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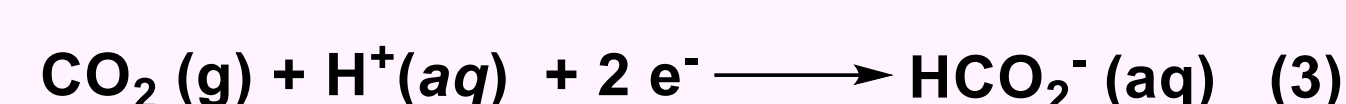
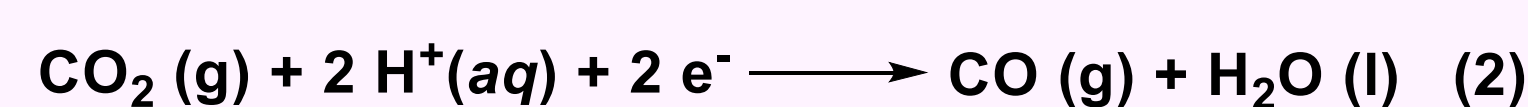
Methods for Increasing the Electron Richness of Iron Tricarbonyl Diimine Complexes

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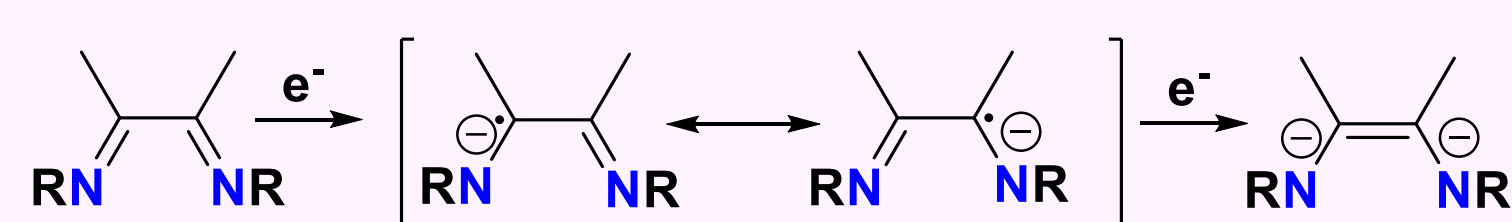


Introduction

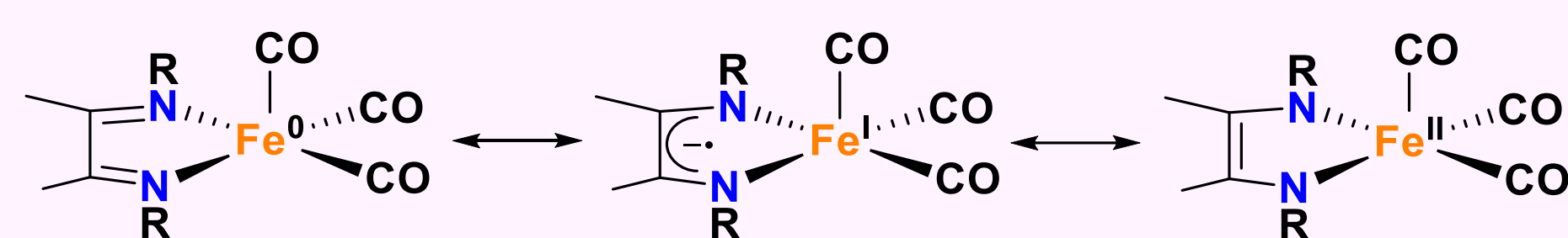
The goal of our research is to synthesize new iron complexes that can reduce carbon dioxide or protons (Equations 1-3).



Both reactions require the transfer of two electrons to the substrate, which can be facilitated by a redox active catalyst. We are focusing on the use of α -diimine ligands because they can potentially be reduced by two electrons.



We propose that iron complexes of α -diimine ligands can be tuned electronically to be selective for the reduction of either protons or carbon dioxide. The oxidation state of the metal and ligand in iron tricarbonyl α -diimine complexes can be assessed based on bond lengths determined by X-ray crystallography.



C-N Bond Lengths Increase
C-C Bond Length Decreases

R group e⁻ donating R group e⁻ withdrawing
Reduction at iron Reduction at ligand
Preference for H⁺ binding Preference for CO₂ binding

The Carroll lab has synthesized a series of iron tricarbonyl diimine complexes, and in all cases, the ligand bond lengths suggest that it exists in the monoanionic form. Additionally, none of these complexes exhibit reactivity with H⁺ or CO₂. Therefore, the main goal of the work reported here is to increase the electron richness of the iron center because this may increase the likelihood for the reactions of interest to occur reactions to occur. We have taken two approaches to accomplish this goal. First, we chose a new diimine ligand that should be more electron donating. Second, we reacted one of the known iron complexes with a reducing agent, in order to reduce either the metal center or the ligand.

