Electronic Supplementary Information

Intermediates in the Reduction of N₂ to NH₃: Synthesis of Iron η^2 Hydrazido(1-) and Diazene Complexes

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Table of Contents

Experimental procedures. S-2 – S-5.

References. S-5. Figure S1. ³¹P{¹H} NMR spectra of addition of KO^tBu to *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺ S-6. Figure S2. ³¹P{¹H} NMR spectra of addition of DBU to *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺ S-7. Figure S3. ³¹P{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺ S-8. Figure S4. ¹H NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_{2}H_{4}$)]²⁺ S-8. Figure S5. ¹H HMQC NMR spectrum of cis-[Fe(DMeOPrPE)₂(¹⁵N₂H₄)]²⁺S-9. Figure S6. ¹⁵N NMR spectrum of cis-[Fe(DMeOPrPE)₂(¹⁵N₂H₄)]²⁺ S-9. Figure S7. ¹⁵N{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_2H_4$)]²⁺ S-10. Figure S8. ${}^{31}P{}^{1}H$ NMR spectrum of *cis*-Fe(DMeOPrPE)₂(N₂H₂) S-10. Figure S9. ¹H NMR spectrum of cis-Fe(DMeOPrPE)₂(¹⁵N₂H₂) S-11. Figure S10. ¹H HMQC NMR spectrum of cis-Fe(DMeOPrPE)₂(¹⁵N₂H₂) S-11. Figure S11. ¹⁵N{¹H} NMR spectrum of cis-Fe(DMeOPrPE)₂(¹⁵N₂H₂) S-12. Figure S12. ¹⁵N NMR spectrum of cis-Fe(DMeOPrPE)₂($^{15}N_2H_2$) S-12. Figure S13. ${}^{31}P{}^{1}H$ NMR spectrum of *cis*-[Fe(DMeOPrPE)₂(N₂H₃)]⁺ at 298K S-13. Figure S14. ³¹P{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂(N₂H₃)]⁺ at 193K S-13. Figure S15. ¹⁵N{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_2H_3$)]⁺ at 298K S-14. Figure S16. ¹⁵N{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_2H_3$)]⁺ at 193K S-14. Figure S17. ¹⁵N NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_2H_3$)]⁺ at 193K S-14. Figure S18. ¹H NMR spectrum of cis-[Fe(DMeOPrPE)₂(¹⁵N₂H₃)]⁺ at 298K S-15. Figure S19. ¹H NMR spectrum of cis-[Fe(DMeOPrPE)₂(¹⁵N₂H₃)]⁺ at 193K S-15. Figure S20. ¹H HMQC (15 N coupled) of *cis*-[Fe(DMeOPrPE)₂(15 N₂H₃)]⁺ at 193K S-16. Figure S21. ³¹P NMR spectrum of addition of N_2H_4 to Fe(DMeOPrPE)₂(N_2) S-17. Figure S22. ³¹P{¹H} NMR spectrum of *cis*-Fe(DMeOPrPE)₂(H)₂ S-17. Figure S23. Variable temperature ¹H NMR spectra of *cis*-Fe(DMeOPrPE)₂(H)₂ S-18. Figure S24. Variable temperature ${}^{31}P{}^{1}H$ NMR spectra of *cis*-Fe(DMeOPrPE)₂(H)₂ S-18.

Materials and Reagents. Unless otherwise noted, all manipulations were carried out in a Vacuum Atmospheres Co. glove box (argon-filled). HPLC grade THF, diethyl ether, and hexane (Burdick and Jackson) were dried and deoxygenated by passing them through commercial columns of CuO, followed by alumina under an argon atmosphere. Commercially available reagents were used as received. cis-[Fe(DMeOPrPE)₂(N₂H₄)]^{2+,1} trans-[Fe(DMeOPrPE)₂(H₂)H]^{+,2} and Fe(DMeOPrPE)₂(N₂)² were synthesized as previously reported. [HDBU][OTf] was prepared by reacting DBU with 1M TfOH in diethyl ether and removing the solvent *in vacuo*. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over 3Å molecular sieves prior to use.

