitated further if there is a cleavage of the Fe-Fe bond. That the reactive FeFeTeTe ring in $\text{Fe}_2\text{Te}_2(\text{CO})_6$ may also be an important factor in the overall reaction is also suggested when $\text{Fe}_2\text{Te}_2(\text{CO})_6$ is allowed to react with $\text{Ru}_3(\text{CO})_{12}$ in benzene solvent at room temperature. After four hours, the new cluster $\text{Fe}_2\text{Ru}_3\text{Te}_2(\text{CO})_{17}$ is formed in good yield. The similarities in the infrared spectra of the Fe_2Os_3 and the Fe_2Ru_3 clusters indicate that both have similar structures.

Work is currently under progress to investigate the reactivity of $\text{Fe}_2\text{Te}_2(\text{CO})_6$ and $\text{Fe}_3\text{Te}_2(\text{CO})_9$ towards additional metal fragments as well as small organic

moieties. Our most recent work shows that the telluro iron molecules are susceptible to add fragments arising from the extremely reactive $\text{Mo}(\text{dppe})_2(\text{N}_2)_2$ and organic carbene groups. The novel $\text{Fe}_2\text{Te}_2(\text{CO})_6(\text{CH}_2)$ has been prepared and its full characterisation is presently under way. Overall, our studies on the reactivity and the general potential of tellurium ligands demonstrates that these large ligands can be employed for the generation of clusters having different structural features, and hence contrasting reactivities from the related sulphur-containing clusters.

TABLE I
Infrared spectral data of some telluro complexes

Complex	I.R. (CO stretching frequencies/cm ⁻¹)			
$\text{Fe}_2\text{Te}_2(\text{CO})_6$	2067 (s),	2028 (vs),	1995 (s),	
$\text{Fe}_3\text{Te}_2(\text{CO})_6$	2045 (s),	2025 (s),	2004 (s),	
$\text{Fe}_2\text{PtTe}_2(\text{CO})_6 (\text{PPh}_3)_2$	2031 (s),	1991 (s),	1955 (s),	1947 (sh),
$\text{Fe}_2\text{PdTe}_2(\text{CO})_6 (\text{PPh}_3)_2$	2033 (s),	1992 (s),	1958 (s),	1948 (sh),
$\text{Fe}_2\text{NiTe}_2(\text{CO})_6 (\text{PPh}_3)_2$	2041 (s),	2016 (s),	1990 (m)	
$\text{Ru}_4\text{Te}_2(\text{CO})_{11}$	2087 (w),	2044 (s),	2026 (m),	1989 (m),
	1827 (w),			
$\text{Fe}_2\text{Os}_3\text{Te}_2(\text{CO})_{17}$	2127 (w),	2899 (m),	2069 (w),	2057 (m),
	2053 (vs),	2044 (m),	2039 (m),	2022 (m),
	2015 (w),	1996 (m),	1989 (w),	1973 (m),
	1965 (w),			
$\text{Fe}_2\text{Ru}_3\text{Te}_2(\text{CO})_{17}$	2122 (w),	2093 (m),	2068 (w),	2053 (vs),
	2039 (m),	2028 (w),	2020 (m),	2005 (m),
	1994 (m),	1985 (w).		

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