



REDUCTION OF 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, *N*-benzylidenebenzylamine, nitrobenzene, AND benzonitrile USING A SYNTHETIC MODEL OF [Fe]-HYDROGENASE.

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Hydrogen as fuel

In hydrogen fuel sources, platinum is often used as an electrocatalyst for H⁺ to H₂ conversion.¹ Proton exchange membrane or polymer electrolyte membrane (PEM) fuel cells are used, transporting protons to the cathode, which then combine with air and electrons to form water.² Hydrogen fuel is two to three times more efficient than gasoline, with zero or close to zero emissions.

[Fe]-hydrogenase

[Fe]-hydrogenase is one of three different kinds of redox proteins, but is unique due to it having a single metal atom present. Found in methanogenic archaea, it is used in an intermediate reaction during the reduction of CO₂ to CH₄, where it stereospecifically transfers H⁺ to the Pro-R position of the methenyl- H₄MPT⁺.³⁻⁴

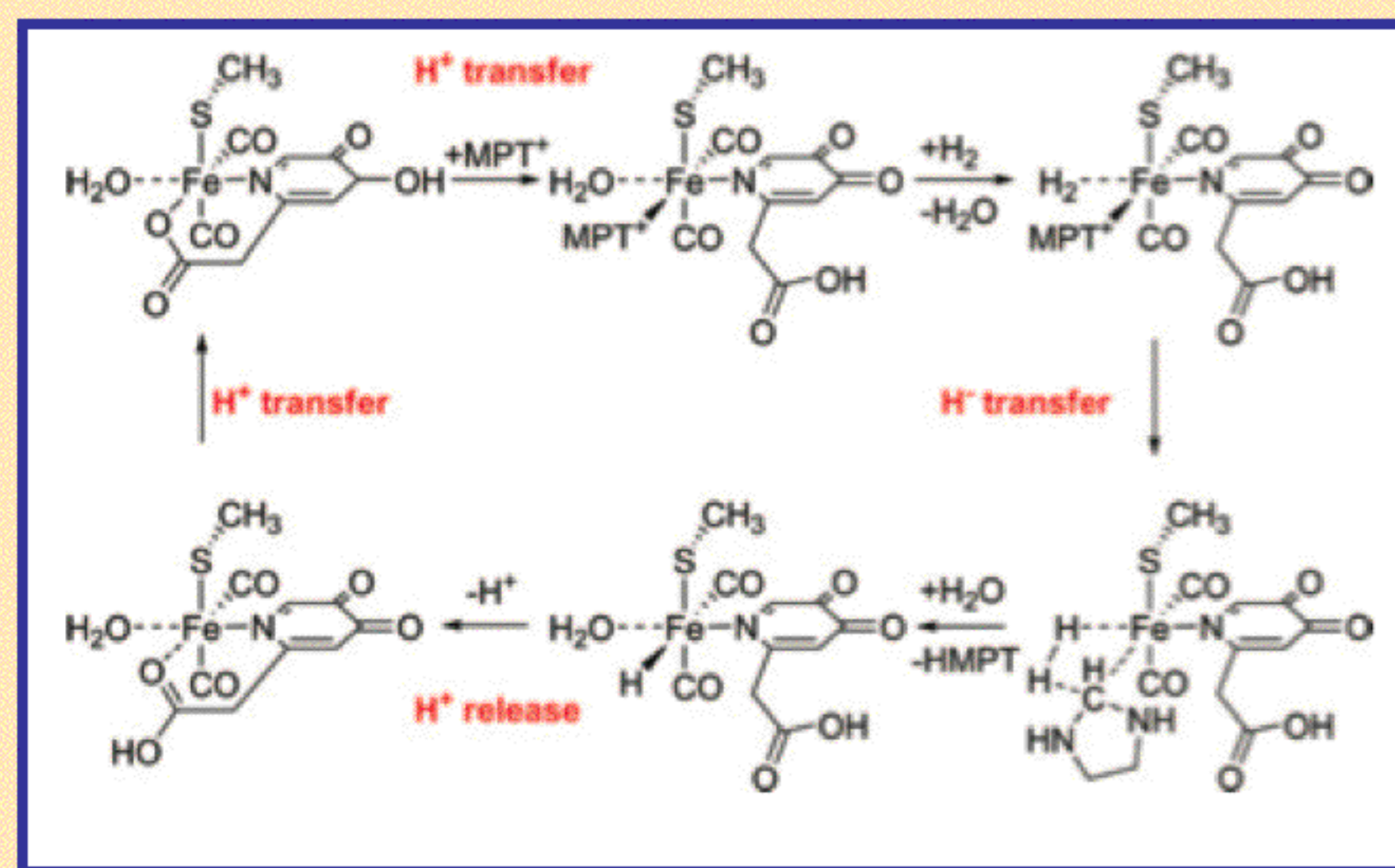


Figure 1: The reduction of methenyl- H₄MPT⁺ with [Fe]-hydrogenase, showing the addition of hydrogen to the catalyst.¹

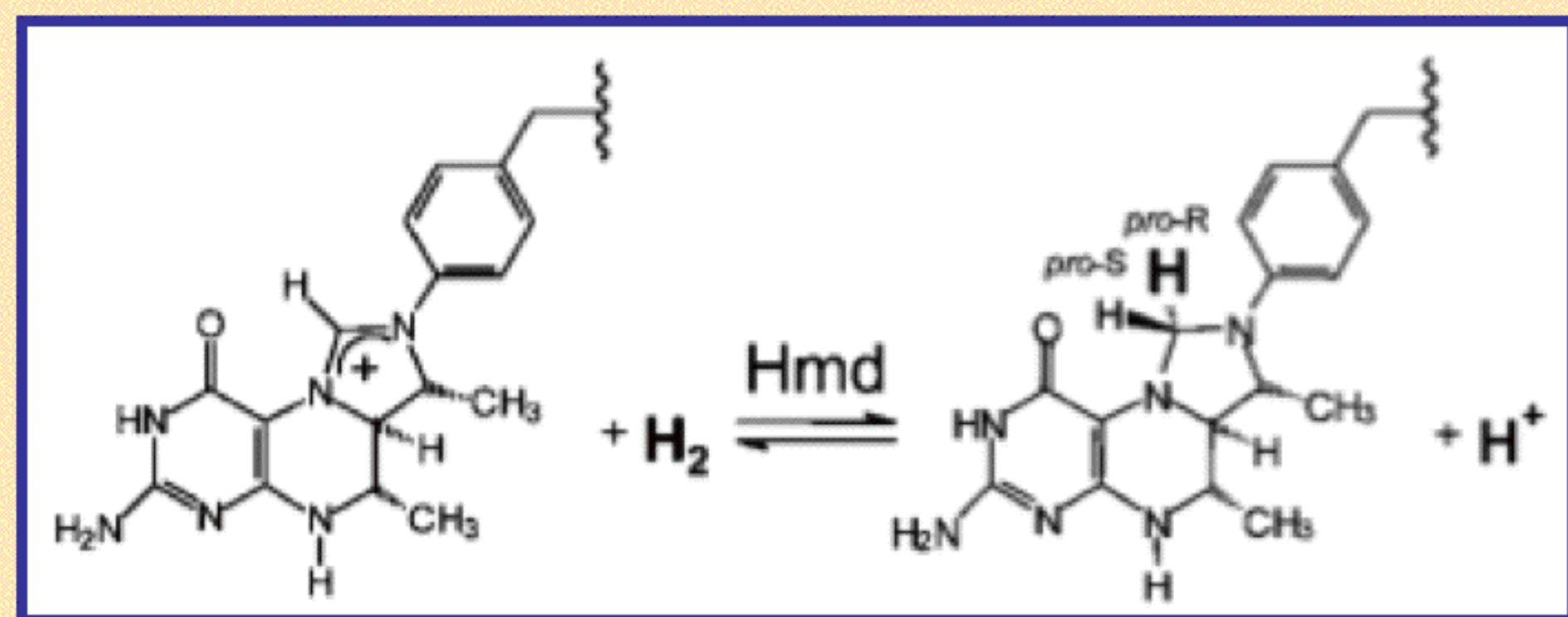


Figure 2: The reduction of methenyl- H₄MPT⁺ with [Fe]-hydrogenase, showing the addition of hydrogen to methenyl- H₄MPT⁺.⁴

Experimental

The synthetic model of [Fe]-hydrogenase, **4**, was made in two steps. The starting material was synthesized by the addition of liquid bromine to iron pentacarbonyl using a drip funnel; this reaction is shown in Figure 2. The product, **2**, was then mixed with 2-aminopyridine and recrystallized in acetonitrile as shown in Figure 3.

