## Asking Ligands to Lend a Hand



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n classical transition-metal-catalysts, the ligand is a spectator, while all key transformations such as oxidative addition,  $\beta$ -hydride elimination and reductive elimination occur at the metal center. Herein, the ligand plays no direct role in the catalytic cycle and its function is limited to stabilizing the metal center and tuning its coordination environment. In recent years, participating ligands, which play an active role during the course of reaction, have received greater

attention (**Scheme 1**). The use of such ligands has allowed for the development of more active/selective catalysts and opened up new reaction pathways. There are many ways in which a ligand can influence the metal center to accelerate the catalytic transformation. For example, hemilabile ligands allow reversible dissociation of a donor unit to adapt to the stereoelectronic requirements of the reaction intermediates.<sup>1</sup> Redox-non-innocent ligands participate in transferring electrons to/from the metal.<sup>2</sup> There is a class of ligands that directly participate in bond making/breaking and undergo reversible chemical transformation during the catalytic cycle.<sup>3,4</sup> These modes of ligand cooperativity have been discussed in many excellent reviews including those by Caulton,<sup>1</sup> Milstein<sup>3</sup> and Grützmacher<sup>4</sup>. Herein, we aim to address two distinct strategies to achieve 'ligand-driven-chemistry' – the use of (a) electronically asymmetric ligand, and (b) protic ligands. A brief discussion on the role of ligands in water activation for functionalization of organic compounds is given at the end.

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## Conventional Metal Catalysis

Scheme 1. Conventional metal catalysis vs ligand driven catalysis.

## A. Electronically asymmetric ligands

Electronically asymmetric ligands have donor components differing in their electronic characteristics (**Scheme 2**).<sup>5-9</sup> These ligands are particularly useful for catalytic transformations involving two electronically different reactants. The difference in the electronic characteristics of the donor components enables the two electronically different reactants to bind the metal center in a specific arrangement. This has a major consequence on the subsequent reactions occurring at the metal center. For example, as shown in **Scheme 3**, there is no preference for the productive arrangement (arrangement **A**) involving two electronically distinct reactants (S1 and S2) on the metal center over the unproductive arrangements (**B** and **C**) employing an electronically symmetric ligand. In contrast, an

Substrate

**Ligand - Driven Catalysis** 

