

09.X-1 THE STEREOCHEMICAL VERSATILITY OF CHLORO-MERCURY ANIONS IN CRYSTALLIZING TRANSITION METAL COMPLEXES. By Ward T. Robinson, Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

A set of ten low temperature crystal structure analyses illustrates the extensive structural variety characteristic of anions containing both chlorine and mercury atoms. Correlations between these structures and related anions in the literature (Battaglia, Corradi, Antolini, Manfredini, Menabue, Pellacani and Ponticelli, J. Chem. Soc. Dalton Trans., 1986, 2529) will be illustrated.

Six different discrete anions, each containing from 1 to 4 mercury atoms, and also 2 polymeric anionic structures have been distinguished. Crystal structures of complexes with identical empirical formulae for the anion can contain totally different structural units whereas genuine geometrical isomerism accounts for differences between their counter cations.

Stoichiometric similarities and structural differences will be summarized and highlighted.

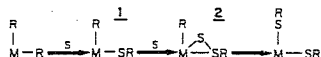
09.X-2 ORGANOTUNGSTEN COMPLEXES WITH OXYGEN AND SULPHUR LIGANDS. By Peter Legzdins, Steven J. Rettig and James Trotter, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6.

Treatment of the diiodide dimer, $[\text{CpW}(\text{NO})\text{I}_2]_2$, Cp = cyclopentadienyl, with the Grignard reagent RMgCl , R = CH_2SiMe_3 , and then with water produces a novel formally 16-electron dialkyl complex, $\text{CpW}(\text{NO})\text{R}_2$. The complex has the usual "piano-stool" molecular structure, and the linear WNO group, and short W-N and long N-O bonds (1.757(8) and 1.226(10) Å, respectively) indicate considerable W→NO back-bonding.

A solution of $\text{CpW}(\text{NO})\text{R}_2$ when exposed to O_2 at room temperature gives rise to an oxo complex, $\text{CpW}(\text{O})_2\text{R}$, also a formally 16-electron complex, with tungsten-oxygen distances (1.720(4) Å) consistent with the presence of W=O double bonds.



Reaction with sulphur proceeds in a different manner, with sequential insertion of sulphur into the metal-carbon single bonds ($\text{M} = \text{CpW}(\text{NO})$):



The molecular structures of the sulphur-containing complexes resemble those of the parent dialkyl complex, with linear WNO groupings, short W-N and long N-O bonds (1.778 and 1.213 Å). The organosulphur ligands are attached to W by essentially single bonds, so that 1 can be viewed as a 16-electron complex, while 2 can be formulated as an 18-electron species in which the $\text{n}^2-\text{S}_2\text{R}$ ligand functions as a formal 3-electron donor.

09.X-3 TRENDS IN TRANSITION METAL CARBYNE CHEMISTRY By J.A.K. Howard, O. Johnson, E. Baumann, P. Sherwood, R. Musgrove, and F.G.A. Stone, Department of Inorganic Chemistry, University of Bristol, England.

The formation of transition metal carbyne complexes has been developed and rationalised during the past few years using the database of our own experimental work and with consideration of the isolobal analogy (1).

The dimetal species, once a novelty, have become routine starting complexes for more adventurous cluster formation. The route leading to cyclization of 8 metal atoms is well documented (2) and we have recently produced new variations of these larger clusters.

Recognition that the fragments $[\text{W}(\text{CO})_2(\eta\text{-C}_5\text{R}_5)]$ and $[\text{W}(\text{CO})_2(\eta\text{-C}_2\text{B}_9\text{R}_2)]^-$ are isolobal, lead us to use the anion, which by seemingly focussing the electron density onto the tungsten centre produces carbyne metal species which undergo unusual reactions. For example, the hydroboration of the carbaborane cage (3) and the polyhedral rearrangement of the 11-vertex ligand (4).

The ligating properties of the (pyrazolyl)borato anions $[\text{R}^-\text{Bpz}_3]^-$ have also been exploited in this area with the formation of several of the analogues of the "Cp-W" complexes, e.g. $[\text{W}(\equiv\text{CR})(\text{CO})_2(\text{R}^-\text{Bpz}_3)]$, $[\text{Rh}_2(\mu_3\text{-CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_7)_2(\text{HBpz}_3)]$ and $[\text{FeRhW}(\mu_3\text{-CR})(\mu\text{-MeC}_2\text{Me})(\text{CO})_4(\eta\text{-C}_9\text{H}_9)(\text{HBpz}_3)]$.

Some details of these preparations appear in the literature, others will be discussed in more detail with the systematics of structural type emerging from the work.

1. R. Hoffmann, *Angew.Chem., Int.Ed.Engl.*, 1982, 21, 711.
2. G.P. Elliott, J.A.K. Howard, T. Mise, C.M. Nunn, and F.G.A. Stone, *Angew.Chem., Int.Ed.Engl.*, 1986, 25, 190.
3. M. Green, J.A.K. Howard, A.P. James, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Chem.Commun.*, 1983, 1113.
4. M.J. Atfield, J.A.K. Howard, A.N. de M. Jelfs, C.M. Nunn, and F.G.A. Stone, *J.Chem.Soc., Chem. Commun.*, 1986, 918.