Electronic Supplementary Information

Intermediates in the Reduction of N₂ to NH₃: Synthesis of Iron η² Hydrazido(1-) and Diazene Complexes

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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+\(^+\), 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. \(^{31}\)P\(^{1}\)H, \(^{15}\)N, and \(^{1}\)H NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer at an operating frequency of 202.45 \((^{31}\)P\)\), 50.69 \((^{15}\)N\)\), and 500.62 \((^{1}\)H\) MHz. The \(^{1}\)H and \(^{31}\)P chemical shifts were referenced to the solvent peak and to an external standard of 1\% H\(_3\)PO\(_4\) in D\(_2\)O, respectively. The \(^{15}\)N chemical shifts were referenced to an external standard of neat nitromethane set to 0 ppm. Note that the \(^{1}\)H 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)\(_2\)(N\(_2\)H\(_2\)). To a stirring solution of cis-[Fe(DMeOPrPE)\(_2\)(N\(_2\)H\(_4\))]\([BPh_4]\)\(_2\) (50 mg, 0.0335 mmol) in THF (3 mL), solid '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$$_8$): $\delta$ 75.8 (t, $^2$J$_{P-P}$ = 38 Hz), $\delta$ 71.2 (t, $^2$J$_{P-P}$ = 38 Hz). ESI+: $m$/z calcd for Fe(DMeOPrPE)$_2$(N$_2$H$_2$), 850.44. Found: [M+H$^+$]$^+$, 851.4. The $^{15}$N isotopologue was synthesized in the same manner using cis-[Fe(DMeOPrPE)$_2$($^{15}$N$_2$H$_4$)][BPh$_4$]$^2$ as the starting material. $^{31}$P{$^{1}$H} NMR (THF-$_d$$_8$): $\delta$ 75.8 (t, $^2$J$_{P-P}$ = 38 Hz), $\delta$ 71.2 (t, $^2$J$_{P-P}$ = 38 Hz). HMQC $^1$H NMR (THF-$_d$$_8$): $\delta$ 2.1 (br, s). $^{15}$N{$^{1}$H} NMR (THF-$_d$$_8$): -315.2 (s). $^{15}$N NMR (THF-$_d$$_8$): $\delta$ -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)$_2$(N$_2$H$_2$) (0.04 mmol, 35 mg) in Et$_2$O (0.6 mL) was added 83 $\mu$L of 1M TfOH in Et$_2$O. The solution changed in color from yellow to orange. The NMR data ($^{31}$P{$^{1}$H} and $^{15}$N) showed quantitative conversion to cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)]$^{2+}$. The product was not isolated from this route.

**Stepwise protonation of cis-Fe(DMeOPrPE)$_2$(N$_2$H$_2$).** To a J. Young NMR tube containing cis-Fe(DMeOPrPE)$_2$(N$_2$H$_2$) (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)$_2$(N$_2$H$_3$)]$^+$. Then one equivalent of 1M TfOH was added and quantitative conversion to cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)]$^{2+}$ 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)$_2$(N$_2$H$_2$).** Anhydrous hydrazine was added to a stirring THF/Et$_2$O solution of Fe(DMeOPrPE)$_2$(N$_2$). The solution was stirred for 2 hours. The product was not isolated from this procedure. The $^{31}$P{$^{1}$H} NMR spectrum showed a mixture of
Fe(DMeOPrPE)$_2$N$_2$, cis-Fe(DMeOPrPE)$_2$(N$_2$H$_2$), cis-Fe(DMeOPrPE)$_2$(H)$_2$, and uncoordinated DMeOPrPE (see Fig. S22).

Synthesis of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)][BPh$_4$]. To a stirring solution of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)][BPh$_4$]$_2$ (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: $\delta$ 77.1 (br, s), 72.8 (br, s), 68.8 (d, $^1$J$_{PP} = 129$ Hz), 66.4 (d, $^1$J$_{PP} = 129$ Hz).

ESI+: m/z calcd. for cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)]$^+$, 851.44. Found: [M]$^+$, 851.4. The $^{15}$N isotopologue was synthesized in the same manner using cis-[Fe(DMeOPrPE)$_2$(15N$_2$H$_4$)][BPh$_4$]$_2$ as the starting material. $^{31}$P{$^1$H} NMR (THF-$d_8$) at 193K: $\delta$ 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 $^1$H{$^{15}$N} NMR (THF-$d_8$) at 193K: $\delta$ 4.23 (s), 4.14 (s), 3.66 (s), 3.44 (s), 1.05 (s), 0.65 (s). HMQC $^1$H NMR (THF-$d_8$) at 193K: $\delta$ 4.23 (d, $^1$J$_{NH} = 80$ Hz), 4.14 (d, $^1$J$_{NH} = 75$ Hz), 3.66 (d, $^1$J$_{NH} = 90$ Hz), 3.44 (d, $^1$J$_{NH} = 92$ Hz), 1.05 (d, $^1$J$_{NH} = 30$ Hz), 0.65 (d, $^1$J$_{NH} = 30$ Hz). $^{15}$N{$^1$H} NMR (THF-$d_8$) at 193K: -367.6 (s), -369.9 (s), -377.4 (s). $^{15}$N NMR (THF-$d_8$) at 193K: -367.6 (d, $^1$J$_{NH} = 50$ Hz), -369.9 (d, $^1$J$_{NH} = 51$ Hz), -377.4 (d, $^1$J$_{NH} = 80$ Hz).

