In search of very ‘unnatural products’

What distinguishes synthetic organic and inorganic chemistries? Organic chemistry is often associated with the molecules of life – ‘natural products’. What about the bonding situations that don’t occur in nature (as far as we know) – ‘unnatural products’. This is the overall goal of our research. This might seem esoteric, if it weren’t for the majority of modern organic synthetic techniques involving reagents far-removed from those in nature – e.g., the Grubbs, Stille, Sonogashira, Sharpless, Heck, Wittig and Suzuki processes for constructing C-C bonds all involve organometallic species not found in nature. A selection of some of the curious bonding situations that we are currently exploring follows.

1. Metal-Carbon Multiple bonds – carbenes, carbynes and carbides

Metal-Carbon multiple bonding can take many forms: M–CR₃, M=CR₂ and M≡CR (R = an organic group) bonds are now well understood and each provide useful intermediates in synthetic processes. We have recently discovered a simple way to make terminal carbido complexes (M≡C). These allow us in principle to add any substituent we chose to the single carbon atom. This project will explore two aspects: (i) The synthesis of bimetallic compounds in which two metals are linked by a single carbon atom (the simplest ‘carbon wired circuit’); (ii) The synthesis of carbyne complexes with main group elements as the substituent, providing a link between organometallic, main group and transition metal chemistries.

The picture shows the inner coordination sphere of a tetrametallic complex in which two molybdenum atoms are linked by single carbon atoms to a dipalladium-dibromide core. The molecule is formed by the oxidative addition of a bromocarbyne (Me≡CBr) C–Br bond to palladium(0).

2. Metal-Boron Dative Bonding

The coordination chemistry of the transition metals typically involves a set of ligands (L₂) acting as electron pair donors to a Lewis acidic transition metal. Can we reverse this and engineer situations where the metal acts as an electron pair donor to a Lewis acid, e.g., boron(III)? This has been hypothesised for four decades, but we have only recently isolated the first genuine examples. These strange molecules have a transition metal-boron dative bond (“LₙM→BR₃”) housed within a cage structure – “metallaboratranes”. This project will explore these unusual molecules including both the synthesis of new examples and an investigation of the previously unexplored reactivity of the novel M→B bond.

The picture shows the inner coordination sphere of a platinaboratranne which has a direct dative bond from platinum to boron.

SKILLS ACQUISITION: Anaerobic synthetic techniques, infra-red, NMR (multinuclear, multi-dimensional, variable temperature), mass-spectrometry and X-ray crystallography.