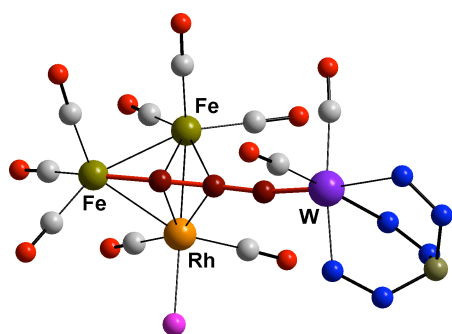


Our work covers a wide range of topics in coordination and organometallic chemistry. Particular foci include unsaturated ligands involving metal-carbon multiple bonding and the interface of transition and main group chemistries. In attempting to understand and ideally control the reactivity of such systems, 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(methimazolyl)chelates.



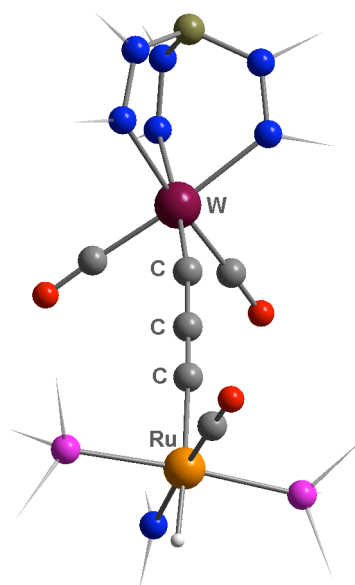
Tricarbido Molecular Wires: $L_nM\equiv C-C\equiv C-ML_n$

There has been enormous growth in recent years in the synthesis of compounds with two metal centres linked solely by a chain of carbon atoms. However, this work has focused almost exclusively on even numbered carbon chains, i.e., $L_nM(C\equiv C)ML_n$. We have now developed a route to bimetallics spanned by a three-carbon (tricarbido) chain, $L_nM\equiv C-C\equiv C-ML_n$ (see right), that should have wide applicability. This is based on the fluorodesilylation of silypropargylidyne complexes of the group 6 metals, and



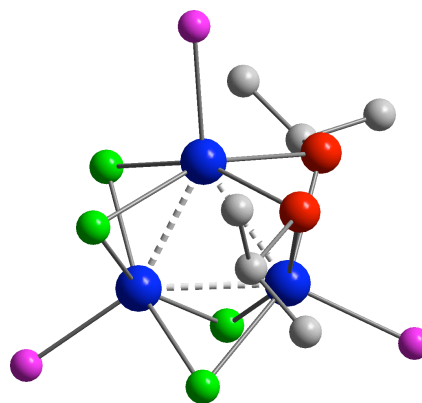
trapping of the desilylated species with a range of transition metal complexes. The

resulting bimetallic complexes serve as precursors to polymetallic species of higher nuclearity through coordination of the localised $-C\equiv C-$ triple bond to further metal centres (see left). (with R. Dewhurst, M.K. Smith, A.C. Willis)



Organometallic Chemistry of Unsaturated Organoselenium Compounds

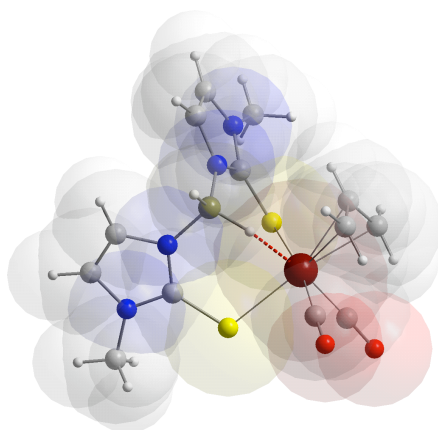
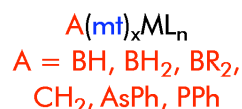
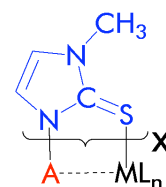
Selenoalkynes, $R-C\equiv C-SeR'$ and alkynylselenolates $R-C\equiv C-Se^-$ offer a number of potential points of reactivity in combination with transition metals. We have been investigating the organometallic chemistry of such species, in parallel with that of isoelectronic isoselenocyanates, $R-N=C=Se$. In both cases the C-Se bonds have been found to be particularly fragile, facilitating either intramolecular rearrangements, or