Instrumentation and Procedures. ³¹P{¹H}, ¹⁵N, and ¹H NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer at an operating frequency of 202.45 (³¹P), 50.69 (¹⁵N), and 500.62 (¹H) MHz. The ¹H and ³¹P chemical shifts were referenced to the solvent peak and to an external standard of 1% H₃PO₄ in D₂O, respectively. The ¹⁵N chemical shifts were referenced to an external standard of neat nitromethane set to 0 ppm. Note that the ¹H NMR data for the methyl and methylene regions in complexes containing the DMeOPrPE ligand were generally broad and uninformative and therefore are not reported in the synthetic descriptions below. The NMR samples were sealed under argon in 7 mm tubes fitted with Teflon valves. Mass spectra were obtained using an Agilent 1100 LC/MS Mass Spectrometer. The samples were dissolved in THF and introduced into the ionization head (ESI) using the infusion method.

Synthesis of *cis*-Fe(DMeOPrPE)₂(N₂H₂). To a stirring solution of *cis*-[Fe(DMeOPrPE)₂(N₂H₄)][BPh₄]₂ (50 mg, 0.0335 mmol) in THF (3 mL), solid ^{*t*}BuOK (13 mg, 0.117 mmol) was added. The solution immediately changed color from bright red-orange to yellow with formation of a white precipitate. The solution was stirred for 15 min and then filtered through Celite. The solvent was removed *in vacuo* and the product was extracted with hexane. The hexane was then removed and the product was isolated as a yellow oil in 96% yield. The product contained uncoordinated DMeOPrPE ligand (~16% by ${}^{31}P{}^{1}H{}$ NMR). ${}^{31}P{}^{1}H{}$ NMR (THF-*d*₈): δ 75.8 (t, ${}^{2}J_{P-P}$ = 38 Hz), δ 71.2 (t, ${}^{2}J_{P-P}$ = 38 Hz). ESI+: *m/z* calcd for Fe(DMeOPrPE)₂(N₂H₂), 850.44. Found: [M+H⁺]⁺, 851.4. The ${}^{15}N$ isotopologue was synthesized in the same manner using *cis*-[Fe(DMeOPrPE)₂({}^{15}N_{2}H_{4})][BPh_{4}]_{2} as the starting material. ${}^{31}P{}^{1}H{}$ NMR (THF-*d*₈): δ 75.8 (t, ${}^{2}J_{P-P}$ = 38 Hz), δ 71.2 (t, ${}^{2}J_{P-P}$ = 38 Hz). HMQC ${}^{1}H$ NMR (THF-*d*₈): δ 2.1 (br, s). ${}^{15}N{}^{1}H{}$ NMR (THF-*d*₈): -315.2 (s). ${}^{15}N$ NMR (THF-*d*₈): δ -315.2 (d, ${}^{1}J_{N-H}$ = 51 Hz).

Protonation of *cis*-**Fe(DMeOPrPE)**₂(**N**₂**H**₂). To a J. Young NMR tube containing *cis*-Fe(DMeOPrPE)₂(N₂H₂) (0.04 mmol, 35 mg) in Et₂O (0.6 mL) was added 83 μ L of 1M TfOH in Et₂O. The solution changed in color from yellow to orange. The NMR data (³¹P{¹H} and ¹⁵N) showed quantitative conversion to *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺. The product was not isolated from this route.

Stepwise protonation of *cis*-Fe(DMeOPrPE)₂(N₂H₂). To a J. Young NMR tube containing *cis*-Fe(DMeOPrPE)₂(N₂H₂) (0.036 mmol, 31 mg) in THF (0.6 mL) was added 16 mg of [HDBU][OTf] in THF. The NMR data (${}^{31}P{}^{1}H{}$ and ${}^{15}N$) showed quantitative conversion to *cis*-[Fe(DMeOPrPE)₂(N₂H₃)]⁺. Then one equivalent of 1M TfOH was added and quantitative conversion to *cis*-[Fe(DMeOPrPE)₂(N₂H₃)]²⁺ was observed by ${}^{31}P{}^{1}H{}$ and ${}^{15}N$ NMR spectroscopy. The products were not isolated during this procedure.

