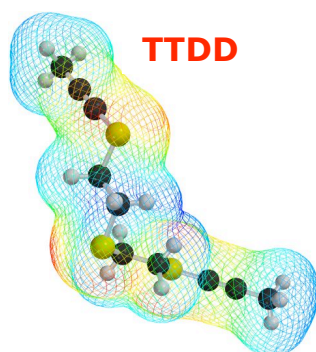


Our work covers a wide range of topics in coordination and organometallic chemistry, focusing primarily on ligand reactivity and transformations. Particular foci include unsaturated ligands involving metal-carbon, metal-phosphorus and phosphorus-carbon multiple bonding and the interface of transition 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. Recently this work has focused on two classes of ligands; based either on polythiamacrocycles or poly(methimazoly)chelates.

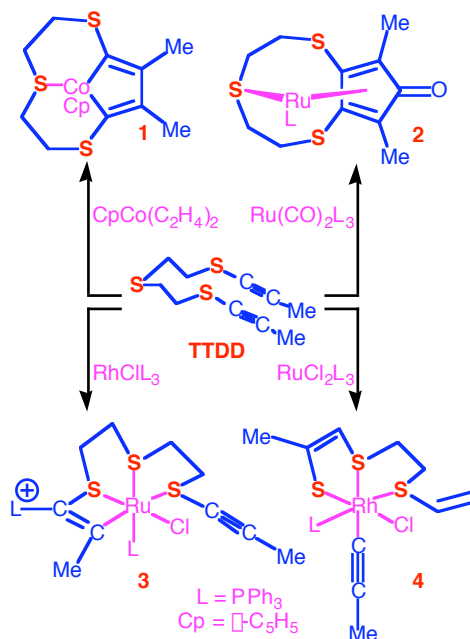


Crystallographic characterisation of new compounds has been carried out in collaboration (with Drs A.C. Willis, A.J. Edwards, Professor A.D. Rae)

Polydentate Thioether Ligands



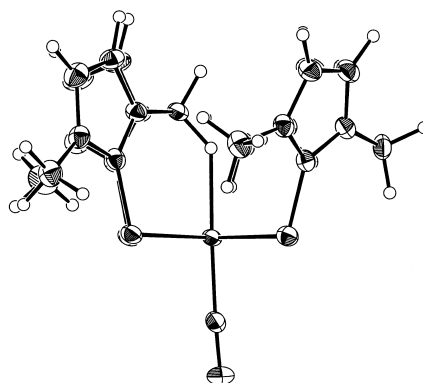
Thioethers are typically weak ligands for transition metals, however the coordinative ability may be enhanced by inclusion of sulfur donors within a macrocycle – i.e., sulfur analogues of crown ethers. Synthetic routes to such macrocycles are currently under investigation in this group. Our strategy is based on the metal-mediated cyclisation of the new π,π -diyne **TTDD**. In some reactions of **TTDD** with metal complexes, the expected cyclisation products are obtained by analogy with hydrocarbon π,π -dienes, e.g., the cobaltacyclopentadiene **1** and the cyclopentadienone complex **2**. In other cases however, the reactivity is diverted as a result of participation or even fragmentation of the thioether groups, e.g., in the formation of the metallacycles **3** and **4**. (with L.M. Caldwell, H. Neumann, M. Schultz)



Methimazolyborates and Metallaboratranes

We have isolated a range of cage structures based on a variety of transition metals ligated by tris(methimazoly)borates, $\text{HB}(\text{mt})_3\text{ML}_n$ (mt = methimazoly). A remarkable feature of these compounds is the possibility of forming direct transannular dative bonds between the metal and boron. En route to these novel

species, intermediates involving *agostic* B-H-M interactions are implicated. Accordingly, we have turned our attention to the isolation of such species, by investigating in detail the coordination chemistry of the simpler bis(methimazolyl)borates, $\text{H}_2\text{B}(\text{mt})_2$. A clear propensity for *agostic* interactions has indeed been established with a number of instances being identified. Amongst these, the complex $\text{W}(\text{CO})\{\text{H}_2\text{B}(\text{mt})_2\}_2$ is particularly informative in that it contains two borate ligands, one with an *agostic* B-H-W interaction, whilst the other is simply bidentate. (with E.R. Humphrey, H. Neumann, N. Tshabang)

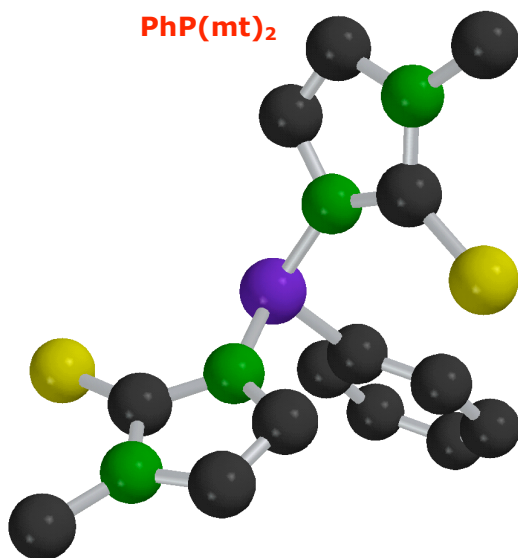


$\text{W}(\text{CO})\{\text{H}_2\text{B}(\text{mt})_2\}_2$

Transition Metal Propargylidynes: $\text{LnM}\equiv\text{C}-\text{C}\equiv\text{C}-\text{R}$

Appreciation of the conceptual analogies between the $\text{C}\equiv\text{C}$ triple bond of alkynes and the $\text{M}\equiv\text{C}$ triple bond of alkylidynes may provide insights in both the design and interpretation of alkylidyne chemistry. We are currently exploring a special case in which both $\text{C}\equiv\text{C}$ and $\text{M}\equiv\text{C}$ bonds are conjugated within the same metallacumulene. Synthetic routes to a range of these have been developed in preparation for a study of their reactivity. (with R. Dewhurst)

Methimazolyl Phosphines and Arsines



In an extension of our work on methimazolylborates, we have explored the synthesis of phosphine and arsine based ligands which bear methimazolyl substituents. These offer both pnictogen and thione groups for coordination a metal centre. The syntheses of these new ligands is based on the reactions of *N*-trimethylsilylmethimazole with the appropriate haloarsine or phosphine. This approach has been applied to the synthesis of a range of phosphines and arsines, including the hexadentate derivative, $(\text{mt})_2\text{PC}_2\text{H}_4\text{P}(\text{mt})_2$. Furthermore, our recent isolation of the corresponding silylated selone provides access to selenium analogues (with R. Dewhurst, E.R. Humphrey, and J.D. Woollins [U. St Andrews])

<http://www.rsc.anu.edu.au/hill.html>