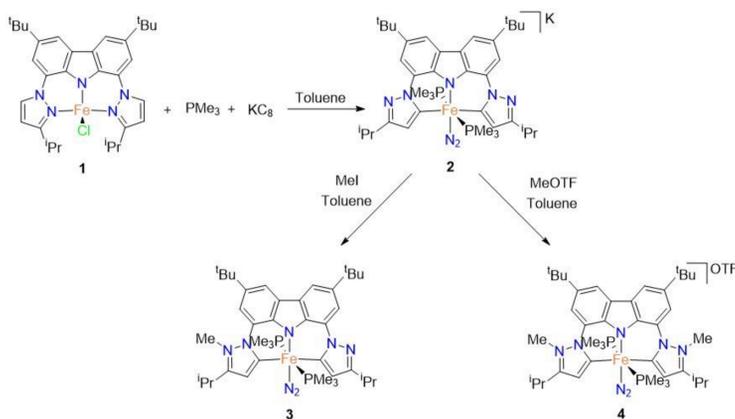


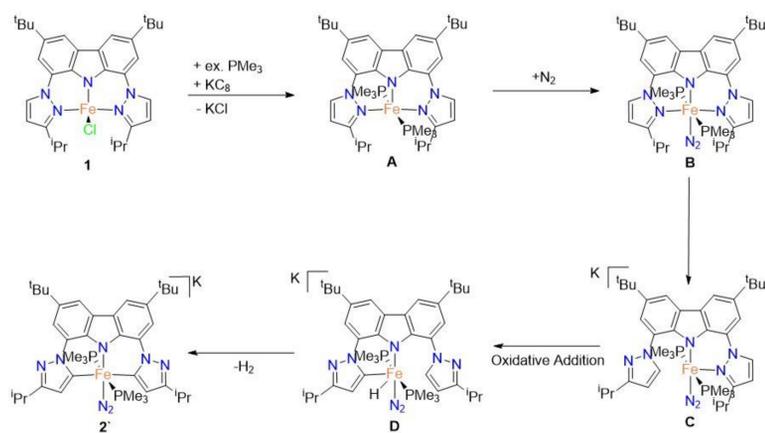
## Abstract

Ammonia production is a process that is integral to a variety of industries ranging from agriculture, textiles, and pesticide production. The Haber-Bosch process has supplied the global demand for ammonia since the beginning of the 20th century, but presents the issue of being incredibly energetically costly. The catalytic reduction of ambient atmospheric dinitrogen is a potential solution to the issue presented by the Haber-Bosch process and through the use of organometallic compounds inspired by the bacterial family of nitrogenases, there is potential for much more energy efficient production of ammonia. A series of iron complexes bearing CNC-pincer ligands have previously been synthesized in this lab and have shown the potential to catalytically reduce dinitrogen to ammonia. Computational analysis was used to further elucidate the mechanistic conversion of complex **1** to complex **2**. Further, complexes **7** and **8** were probed by running a series of reactions to better study N<sub>2</sub> as a labile ligand.

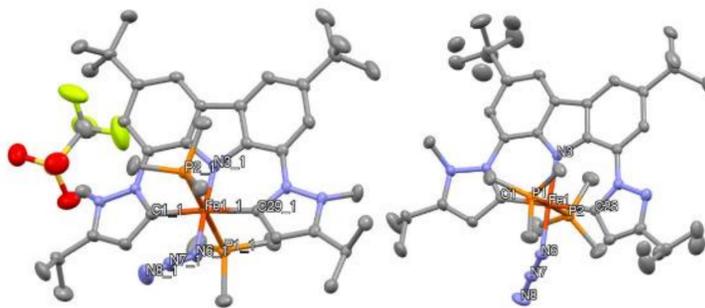
### Scheme 1. Previously synthesized Fe-N<sub>2</sub> complexes



### Scheme 2. Mechanistic pathway for conversion of **1** to **2**



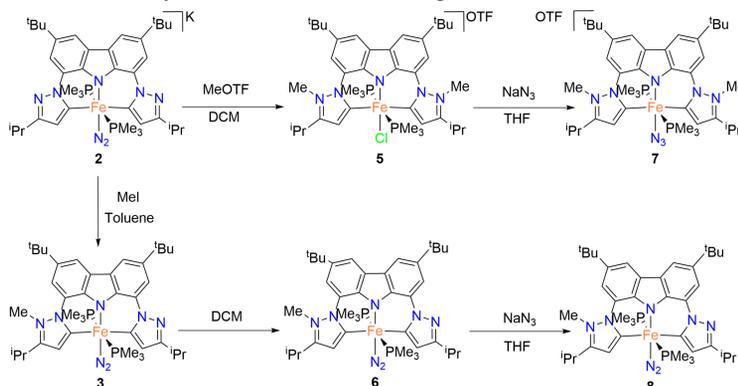
**Figure 1.** Molecular structures of **7** and **8** with hydrogen atoms omitted for clarity



