**Beyond Steric Crowding: London Dispersion Effects in Ligands and their Unusual Consequences**

The main theme of the lecture is an account of the methods that we have employed to generate and use London dispersion (LD) energies in ligands to synthesize new molecules with new types of bonding, structures and reactivity. The LD energies arise from instantaneously induced dipoles (akin to miniature magnets) generated when the atoms in a molecule are  in close proximity to those in a neighbouring molecular unit.

This causes the atoms to become attracted to each other. Generally speaking, such attractions have been discounted as being of little significance in molecular chemistry owing to the fact that they are usually weak, e.g. < 1.0 kcal/mol of energy between a pair hydrogen atoms. Nonetheless, if there are many such H—H interactions (as there can be when there are large hydrocarbon ligands) the LD energies may become large enough to significantly affect the structure and physical or chemical properties of the molecule.

Thus, if the LD interactions can be accurately directed, it may be possible to use them to attain several goals. The designed inclusion of LD interactions in molecules in order to direct physical and chemical behaviour is the central theme. The research in PP’s lab represents an attempt to attain such goals by employing a range of ligands that  are, in effect, dispersion energy donors (i.e DED).

Much of the effort has focused on substituted terphenyl ligands. These ligands comprise a central aryl ring which is substituted by two further aryl rings with alkyl substituents so that they can interact strongly with other  terphenyl ligands that are suitably oriented toward each other. Quantum mechanical calculations , as well as experimental data have shown that the LD interactions produced by the terphenyl DED ligands are crucial for the stability of many new compounds of heavier main group  (e.g. aluminum, gallium, silicon, germanium, tin) and transition elements (e.g.  quintuple bonded chromium species ) with multiple bonds.

The DED ligands provide extra stabilization energies of up to ca. 50 kcal/mol-- an amount that exceeds covalent bond strengths in compounds of many of the heavier elements.  In many cases this allows the isolation of otherwise unstable compounds. Other examples of LD effects include the inducement of disproportionation reactions to generate low-coordinate copper(II) complexes, the generation of transition metal compounds with new element-element combinations such as aluminum-copper or gallium-copper bonds. A new class of DED ligands, related to the terphenyls, but featuring cyclohexyl instead of aryl substituents on the central aryl rings, is also being developed. These have been shown to produce significantly (2-3 times) higher LD energies than the terphenyls currently employed and may be expected to stabilize an even greater range of new reactions and species.