Ligand design in organometallic chemistry taken to the extreme: when the metal is no longer needed

Ligand design has been playing a very important role in the optimization of transition-metal catalyzed processes. In the past decade, our research group has been working on the synthesis and coordination chemistry of ambiphilic molecules having both a group XIII Lewis acid and a Lewis base within the same framework.[1] Contrarily to Frustrated Lewis Pairs (FLPs) the molecules studied do not contain significant steric bulk.[2] Along the road, we discovered that some ambiphilic molecules were more active for small molecule activation than the related coordination complexes. Indeed, as in FLP chemistry, the Lewis acid and the Lewis base can cooperate and behave similarly to a transition metal in 2-electron transfer processes, making possible some metal-free transformations that were thought to be exclusive to transition metals.[3]

By fine tuning of the steric and electronic properties of both partners in these "metal-free organometallic" species, the same way organometallic chemists design ligands for transition metals, it is possible to obtain catalytic activities that are as good, and sometime better, than traditional transition metal systems. This talk will detail the reactivity of ambiphilic molecules in the hydroboration of carbon dioxide,[4] hydrogenation of carbon dioxide,[5] borylation of heteroarenes[6] and in dehydrogenative diboration of hydroboranes.[7]

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