



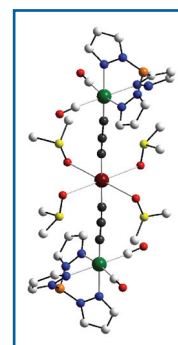
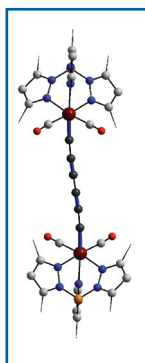
INORGANIC CHEMISTRY

Synthetic Organometallic and Coordination Chemistry Professor Anthony Hill

Our work covers a wide range of topics in coordination and organometallic chemistry. Particular foci include unsaturated ligands involving metal-carbon multiple bonding and the interface of transition and main group chemistries. In attempting to understand and ideally control the reactivity of such systems, the nature of the metal centre is of paramount importance and this may be tuned through variations in oxidation state, d-configuration and, most importantly, the nature of the co-ligands. Accordingly, considerable effort is directed towards the synthesis of new co-ligands which themselves do not directly take part in ligand transformations but may moderate these indirectly. This work is currently centred on two classes of ligands; polythiamacrocycles and poly(methimazoly)chelates.

Dimetallapolycarbyls: Tri-, Tetra-, Hexa- and Octa-carbido Molecular Wires: $L_nMC_xML_n$ ($x = 3, 4, 6, 8$)

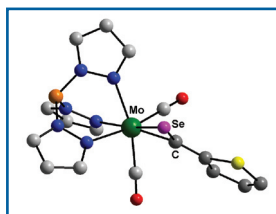
The vast majority of compounds in which two metal centres are linked by a linear chain of carbon ('molecular wires') are based on an even number of carbon atoms. This is simply because the majority of routes to such compounds involve alkyne, diyne and poly-yne modifications, *i.e.*, the carbon is introduced in packets of two, $-C\equiv C-$. Furthermore, such chains are typically bound to metal centres *via* a simple metal-carbon single bond. This has resulted in a number of gaps in what is otherwise an intensely studied field. We have, therefore, targeted the development of synthetic routes that will afford access to (i) bimetallics with *odd* numbered carbon chains and (ii) carbon chains that are bound to the metal centres *via M-C multiple bonding*. Highlights this year have included the syntheses of the first bis(tricarbido) trimetallics centred on ruthenium, iridium and mercury (see right); the first example of the catalytic demercuration of bis(metallapolycarbido)mercurials; and the first bimetallic hexacarbido complex with a hexa-2,4-diyne-1,6-diylidyne bonding pattern (see left). These results provide the basis for the award of ARC Grant DP0556236 to commence in 2005. (*With R Dewhurst, A C Willis*)

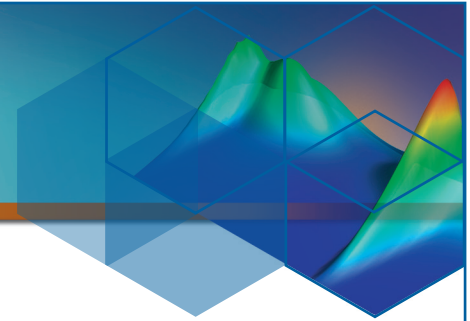


Metal butadiynyls L_nMC_4H are also key building blocks for the construction of bimetallics spanned by the tetracarbido linkage $L_nMC_4ML_n$. Whilst numerous examples now exist, surprisingly little subsequent functionalisation of the C_4 unit has been reported. In addressing this, we have succeeded in obtaining the first transition metal examples of bimetallics spanned by CCCHC, CCCCHC and CCCHCH linkages, the latter *via* the hydrometallation of a terminal σ -butadiynyl complex. (*With M J Bartlett, M K Smith*)

Organometallic Chemistry of Unsaturated Organoselenium Compounds

Last year we reported the remarkable fragility of C-Se bonds in isoselenocyanates and alkynyl selenoethers when presented with various organotransition metal complexes. Rather than viewing this as a problem, we have taken a different approach and exploited this reactivity. Effective single-atom selenium transfer reagents are rare, however, we have been able to show that isoselenocyanates are able to serve this purpose. This has been demonstrated in the reactions of $RNCSe$ ($R = C_6H_2Me_3-2,4,6$) with a range of alkylidynes which provide the first examples of group 6 selenoaryl complexes, including both



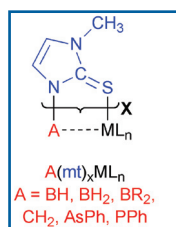


mononuclear (see above left) and binuclear examples. The side product in these reactions is the free isonitrile RNC and it could be shown that isonitriles can thereby serve to catalytically activate elemental selenium. (With L M Caldwell, A C Willis)

Methimazolyl Chelate Complexes

Previous annual reports have described a range of 'scorpionate' ligands in which a bridgehead group ('A') bound to two or three ('x') methimazolyl heterocycles ('mt') acts as a chelate to a metal centre ('ML_n') [ARC Grant DP034270]. The majority of recent work has involved boron derivatives with which the metal associates *via* a transannular dative M→B bond within a cage structure (metallaboratranes). These were previously limited to our own studies of examples involving

zerovalent metals from group 8, wherein the M→B bond was bridged by three *mt* buttresses. Thus, questions arose as to (i) their generality and (ii) the need for three *mt* bridges. Both questions have been partially addressed. Firstly, the metallaboratrane class of compounds has now been successfully extended to include metals from group 9 (Ir, Rh) and 10 (Pt), 0, +1 and +2 metal oxidation states, d⁸ and d¹⁰ electronic configurations and geometries involving 5 or 6 coordinate metals. Thus the metallaboratrane motif appears to be generally accessible for late transition metals with high d-occupancies. Furthermore, the isolation of a di-buttressed iridaboratrane, devoid of the geometric constraints of the

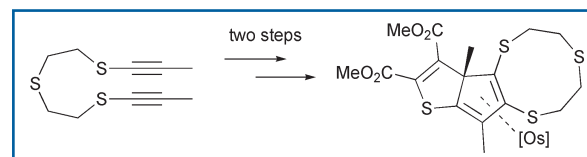


previous tri-buttressed examples, substantiates the claim that there is a genuine electronic basis for invoking M→B bonding and that it is not simply a ramification of a constrained cage geometry.

The second thrust of this research involves the study of methimazolylborate coordination to early transition metals with low d-configurations and high oxidation states. This might appear to represent a mismatch of metal and donors within the hard and soft acid and base conceptual framework. We have, however, shown that a range of derivatives based on metals from groups 4 (Ti, Zr), 5 (Nb, Ta) and 6 (Mo, W) are indeed accessible, although as might be expected, they are highly reactive. A variety of organometallic H₂B(mt)₂ and HB(mt)₃ complexes have thus been obtained bearing carbonyl, stannyl, alkyne, cyclopentadienyl, allyl, imido or phosphine ligands. (With R J Abernethy, I R Crossley, E R Humphrey, A D Rae, M K Smith, N Tshabang, A C Willis)

Polythioether Macrocycles

The cyclisation of α, ω-dialkynyl polythioethers provides a potential route to macrocyclic thioethers. We have now applied this approach to systems that also incorporate CO or CS within the alkyne coupled ring to provide cyclopentadien-1-one and cyclopentadien-1-thione complexes. In the latter case, the sulfur group is particularly nucleophilic and we have observed a novel [3+2] cycloaddition reaction with an activated alkyne to regioselectively provide an unusual tricyclic tetrathia-macrocyclic. (With A D Rae, M Schultz, A C Willis)



<http://rsc.anu.edu.au/research/hill.php>



Members of the research group