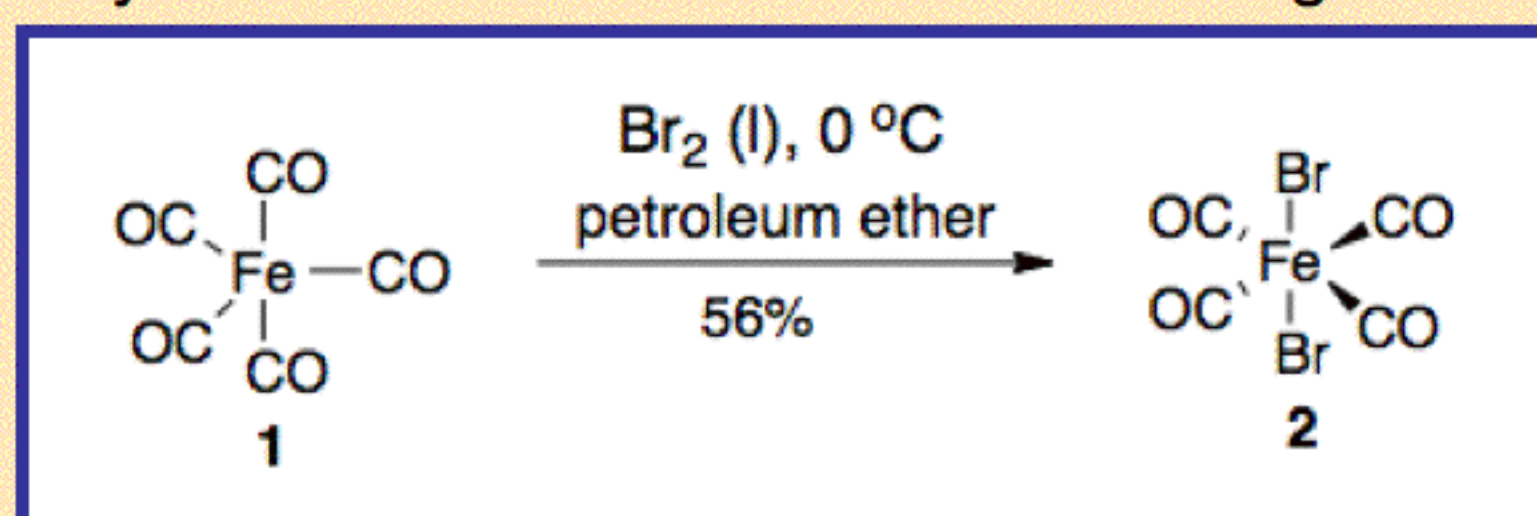


Figure 3: The synthesis of *trans*-dibromotetracarbonyl iron (ii), **2**, from iron pentacarbonyl with liquid bromine, 56%.

