A Five-Coordinate Phosphino/Acetate Iron(II) Scaffold that Binds N_2, N_2H_2, N_2H_4, and NH_3 in the Sixth Site

Caroline T. Saouma,[‡] Curtis E. Moore,[†] Arnold L. Rheingold,[†] Jonas C. Peters*[,‡]

[‡]*Department of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, 91125, U.S.A.*
[†]*Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, 92093, U.S.A.*

Table of Contents

Experimental Procedures……………………………………………………………………..…S-2
Chart S1. Plot of $^{3}J_{HH}$ vs. N-N bond distance in M_2(*trans*-N_2H_2) species………………….. S-11
Figure S1. ^{1}H NMR spectrum of 1 (THF-d_8, 25 ^{o}C)……………………………………….S-12
Figure S2. Overlay of rRaman spectra of ^{14}N-**2** and ^{15}N-**2**…………………………………...S-13
Figure S3. ^{15}N NMR spectrum (d_8-THF, -75 ^{o}C) of **2**……………………………………...S-13
Figure S4. ^{31}P NMR spectrum (d_8-THF, -75 ^{o}C) of **2**…………………...…………………S-13
Figure S5. ^{31}P NMR spectrum (d_8-THF, -75 ^{o}C) of **3**……………………………………...S-14
Figure S6. ^{1}H NMR spectrum (d_8-THF, -75 ^{o}C) of ^{15}N-**3**…………………………………..S-14
Figure S7. ^{1}H NMR spectrum (d_8-THF, 0 ^{o}C) of **1**/^{15}N-**2** and **1**/^{15}N-**3**……..………………..S-15
Figure S8. CV of **2** recorded at -35 ^{o}C……………………………………………………..S-16
References....…………………………………………………………………………..S-17

General Considerations

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by sparging with Ar followed by passage through an activated alumina column from S.G. Water (Nashua, N.H.). Nonhalogenated solvents were tested with a standard purple solution of benzophenone ketyl in THF to confirm effective oxygen and moisture removal. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3-Å molecular sieves prior to use. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

Caution: All manipulations with anhydrous hydrazine were done at ambient or reduced temperatures, and the waste disposed of appropriately. Anhydrous hydrazine is both highly toxic and highly explosive, with an auto-ignition temperature that is highly dependent on the presence of impurities. Prior to working with anhydrous hydrazine, we encourage others to consult appropriate sources to familiarize themselves with the dangers. We found "Wiley Guide to Chemical Incompatibilities" (Pohanish, R. P. and Greene, S. A.; Wiley) to be an excellent reference for such matters. Though we did not distill our anhydrous hydrazine, a procedure is described in the literature (Lucien, H. W., J. Chem. Eng. