Rhenium(I) transformational chemistry to generate novel pincer complexes and enhance photochemical carbon dioxide reduction

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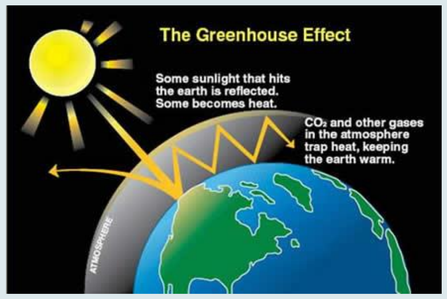
Rational for Research

Rhenium (I) complexes have potential application in organic light-emitting diodes (OLED), chemosensors and biotechnology probes, and the photochemical reduction of carbon dioxide to carbon monoxide.

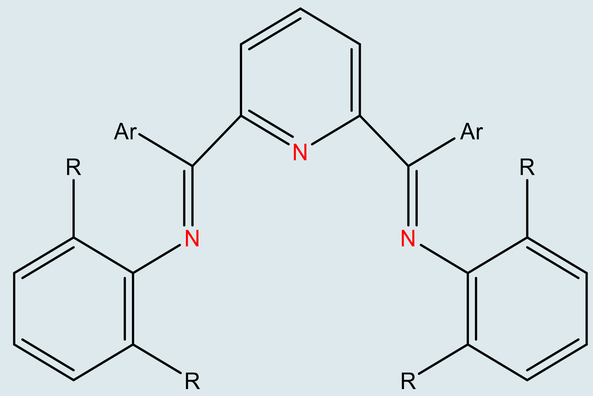


Past research has shown the structure and catalytic activity of rhenium bidentate complexes, however there are some limitations to their activity. These limitations are explored through the construction of novel pincer compounds as well as addressing the unexplored and structurally restricted tridentate species. The novel molecular scaffolds provide a unique environment for the catalytic reduction of carbon dioxide. Having the ability to use a renewable energy source (sunlight) to reduce the prevalence of the most abundant greenhouse gas (carbon dioxide)in the environment can lead to the wide-scale industrial application which was otherwise not feasible.

Objectives:

1) Using modern organic and inorganic synthesis techniques the three different bis(imino)pyridine ligands are synthesized from 2,6-diacetyl pyridine and complexed to a $Re(CO)_5X$ (X = Br or Cl).
2) Characterization techniques like multinuclear NMR and mass spectroscopy are utilized to gain information of the properties of the synthesized catalysts as well as to confirm the production of the correct product

The bis(imino)pyridine ligand



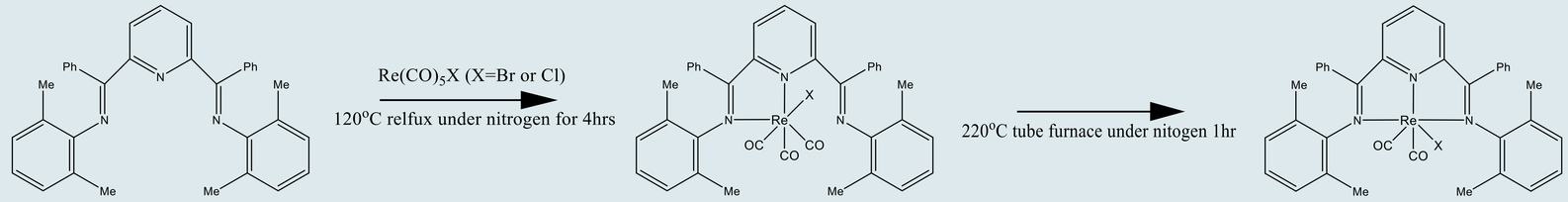
This ligand is a rigid planar molecule that will complex to $Re(CO)_5X$ (X=Br or Cl) at the red coloured nitrogen's comprising the pyrimidine ring and imine components. The pyridine nitrogen will always complex, however when forming the bidentate one imine nitrogen will complex. In the tridentate synthesis all three nitrogen's complex.

Ar = Phenyl
R' = Me, Isopropyl, H

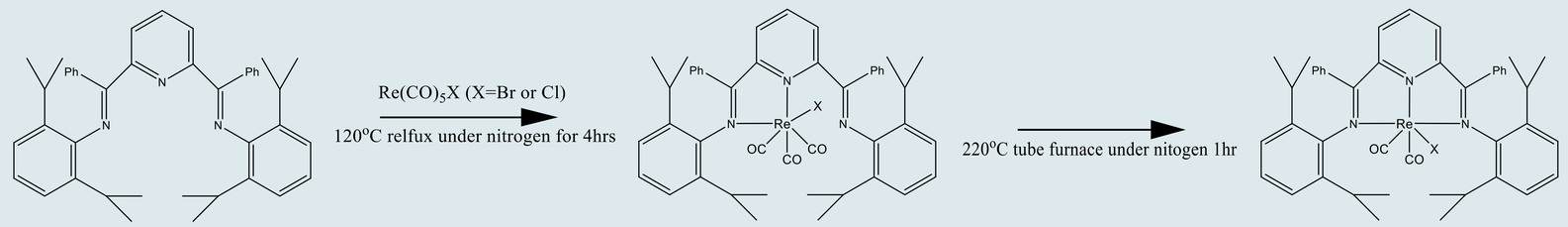
Methods and Results

1)

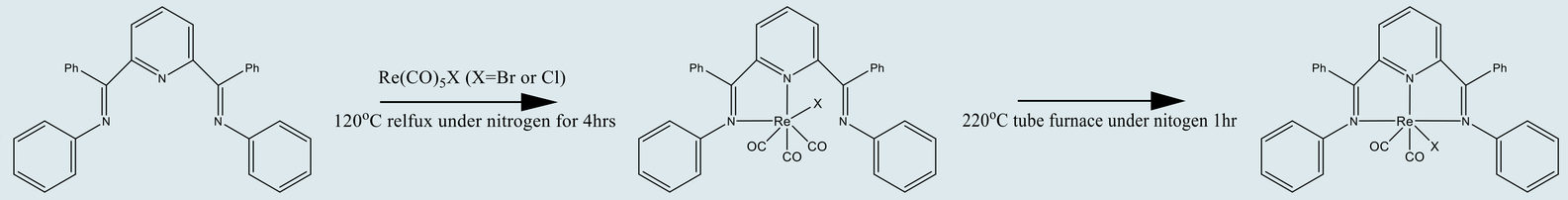
Ligand 1



Ligand 2



Ligand 3



2) The elemental analysis is a pivotal requirement to the process. After each ligand and bidentate is synthesized and purified the first step is to conduct an 1H NMR. The NMR data is then analyzed for any impurities and compared to the literature to check the similarity. Since we are looking to synthesize the novel tridentate molecule it is imperative that we know the reactants are pure. Thus far the tridentate synthesis of ligand 2 was a success and its photochemical reductive properties were tested and the results showed that the structure was able to reduce CO_2 to CO by a fellow researcher in the Richeson Lab. The next steps are to synthesize the tridentate complex of the other ligand scaffolds and to perform and elemental analysis of these compound. That includes: IR spectroscopy, ^1H NMR, mass spectroscopy and x-ray crystallography. The elemental analysis will prove that the compound obtained was exactly what we are looking for. The remaining tridentate catalyst can then be subjected to photochemical reduction tests to test its catalytic ability to reduce CO_2 to CO.

Conclusion

The bidentate compounds of all three ligands were successfully synthesized as well as the synthesis of the tridentate molecule of ligand 2. Next steps are to finish the synthesis of the tridentate molecules of the other two ligands and conduct and elemental analysis of all three.

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