Results

Characterization and Electrochemical Analysis of an Electron Rich α -Diimine Ligand

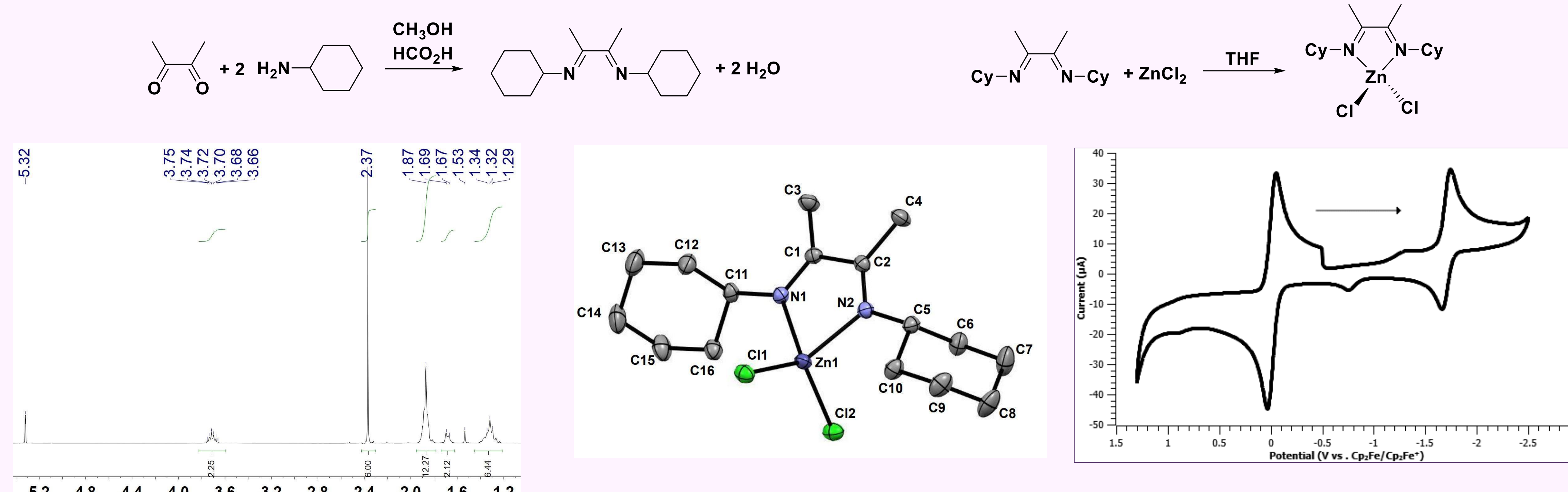


Figure 1. ¹H NMR spectrum of Zn(CyDABMe)Cl in CDCl₃.

Figure 2. Molecular structure of Zn(CyDABMe)Cl₂ with 50% probability and hydrogen atoms excluded.

Figure 3. Cyclic voltammogram of 10 mM Zn(CyDABMe)Cl₂ in acetonitrile. Conditions: 0.1 M [Bu₄N][PF₆], glassy carbon working electrode, platinum counter electrode, Ag pseudoreference electrode.

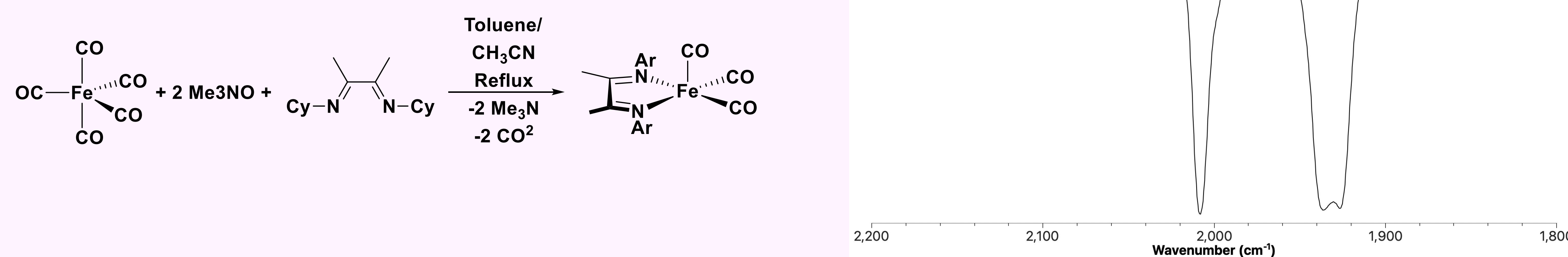


Figure 4. IR spectrum of Fe(CyDABMe)(CO)₃ in hexane.