Protonation of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)]$^+$. To a J. Young NMR tube containing cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)]$^+$ (0.036 mmol, 42 mg) in THF (0.6 mL) was added 36 μL of 1M TfOH in Et$_2$O. The solution changed in color from yellow to orange. The NMR data ($^{31}$P{$^1$H} and $^{15}$N) showed quantitative conversion to cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)]$^{2+}$. The product was not isolated from this route.
Synthesis of Fe(DMeOPrPE)$_2$(H)$_2$. A solution of Fe(DMeOPrPE)$_2$(N$_2$) in THF was charged with 1 atm of H$_2$ in a 50 mL Fischer-Porter tube and vigorously stirred for 6 hrs. The yellow oil was isolated by removing the solvent in vacuo. $^{31}$P{$^1$H} 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). $^1$H 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 $^1$H and $^{31}$P 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)$_2$H(H$_2$)]PF$_6$ (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 by removing the solvent in vacuo. The NMR spectra of the product synthesized by this route were identical to those described above.

References

Figure S1. $^{31}$P{$^1$H} NMR spectra at 298K of titration of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)]$^{2+}$ with varying equivalents of KO'Bu.
Figure S2. $^{31}$P$\left\{^1\text{H}\right\}$ NMR spectra at 298K of titration of $cis$-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)]$^{2+}$ with varying equivalents of DBU.
Figure S3. $^{31}$P($^1$H) NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_4$)][2BPh$_4$].

Figure S4. $^1$H NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(^{15}N$_2$H$_4$)][2BPh$_4$].
Figure S5. $^1$H HMQC NMR spectrum of \textit{cis}-[Fe(DMeOPrPE)$_2$(\textsuperscript{15}N$_2$H$_4$)][2BPh$_4$].

Figure S6. $^{15}$N NMR spectrum of \textit{cis}-[Fe(DMeOPrPE)$_2$(\textsuperscript{15}N$_2$H$_4$)]$^{2+}$. 
Figure S7. $^{15}$N{$^1$H} NMR spectrum of $\text{cis-}[\text{Fe(DMeOPrPE)}_2(15\text{N}_2\text{H}_4)]^{2+}$.

Figure S8. $^{31}$P{$^1$H} NMR spectrum of $\text{cis-Fe(DMeOPrPE)}_2(\text{N}_2\text{H}_2)$. The resonance at -26.6 ppm is uncoordinated DMeOPrPE.
Figure S9. $^1$H NMR spectrum of cis-Fe(DMeOPrPE)$_2$(N$_2$H$_2$)$_2$.

Figure S10. $^1$H HMQC ($^{15}$N coupled) NMR spectrum of cis-Fe(DMeOPrPE)$_2$(N$_2$H$_2$)$_2$.
Figure S11. $^{15}$N{$_1^1$H} NMR spectrum of $cis$-Fe(DMeOPrPE)$_2$($_{15}$N$_2$H$_2$).

Figure S12. $^{15}$N NMR spectrum of $cis$-Fe(DMeOPrPE)$_2$($_{15}$N$_2$H$_2$).
**Figure S13.** $^{31}$P$\{^1$H$\}$ NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)]$^+$ at 298K. The resonance at -26.65 ppm is uncoordinated DMeOPrPE.

**Figure S14.** $^{31}$P$\{^1$H$\}$ NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(N$_2$H$_3$)]$^+$ at 193K. The resonance at -29.0 ppm is uncoordinated DMeOPrPE.
Figure S15. $^{15}$N{$^1$H} NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(15N$_2$H$_3$)]$^+$ at 298K.

Figure S16. $^{15}$N{$^1$H} NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(15N$_2$H$_3$)]$^+$ at 193K.

Figure S17. $^{15}$N NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(15N$_2$H$_3$)]$^+$ at 193K.
Figure S18. $^1$H NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(^{15}$N$_2$H$_3$)]$^+$ at 298K.

Figure S19. $^1$H NMR spectrum of cis-[Fe(DMeOPrPE)$_2$(^{15}$N$_2$H$_3$)]$^+$ at 193K. The hydrazido proton resonances are located at 4.2 and 0.7 ppm.
Figure S20. $^1$H HMQC ($^{15}$N coupled) of cis-[Fe(DMeOPrPE)$_2$(H$_2$N$_3$)]$^+$ at 193K.
**Figure S21.** $^{31}$P NMR spectrum of addition of N$_2$H$_4$ to Fe(DMeOPrPE)$_2$(N$_2$). Peak assignments: δ 99, 85 cis-Fe(DMeOPrPE)$_2$(H)$_2$; δ 81 Fe(DMeOPrPE)$_2$(N$_2$); δ 78 unknown; δ 76, 71 cis-Fe(DMeOPrPE)$_2$(N$_2$H$_2$); δ -26 DMeOPrPE.

**Figure S22.** $^{31}$P{$_1$H} spectrum of cis-Fe(DMeOPrPE)$_2$(H)$_2$ at -20°C.
Figure S23. $^1$H 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$^\{^1\text{H}\}$ spectra of Fe(DMeOPrPE)$_2$(H)$_2$ showing \textit{cis} to \textit{trans} isomerization.