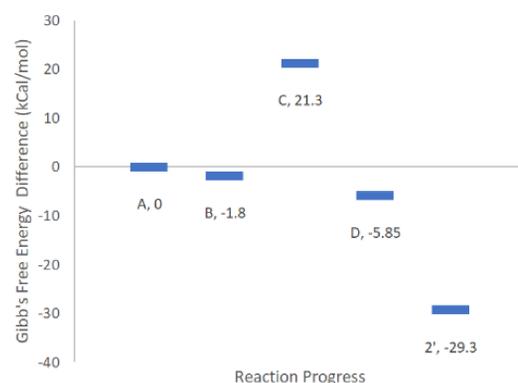
**Table 1.** Selected bond angles and measurements comparing **7** and **8**

	<b>7</b>	<b>8</b>
Fe-N <sup>Cbz</sup> (Å)	1.906(1)	1.897(1)
Fe-C <sup>Me,a</sup> (Å)	1.978(2)	1.970(1)
Fe-C (Å)	---	2.006(1)
Fe-N <sub>6</sub> (Å)	1.964(2)	1.981(1)
N <sub>6</sub> -N <sub>7</sub> (Å)	1.199(3)	1.188(2)
N <sub>7</sub> -N <sub>8</sub> (Å)	1.160(3)	1.163(2)
N <sup>Cbz</sup> -Fe-Cl (degrees)	177.57	177.82
C-Fe-C (degrees)	174.51	173.59
P-Fe-P (degrees)	178.79	174.57

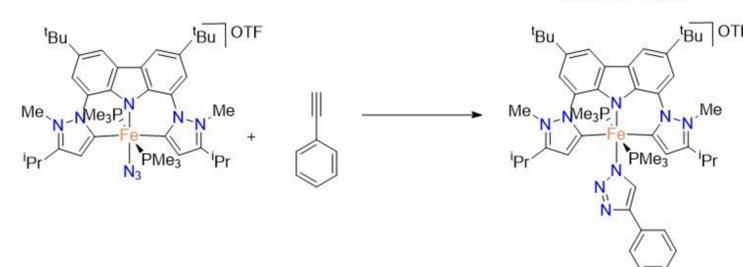
### Scheme 3. Synthesis of azide analogs **7** and **8**



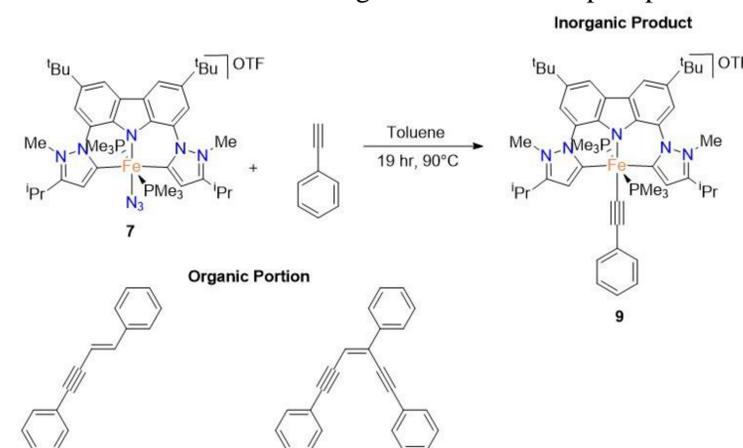
**Figure 1.** Reaction process diagram to produce **2**



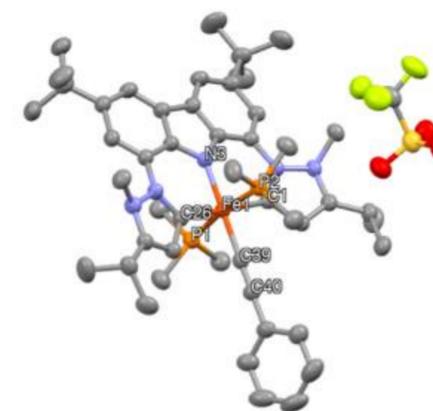
### Scheme 4. Proposed reaction of **7** and phenylacetylene



### Scheme 5. Reaction of **7** to give **9** and C-C coupled products



**Figure 3.** Molecular structure of **9** with hydrogens omitted for clarity



## Conclusion

Based on the results presented here, we were able to further understand the mechanistic steps of the synthesis from complex **1** to **2** which revealed the double sp<sup>2</sup> C-H bond activation in order to flip both pyrazole moieties of the pincer ligand and ultimately yield a CNC coordination to our reduced iron center. Furthermore, probing the reactivity of the iron azide species for 2,3 cycloaddition reactions with phenylacetylene revealed the surprising head-to-head dimerization and trimerization products. Future work will be done to probe the reactivity of **4** and isolate crystals of a previously synthesized organic azide analog of this complex.

## Contact

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