



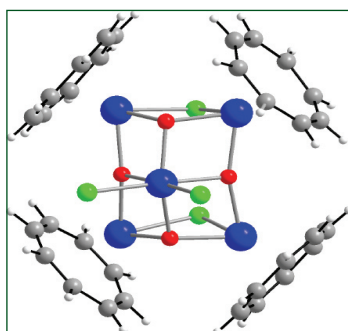
# SYNTHETIC ORGANOMETALLIC AND COORDINATION CHEMISTRY

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Our work covers a diversity of challenges 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; 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 necessarily take part in the transformations of other ligands but may moderate these indirectly.

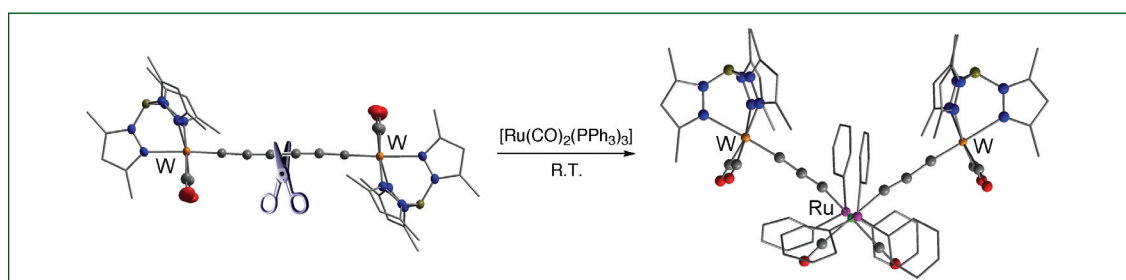
## Cyclooctatetraene ( $C_8H_8$ ) Chemistry

We have initiated a study of the chemistry of coordinated cyclooctatetraene ( $C_8H_8$ ), specifically involving the early transition metals. The key feature of  $C_8H_8$  in an organometallic context is that it may, as a ligand, provide 2, 4, 6 or 8 valence electrons to a metal centre and this is manifest in the adopted geometry. We have thus used the hapticity of  $C_8H_8$  as a 'reporter' to assess the nature of bonding of other co-ligands. Specifically, the facility with which poly(azolyl)borate ligands may enter into 3-centre, 2-electron B-H-Metal interactions has been assessed with respect to the synthesis of a range of complexes of the form  $[ZrCl(C_8H_8)(L)]$  ( $L = H_2B(pz)_2, H_2B(mt)_2, HB(pzMe_2)_3$  etc). Tangential to the systematic chemistry, we have isolated an aesthetically beautiful side product (shown) that comprises a pyramidal array of five zirconium centres bridged by oxide and chloride ligands and encapsulated by four planar cyclooctatetraene ligands. *(With M K Smith)*



## Carbon Wires with Metal Carbon-multiple Bonding

It has long been argued that connecting two metals by a linear chain of carbon atoms would provide a means of electronic communication between the metals - 'a carbon wire'. Reflecting their ease of synthesis, effort has generally focused on poly-yne-diyl carbon chains that bind to the metal centres as simple  $\sigma$ -acetylides with at best modest retrodonation into the unsaturated  $\pi$ -system of the carbon spacer. Our approach has been to turn to the strongest known  $C_1$ - $\pi$ -acid ligands - alkylidynes with metal-carbon triple bonds - on the grounds that metal to ligand charge transfer will be most favoured in such systems. Recent advances within the group have included the first examples of dimetallaocotatetraynes for which a valence-localised bonding description of the form  $L_n W \equiv C-C \equiv C-C \equiv C-W L_n$  has been shown to be appropriate as distinct from the more