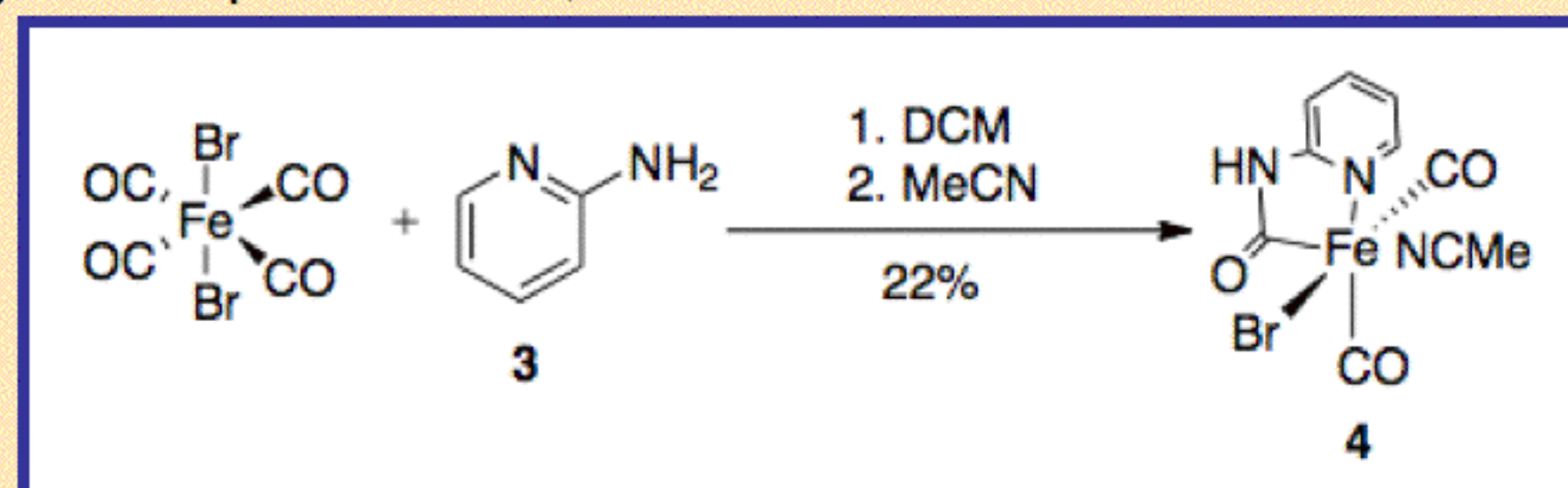


Figure 4: The synthesis of FeBr(C₆H₅N₂O)(CO)₂(MeCN), **4**, from *trans*-dibromotetracarbonyl iron (ii) with 2-aminopyridine and acetonitrile, 22%.

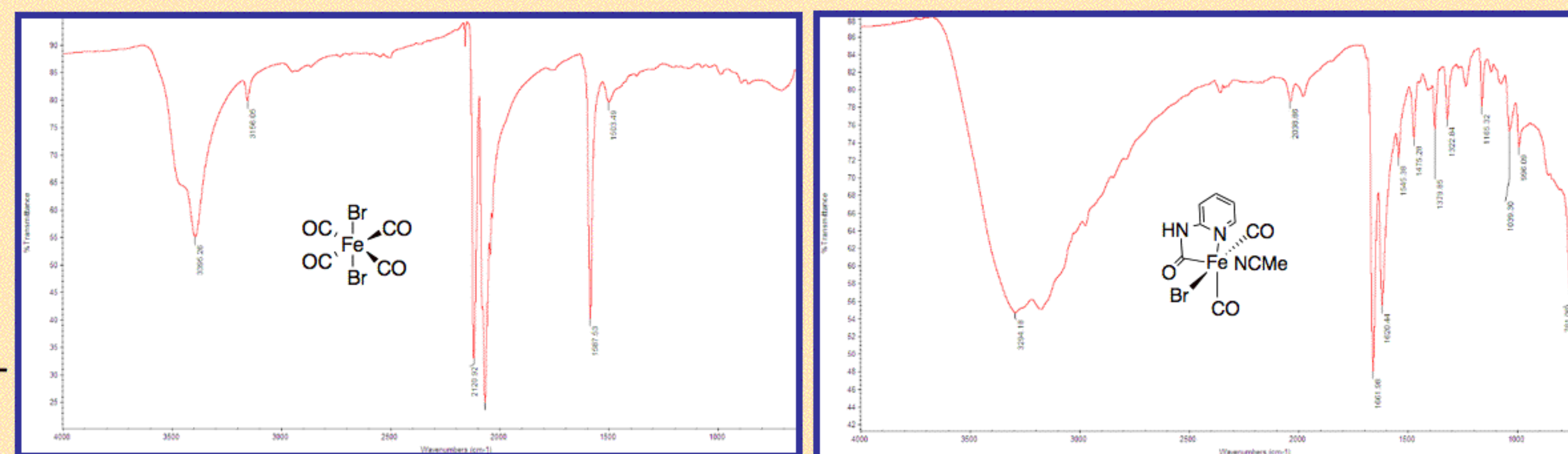


Figure 5: The infrared spectra of *trans*-dibromotetracarbonyl iron (ii) (left) and FeBr(C₆H₅N₂O)(CO)₂(MeCN) (right).

