

Activation of Hydrogen by Sterically Modulated Coinage Metal Catalysts via Mutual Quenching of Hard/Soft Acid/Base Mismatches

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To mitigate the devastating environmental impacts of climate change in the coming decades, it is imperative that we replace the use of fossil fuels with renewable energy sources such as wind, solar, and hydroelectric. However, as these renewable energy sources are inherently intermittent, there exists a need for efficient, sustainable mechanisms to store renewable energy for later use. While the direct use of dihydrogen (H_2) as a combustible fuel would allow for energy storage without the harmful release of carbon dioxide (CO_2) upon combustion, the practicality of H_2 as a synthetic fuel is limited by its low volumetric energy density. Instead, combining sustainable H_2 production (e.g. electrolysis using energy from renewable sources) with subsequent carbon fixation (e.g. the hydrogenation of CO_2) represents a promising pathway to the sustainable production of high-density synthetic fuels.¹ We hypothesize that such a process could be catalyzed by an IPr^{**} -supported catalyst containing a hard/soft acid/base (HSAB) mismatch, with a polarizable coinage metal acting as a soft acid (Fig. 1A).²⁻⁴ Following hydrogen production driven by energy generated from renewable sources, such a catalyst would facilitate the heterolysis of H_2 , yielding one nucleophilic hydride poised to attack a carbon source such as CO_2 , and one electrophilic hydride poised for a subsequent proton transfer event to complete the catalytic cycle (Fig. 1B).

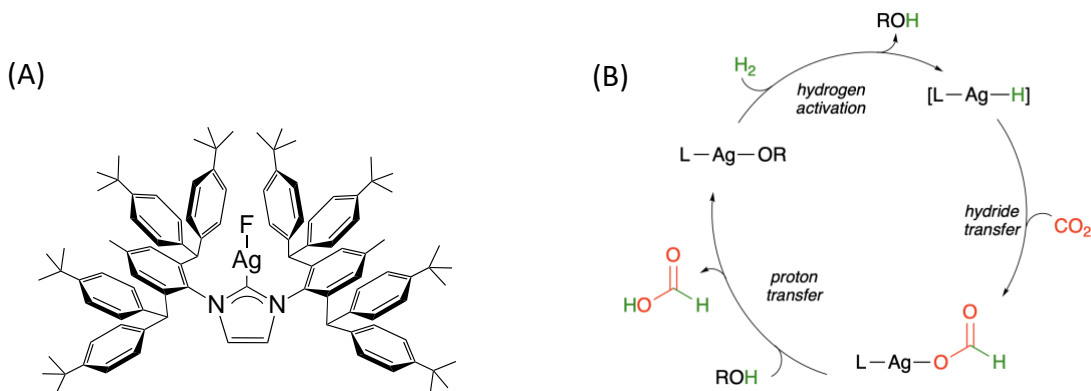


Figure 1. (A) Structure of a proposed IPr^{**} -supported HSAB mismatch catalyst (IPr^{**} -Ag-F). (B) Hypothetical catalytic cycle for H_2 activation and CO_2 hydrogenation via a proposed HSAB mismatch catalyst.

This year, we successfully synthesized and metalated the IPr^{**} ligand, isolating and characterizing an IPr^{**} -Ag-Cl complex³ as we attempted to construct an IPr^{**} -supported HSAB mismatch catalyst. Although the Ag-Cl bond in this complex is likely not active in H_2 activation (because Cl^- is a very weak base), this IPr^{**} -Ag-Cl complex is an immediate precursor to our proposed silver catalysts, for which the chloride ion would be substituted for a stronger, harder base. Although our initial attempt to introduce a hard base (*tert*-pentoxide) to the silver complex did not yield the desired product (IPr^{**} -Ag-O^tPent), the replicable synthesis of IPr^{**} -Ag-Cl represents an important step towards our ultimate goal of constructing a catalogue of IPr^{**} -supported HSAB mismatch catalysts.

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