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NOVEL LIGAND SYNTHESIS FOR CO_2 HYDROGENATION

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Abstract

As the world continues to rely heavily on fossil fuel usage, it is imperative that new carbon sources be found. Ideally, CO_2 could be used as such a source. It is cheap and so abundant in the atmosphere that it contributes to global warming via greenhouse effect. Being able to mimic the carbon cycle as plants do, by using the CO_2 in the air as a carbon source, would be an extremely powerful tool. This would mitigate pollution, as it would allow us to control exactly what is in our fuel, affording cleaner combustion byproducts and help reach a net zero carbon footprint. Unfortunately, CO_2 is weakly electrophilic and unreactive, necessitating a catalyst for conversion to fine chemicals and fuel. Hydrogenation of CO_2 involves the addition of H_2 and breaking the carbonyl π bond. By adding variable amounts of electrons and protons to CO_2 it is possible to produce methanol and formate. The proposed catalytic cycle is detailed in the figure below. The work conducted thus far has been focused on novel ligand scaffolds used for homogenous hydrogenations of CO_2 mediated by ruthenium. Homogenous catalysts are preferred due to the ability to analyze them in situ and tuning the catalyst by adjusting thermodynamic and kinetic properties. The studied ruthenium complexes have a pendant amine group in the second coordination sphere to assist in CO_2 binding stability during catalysis. Dimethylammonium dimethylcarbamate (DMC) is used as a soluble CO_2 surrogate in the hydrogenation reactions, as carbon capturing CO_2 with amine compounds has proven to be a useful tactic in removing CO_2 from the atmosphere. The research done has included synthesis of two novel, Milstein-inspired, P-P-P ligands coordinated to ruthenium and preliminary hydrogenation studies. A variety of techniques including single crystal X-ray diffraction, UV-vis analysis, NMR, GCMS, and IC chromatography are used in the analysis of hydrogenation reactions and synthesis of the complexes. This research will be contextualized in terms of what parameters of the catalysts have significant effects on catalytic performance, allowing for rational design of next generation systems. Future work includes synthesis of ligand derivatives that have different electronic and steric properties, and using first-row transition metals, such as cobalt, that are more abundant and economically feasible on an industrial scale.

Proposed Catalytic Cycle for CO_2 Hydrogenation