Alternative synthesis of *cis*-Fe(DMeOPrPE)₂(N₂H₂). Anhydrous hydrazine was added to a stirring THF/Et₂O solution of Fe(DMeOPrPE)₂(N₂). The solution was stirred for 2 hours. The product was not isolated from this procedure. The ³¹P{¹H} NMR spectrum showed a mixture of

Fe(DMeOPrPE)₂N₂, *cis*-Fe(DMeOPrPE)₂(N₂H₂), *cis*-Fe(DMeOPrPE)₂(H)₂, and uncoordinated DMeOPrPE (see Fig. S22).

Synthesis of cis-[Fe(DMeOPrPE)₂(N₂H₃)][BPh₄]. To a stirring solution of cis-[Fe(DMeOPrPE)₂(N₂H₄)][BPh₄]₂ (55 mg, 0.037 mmol) in THF, DBU (12 mg, 0.079 mmol) was added. The solution color immediately changed from red-orange to yellow. The solution was stirred for 15 min and then the solvent was removed in vacuo. The yellow product was extracted with toluene and precipitated by addition of hexane yielding a yellow oil in 93% yield. The product contained uncoordinated DMeOPrPE ligand (~13% by ${}^{31}P{}^{1}H{}$ NMR). ${}^{31}P{}^{1}H{}$ NMR (THF- d_8) at 298K: δ 77.1 (br, s), 72.8 (br, s), 68.8 (d, ${}^1J_{PP} = 129$ Hz), 66.4 (d, ${}^1J_{PP} = 129$ Hz). ESI+: m/z calcd. for cis-[Fe(DMeOPrPE)₂(N₂H₃)]⁺, 851.44. Found: [M]⁺, 851.4. The ¹⁵N isotopologue was synthesized in the same manner using *cis*-[Fe(DMeOPrPE)₂(¹⁵N₂H₄)][BPh₄]₂ as the starting material ${}^{31}P{}^{1}H$ NMR (THF- d_8) at 193K: δ 77.9 (s), 73.7 (s), 72.2 (s), 70.7 (s), 69.2 (d, ${}^{1}J_{PP} = 130$ Hz), 68.7 (d, ${}^{1}J_{PP} = 45$ Hz), 65.9 (d, ${}^{1}J_{PP} = 45$ Hz), 65.7 (d, ${}^{1}J_{PP} = 130$ Hz). HMQC ¹H{¹⁵N} NMR (THF-*d*₈) at 193K: δ 4.23 (s), 4.14 (s), 3.66 (s), 3.44 (s), 1.05 (s), 0.65 (s). HMQC ¹H NMR (THF- d_8) at 193K: δ 4.23 (d, ¹ J_{NH} = 80 Hz), 4.14 (d, ¹ J_{NH} = 75 Hz), 3.66 (d, ${}^{1}J_{\rm NH} = 90$ Hz), 3.44 (d, ${}^{1}J_{\rm NH} = 92$ Hz), 1.05 (d, ${}^{1}J_{\rm NH} = 30$ Hz), 0.65 (d, ${}^{1}J_{\rm NH} = 30$ Hz). ${}^{15}N{}^{1}H{}$ NMR (THF-d₈) at 193K: -367.6 (s), -369.9 (s), -377.4 (s). ¹⁵N NMR (THF-d₈) at 193K: -367.6 (d, ${}^{1}J_{\rm NH}$ = 50 Hz), -369.9 (d, ${}^{1}J_{\rm NH}$ = 51 Hz), -377.4 (d, ${}^{1}J_{\rm NH}$ = 80 Hz).