Synthesis and Reduction of Fe(3,5-(CF₃)₂PhDABMe)(CO)₃

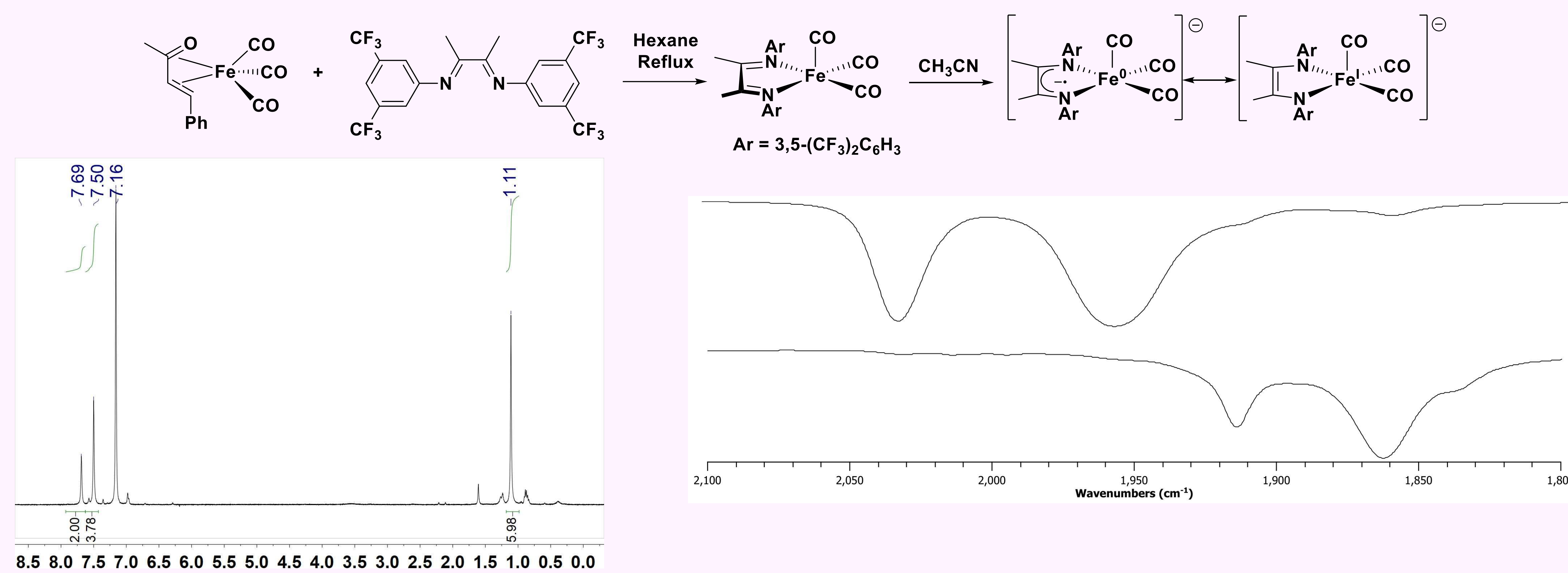


Figure 5. ¹H NMR spectrum of Fe(3,5-(CF₃)₂PhDABMe)(CO)₃ in CDCl₃.

Figure 6. IR spectra of Fe(3,5-(CF₃)₂PhDABMe)(CO)₃ before reduction (top) and after reduction with KC₈ (bottom). Spectra were taken in acetonitrile.

Conclusions

We have successfully synthesized more electron rich iron tricarbonyl diimine complexes. The complex Zn(CyDABMe)Cl₂ was characterized by NMR spectroscopy and X-ray crystallography. The cyclic voltammogram shows that the complex undergoes a quasi-reversible reduction at -1.70 V, which is ~200 mV more negative than reduction potentials of previously synthesized zinc diimine complexes, suggesting that this diimine is more electron rich. Reaction of Fe(CO)₅ with the CyDABMe ligand results in formation of a complex with an IR spectrum that matches that of the related complex, but the CO stretching frequencies are ~10 cm⁻¹ lower energy than previously reported complexes, confirming that the CyDABMe ligand forms a more electron rich complex.

Based on IR and NMR spectroscopy, the complex Fe(3,5-(CF₃)₂PhDABMe)(CO)₃ has been successfully synthesized. The decrease in CO stretching frequencies confirms that reduction of the complex occurs.

In the future, we seek to characterize the new iron complexes by X-ray crystallography and explore their reactivity with acid and carbon dioxide and electrochemical properties.

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