complete fragmentation. Thus, *e.g.*, the reaction of $[\text{Ru}_2\text{Cl}_4(\eta^6\text{-cymene})_2]$ with $\text{Ph-C}\equiv\text{CSe}^i\text{Pr}$ and PCy_3 was found to provide both the vinylidene complex $[\text{RuCl}_2(=\text{C}=\text{CHPh})(\text{PCy}_3)_2]$ and the unusual cluster $[\text{Ru}_3(\mu\text{-Se}^i\text{Pr})_2(\mu\text{-Cl})_4(\text{PCy}_3)_3]$ (shown) by cleavage of the C–Se bond. (*with L.M. Caldwell, M.K. Smith, A.C. Willis*)

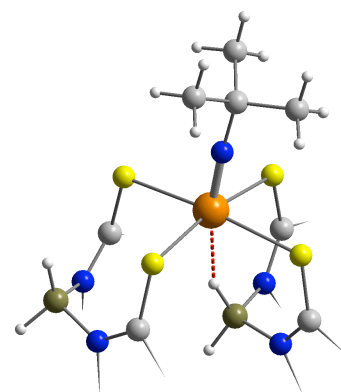
Methimazolyl Chelate Complexes: *Agostic* B–H–Metal Interactions

We have been investigating 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]. Of particular interest is the possibility of transannular interactions between the bridgehead group, A, and the metal. This may be simple dative coordination in the case of $\text{A} = \text{PPh}$, however for $\text{A} = \text{CH}_2, \text{BH}_2$, the question of *agostic* bonding arises. This is of particular relevance to the formation of metallaboratranes via B–H activation.



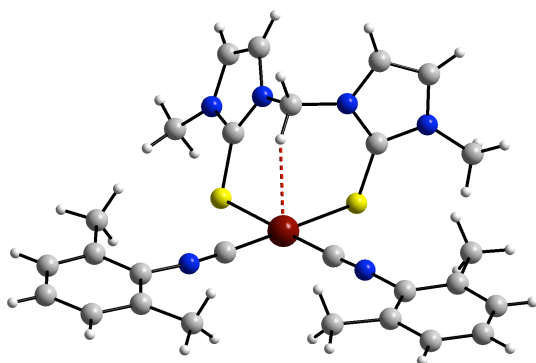
The synthesis of a wide range of complexes featuring such interactions has been achieved for the metals ruthenium, tungsten, rhodium, titanium and molybdenum. The potential hemilability of these B–H–M interactions is currently under investigation. The allyl complex $[\text{W}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\{\text{H}_2\text{B}(\text{mt})_2\}]$ is depicted (left) with the *agostic* B–H–W interaction shown in red.

The imido complex $[\text{Ti}(=\text{NCMe}_3)\{\text{H}_2\text{B}(\text{mt})_2\}_2]$ is unusual in that it displays two distinct coordination modes for the $\text{H}_2\text{B}(\text{mt})_2$ ligands; one simply acts as a bidentate chelate whilst the second also involves the formation of an *agostic* B–H–Ti interaction (shown in red, right).



The facile formation of *agostic* B–H–metal interactions for $\text{H}_2\text{B}(\text{mt})_2$ ligands is in part due to the favourable geometry. We therefore investigated whether such a geometry might induce *agostic* interactions based on elements other than boron. This is indeed the

case as illustrated by the salt $[\text{Rh}(\text{CNC}_6\text{H}_3\text{Me}_2)_2\{\text{H}_2\text{C}(\text{mt})_2\}]\text{BF}_4$ in which the bridgehead CH_2 group is weakly coordinated to both the rhodium centre (shown in red) and the counteranion. (*with R.J. Abernethy, E.R. Humphrey, H. Neumann, M.K. Smith, N. Tshabang, A.C. Willis*)



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