

Design of New Catalytic Reactions Based on Metal-Ligand Cooperation

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We have developed a new mode of metal-ligand cooperation, based on aromatization-dearomatization of pincer-type ligands, and have designed several *environmentally benign catalytic reactions* based on such cooperation, including (a) dehydrogenative coupling of alcohols to form esters and H₂ (b) hydrogenation of esters to alcohols under mild conditions (c) synthesis of amides by coupling of amines and alcohols with liberation of H₂ (d) dehydrogenative coupling of amines and alcohols to form imines (e) selective synthesis of primary amines directly from alcohols and ammonia (f) direct formation of acetals by dehydrogenative coupling of alcohols. These new reactions are efficient, proceed under neutral conditions and produce no waste. They are catalyzed by pincer-type ruthenium complexes based on pyridine and on acridine, and involve as a key mechanistic step aromatization - dearomatization of the hetero-aromatic ligand core. Metal-ligand cooperation of this type has very recently led also to *a distinct approach towards water splitting*, based on consecutive thermal H₂ generation and light-induced O₂ liberation.