From Interaction to Frustration in Bimetallic Late-Transition Metal Systems

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In the early 80s Chisholm proposed that “all the types of reactions which have been studied for mononuclear transition metal complexes will also occur for dinuclear transition metal complexes”.¹ Almost 40 years later, continued research on the area of bimetallic systems has proven that claimed and gone beyond.² Regarding catalytic applications, there are many important transformations that require the concerted action of pairs of active metal sites, paralleling what is often found in metalloenzymes. We recently started to investigate late-transition bimetallic systems characterized by the use of sterically hindered phosphine ligands containing a terphenyl (2,6-C₆H₃-Ar₂) substituent.³ Phosphine ligands occupy a prominent position within organometallic chemistry and homogeneous catalysis, and those providing enough steric shrouding have allowed developing novel catalytic processes and kinetically stabilizing many uncommon low-coordinated structures. In the last two years we have analyzed the effect of the stereoelectronic properties of these terphenyl phosphine ligands in the competition between the formation of M-M bonds versus M···M frustration and investigated the reactivity derived from a variety of bimetallic systems, an example of which is depicted in the Figure below.⁴ Our results pertaining the reactivity of a number of bimetallic pairs based on late-transition metals and group 12 elements will be discussed.