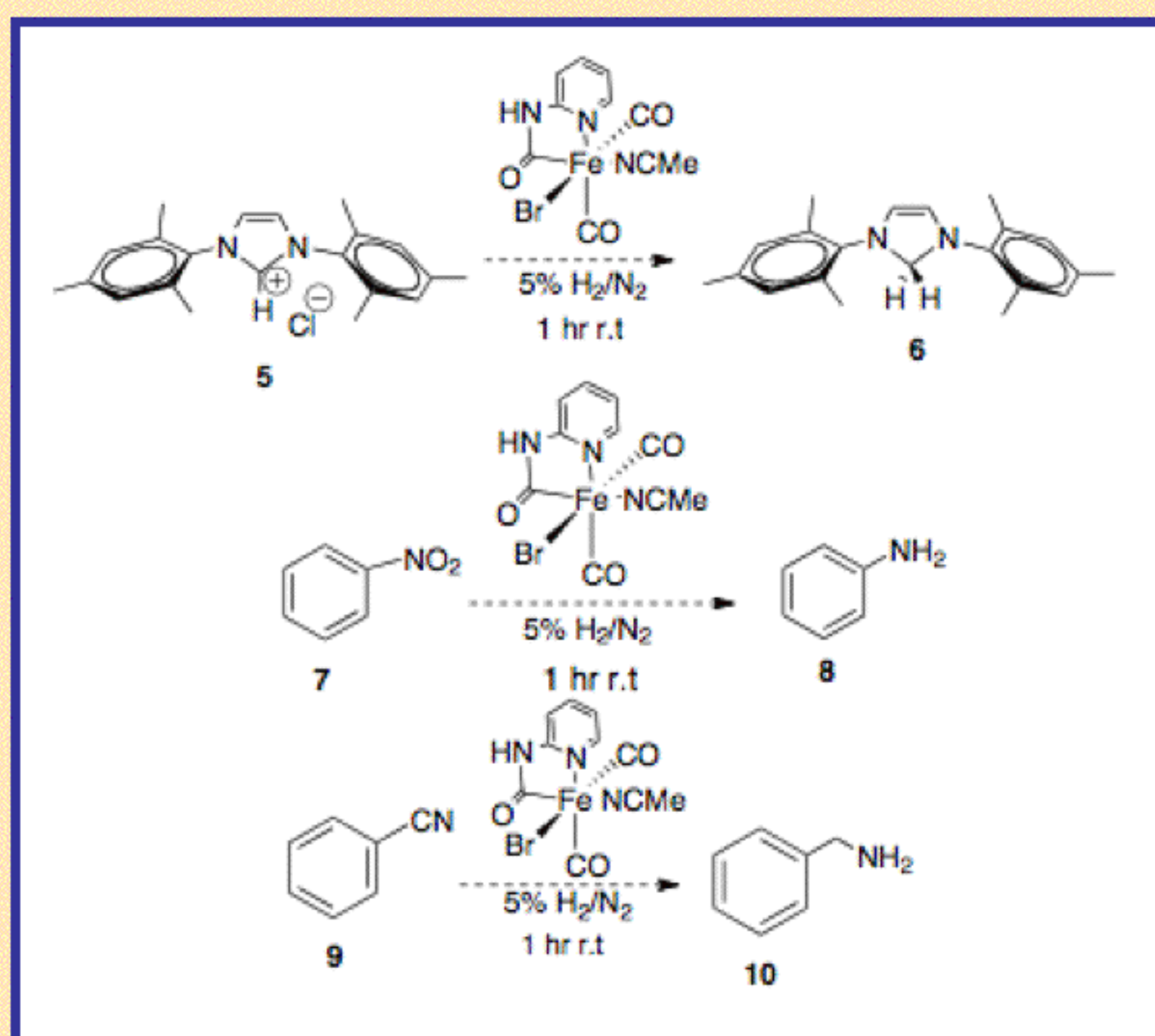


Figure 6: The attempted reduction of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride, nitrobenzene, and benzonitrile with the synthetic [Fe]-hydrogenase precursor at SATP.

Attempted reduction under pressure

After the catalyst proved to be ineffective on compounds **5**, **7**, and **9**, the final reaction was put under 4 atmospheres of pressure and heated to essentially increase the concentration of hydrogen and lower the activation energy of the reaction. This reaction was also not successful.

