Phosphacarbon-containing Organometallics and Ligands: From Conjugated Cyaphides to Heteroborolediides.

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The diagonal relationship between carbon and phosphorus results in compounds of these two elements sharing appreciable similarities in their chemistry, in terms of structural, electronic and reactivity profiles, while also retaining their own unique character. This is most apparent in unsaturated molecular fragments, wherein multiple bonds between phosphorus and carbon exhibit higher energy HOMOs and reduced HOMO-LUMO separations compared with carbon-only systems, though mirror much of their chemistry. As such, the synthesis of ‘phosphacarbon’ analogues of classical organic / organometallic compounds and/or ligands offers a means of chemical and electronic control, while also presenting a significant synthetic challenge.

We have particular interest in incorporating unsaturated phosphacarbon fragments into the ligand sets of organometallic complexes as a means of effecting control over redox response in the context of molecular conduction. In this respect we have worked extensively on the, currently topical, cyaphide ligand ($^{-}C{\equiv}P$; the analogue of cyanide and ethynyl) to achieve metal-mediated conjugation with extended alkynyl chains, as P-doped models for molecular wires. We have also developed a range of ligands exploiting phosphorus within a conjugated scaffold to offer nuanced control of donor/acceptor character. These include cyclic and macrocyclic diketophosphanyls and a novel diphosphaborolediide dianion.

This talk will summarise our work in these two general areas discuss some of our current activity.