To Insert or not to Insert: Divergent Routes to Element–Carbon Bonds

Abstract: Metal-catalyzed routes to element–carbon bonds commonly involve insertion reactions of unsaturated substrates (e.g., heterofunctionalization). However, simple changes to metal or substrate can afford divergent and often unique reactivity. For example, zirconium compounds \((\text{N}_3\text{N})\text{ZrX} (\text{N}_3\text{N} = \text{N(CH}_2\text{CH}_2\text{NSiMe}_3)_3--; \text{X} = \text{anionic ligand})\) are catalysts for several transformations including dehydrocoupling and hydrophosphination. The latter reaction was initially observed for a limited set of substrates, terminal alkynes and carbodiimides. A reinvestigation of the catalysis has shown that, using primary phosphine substrates, alkenes and dienes are easily functionalized with high selectivity for either the secondary product (i.e., one P–H addition) or the tertiary product (i.e., two P–H additions). Surprising photolysis is a critical factor in activity for these catalysts. If insertion is disfavored at the metal center, then it is possible for a low-valent intermediate to de-insert from a M–H bond. This process, termed elimination, can produce new E–C bonds by reactions such as \([1 + n]\) cycloaddition or multicomponent cyclizations. The features that promote these divergent pathways will be explored.