

Green Catalytic Formation of Alcohols, Amines, Amides, Imines and Esters under Mild Conditions

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Overview

A team of researchers headed by Prof. David Milstein at the Weizmann Institute of Science (WIS), have developed a novel set of manganese, ruthenium, and related borohydride complexes (Pincer-type). These catalysts are efficient and environmentally-benign for the synthesis of alcohols, amines, amides, imines, and esters.

The basic building blocks for the chemical and chemical related industries are presently generated in an environmentally harmful manner. These common building blocks are produced in reactions requiring harsh and energetically expensive conditions. Additionally during synthesis as well as in the final products there are environmentally hazardous byproducts.

Consequently there is a strong need for catalysts that function under mild and neutral conditions, using low catalyst loading, employ no corrosive or toxic reagents, and generate no waste. The team of Prof. Milstein have developed a set of catalysts that fit these green requirements and can efficiently produce the basic building blocks of the chemical and biochemical industry.

The Need

Amines, alcohols, amides, imines, and esters, are essential for industries such as research, chemicals, plastics and polymers, dyes, fragrances, fibers, pharmaceuticals, and agrochemicals. However, require conditions of high temperature/pressure and stoichiometric amounts of different hazardous compounds (e.g. activated acid derivatives or large amounts of metal compounds) to synthesize.

Carbon-carbon bond formation reactions are of a fundamental importance in organic chemistry. Yet, they often require the application of strong bases, which may not be compatible with various functional groups and can lead to undesired side reactions.

In addition, there is a strong interest in the replacement of noble metal catalysts by more economical and environmentally friendly catalysts, based on earth-abundant metals. Further there is a need for cheaper and more efficient synthetic methods.

The Solution

A novel set of catalysts based on manganese, ruthenium, and related borohydride complexes (Pincer-type) gives an alternative green option in synthesizing fundamental compounds.

Technology Essence

In recent years, complexes based on π -cooperating π -ligands have exhibited remarkable catalytic activity. These ligands can cooperate with the metal center by undergoing reversible structural changes in the processes of substrate activation and product formation.

Prof. David Milstein's group has discovered a new mode of action for metal-ligand cooperation, involving aromatization/dearomatization of ligands. Pincer-type, pyridine-based complexes of Mn and acridine complexes of Ru have been shown to exhibit such cooperation, leading to facile activation of C-H, C-C, H-H, N-H, and O-H bonds.

Applications and Advantages

Advantages

- Reduced material cost (cheaper catalysts & reagents, reduced need for protecting groups, fewer reaction steps, higher yields, and less work-up.)
- Lower waste treatment cost (catalytic amounts - 1% mol, absence of toxic reagents, and byproducts, minimizes hazardous waste formation.)
- Decreased energy costs (Mild conditions - pressure 10 atm, temperatures of ~110 oC)
- No additives (just substrates and catalyst, except with certain reactions where hydrogen is required)
- New synthetic pathways that were not feasible before (e.g. such as the synthesis of amides and imines directly from alcohols and amines, esters synthesis from alcohols)
- Broad substrate scope and excellent yields

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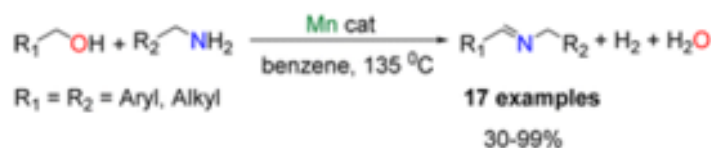
Applications

- Pharmaceuticals
- Dyes
- Cosmetics and fragrances
- Fibers
- Agrochemicals

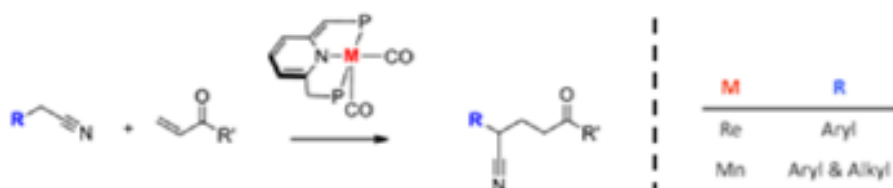
Development Status

The novel catalysts have been used in the following reactions:

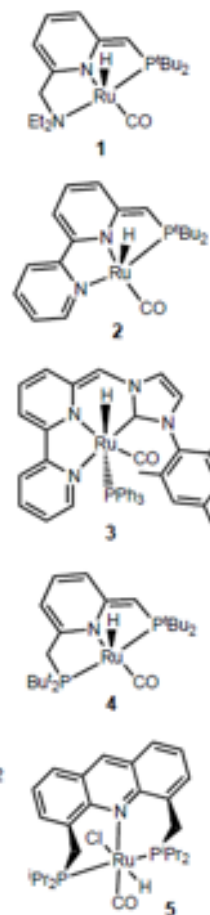
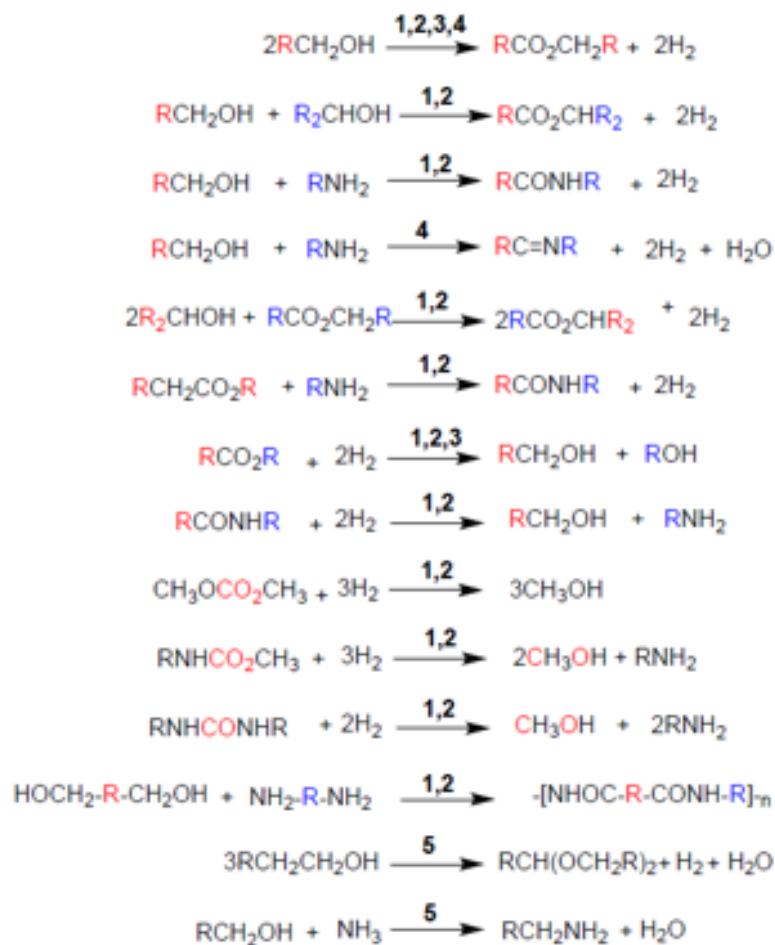
- Synthesis of imines:



- C-C bond formation (Michael addition):



- Synthesis of alcohols, amines, amides, and esters:



Products have been validated using NMR analysis and DFT calculations.



Patent Status

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