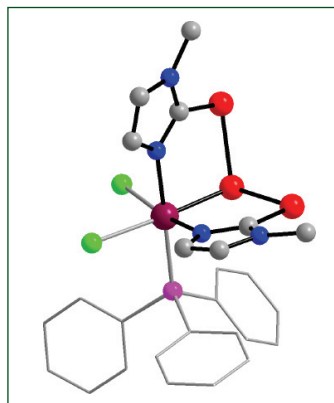
common  $L_nM-C\equiv C-C\equiv C-C\equiv C-ML_n$  description for a hexacarbido linkage. Lessons learned from the discovery of such species have now led us to a '3+1' synthetic strategy for the synthesis of both symmetrical and non-symmetrical dimetallahexatriynes of the form  $L_nW\equiv C-C\equiv C-C\equiv ML_n$  ( $M = Mo, W$ ). We have also now considered the functionalisation of carbon wires. One of the most versatile methods for alkyne functionalisation involves hydrometallation of  $-C\equiv C-$  bonds. We have now shown that this may be extended to carbon wires and reported the first such reaction leading to complexes in which two metals are spanned by the 'C<sub>6</sub>H' ligand to which is also appended a third metal, thus paving the way for protocols allowing the decoration of carbon wires with further tangential metal centres. Our synthesis of the first dimetallaooctatetraynes involved the coupling of two tricarbido-metal precursors. In a remarkable reverse of this process we have reported the cleavage of one Csp-Csp bond of a carbon wire to provide complexes in which the third metal is inserted into the carbon chain. (With R D Dewhurst, M K Smith, A C Willis)

### Alkyne-alkylidyne Coupling and Chalcogenolate Migration Process

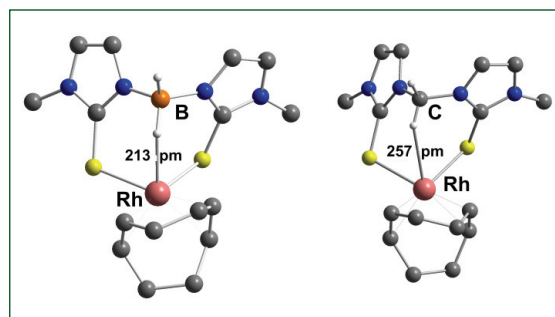
Of relevance to the Fischer Tropsch process is the coupling of small C<sub>1</sub> and C<sub>2</sub> fragments on metal surfaces and such processes have been modelled using bimetallic molecular complexes. Building on our previous studies of intraligand chalcogenolate migration on mononuclear complexes, we have now investigated the coupling of alkylidyne (C<sub>1</sub>) and alkyne (C<sub>2</sub>) units in which the alkyne bears chalcogenolate substituents. In dramatic contrast to simple hydrocarbon chemistry, a far more complex situation arises in which a plethora of novel unsaturated organoselenium ligands have been encountered. (With L M Caldwell, A C Willis)

### Unusual Methimazolyl-derived Ligands

We have in previous years pursued the chemistry of poly(methimazolyl)borates and boranes, however more recent emphasis has turned to alternative polydentate ligands in which the bridgehead boron atom is replaced by other potential donors. Two highlights include the first complexes of bis(methimazolyl)methanes, H<sub>2</sub>C(mt)<sub>2</sub> (mt = methimazolyl) and bis(imidazolyl)polyselenanes. In the former, it could be shown that the geometry



predisposes the chelate towards incipient agostic C-H-Metal interactions allowing direct comparison with isoelectronic B-H-Metal systems as illustrated above for the complexes [Rh(cod){H<sub>2</sub>X(mt)<sub>2</sub>}] (X = B, C<sup>+</sup>). The coordination chemistry of diorganopolyselenanes 'RSe<sub>n</sub>R', has not previously been explored. We have now synthesised the novel ligand Se<sub>3</sub>(mt)<sub>2</sub> via a templation protocol providing the complex [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]{Se<sub>3</sub>(mt)<sub>2</sub>} (shown left) in which the ligand coordinates in a tridentate manner through one selenium and two nitrogen donors. (With I R Crossley, E R Humphrey, M K Smith, N Tshabang, A C Willis)



### B-functionalisation of Poly(pyrazolyl)borates

Poly(pyrazolyl)borates H<sub>x</sub>B(pz)<sub>4-x</sub> are renowned as 'innocent' spectator ligands that generally play no direct role in the subsequent chemistry of their complexes. We are currently studying situations in which this is demonstrably not the case. Specifically, the bridgehead borohydride groups have now been shown to enter into metal-mediated methanolysis reactions providing complexes of, for example, the novel (MeO)<sub>2</sub>B(pz)<sub>2</sub> ligand in which one methoxide group also acts as a donor to the metal centre. (With R J Abernethy, M K Smith, A C Willis)

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