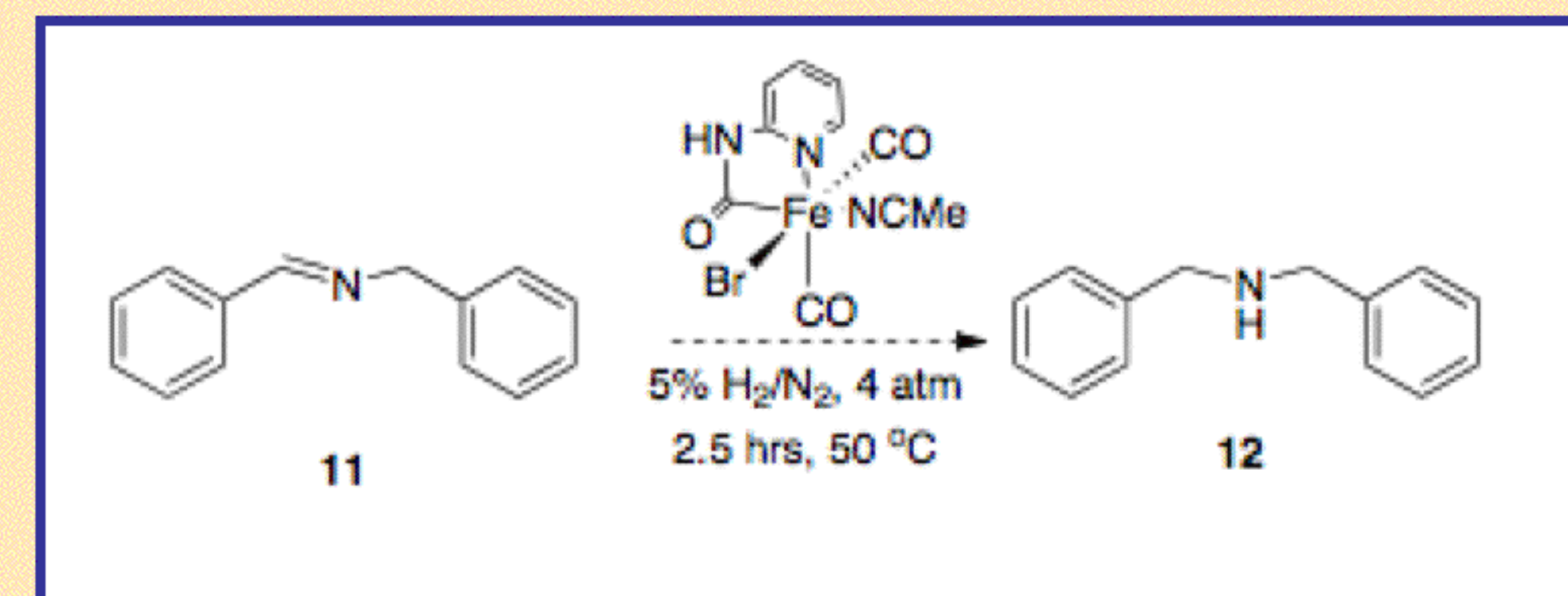


Figure 7: The attempted reaction of *N*-benzylidenebenzylamine with the synthetic [Fe]-hydrogenase precursor at 4 atm and 50 °C.

Results

The synthesis of the starting material for the catalyst and the catalyst itself was analyzed by infrared spectroscopy and showed to be successful with moderate yields. The reductions, however, showed starting material with minor impurities through ¹H NMR spectroscopy.

Conclusions

Using the [Fe]-hydrogenase precursor as a catalyst for the reduction of various nitrogen compounds proved not to be successful. The [Fe]-hydrogenase used to reduce methenyl- H₄MPT⁺ had a chelating N,S-ligand with a tight bite angle.⁵ The combination of the synthetic [Fe]-hydrogenase precursor and a sulfur ligand may be the key ingredient to the reduction of these compounds.

Future Work

The use of [Fe]-hydrogenase in the production of hydrogen as fuel could be an inexpensive alternative to the current platinum electrocatalysts. Hydrogenase electrodes as anodes in biofuel cells could be attached to a metal surface, modified with an agent holding the catalyst in place, if shown to successfully produce the protons needed to couple with oxygen.⁶

Acknowledgements

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