Protonation of *cis*-[**Fe**(**DMeOPrPE**)₂(**N**₂**H**₃)]⁺. To a J. Young NMR tube containing *cis*-[Fe(DMeOPrPE)₂(N₂H₃)]⁺ (0.036 mmol, 42 mg) in THF (0.6 mL) was added 36 μ L of 1M TfOH in Et₂O. The solution changed in color from yellow to orange. The NMR data (³¹P{¹H} and ¹⁵N) showed quantitative conversion to *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺. The product was not isolated from this route. Synthesis of Fe(DMeOPrPE)₂(H)₂. A solution of Fe(DMeOPrPE)₂(N₂) in THF was charged with 1 atm of H₂ in a 50 mL Fischer-Porter tube and vigorously stirred for 6 hrs. The yellow oil was isolated by removing the solvent *in vacuo*. ³¹P{¹H} NMR (DMSO-*d*₆) at 253K: 98.9 (t, ²*J*_{P-P} = 20 Hz), δ 84.8 (t, ²*J*_{P-P} = 20 Hz). ¹H NMR (DMSO-*d*₆) of the hydride region: -14.5 (quintet, ²*J*_{P-H} = 36 Hz), -14.7 (ddt, ²*J*_{P-H} = 37 Hz, ²*J*_{P-H} = 14 Hz, ²*J*_{P-H} = 58 Hz). Both *trans* and *cis* isomers are seen at various temperatures by ¹H and ³¹P NMR spectroscopy (see Figs. S24 and S25), which has previously been observed in analogous iron dihydride complexes.³

Alternative synthesis of $Fe(DMeOPrPE)_2(H)_2$. To a stirring solution of *trans*-[Fe(DMeOPrPE)_2H(H_2)]PF₆ (50 mg, 0.056 mmol) in THF, solid ^tBuOK (13 mg, 0.112 mmol) was added. The reaction was stirred for 2 hours and then filtered through Celite. The yellow oil was isolated my removing the solvent *in vacuo*. The NMR spectra of the product synthesized by this route were identical to those described above.

References

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Figure S1. ³¹P{¹H} NMR spectra at 298K of titration of *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺ with varying equivalents of KO'Bu.



Figure S2. ³¹P{¹H} NMR spectra at 298K of titration of *cis*-[Fe(DMeOPrPE)₂(N₂H₄)]²⁺ with varying equivalents of DBU.











is uncoordinated DMeOPrPE.

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Figure S10. ¹H HMQC (¹⁵N coupled) NMR spectrum of *cis*-Fe(DMeOPrPE)₂(¹⁵N₂H₂).







Figure S13. ³¹P{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂(N₂H₃)]⁺ at 298K. The resonance at -26.65 ppm is uncoordinated DMeOPrPE.





Figure S15. ¹⁵N{¹H} NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_2H_3$)]⁺ at 298K.







Figure S18. ¹H NMR spectrum of cis-[Fe(DMeOPrPE)₂(¹⁵N₂H₃)]⁺ at 298K.



Figure S19. ¹H NMR spectrum of *cis*-[Fe(DMeOPrPE)₂($^{15}N_2H_3$)]⁺ at 193K. The hydrazido proton resonances are located at 4.2 and 0.7 ppm.





Figure S21. ³¹P NMR spectrum of addition of N₂H₄ to Fe(DMeOPrPE)₂(N₂). Peak assignments: δ 99, 85 *cis*-Fe(DMeOPrPE)₂(H)₂; δ 81 Fe(DMeOPrPE)₂(N₂); δ 78 unknown; δ 76, 71 *cis*-Fe(DMeOPrPE)₂(N₂H₂); δ -26 DMeOPrPE.



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Figure S23. ¹H spectrum of hydride region of $Fe(DMeOPrPE)_2(H)_2$ (red spectrum acquired at 80°C, blue spectrum acquired at -40°C).



Figure S24. Variable temperature ${}^{31}P{}^{1}H$ spectra of Fe(DMeOPrPE)₂(H)₂ showing *cis* to *trans* isomerization.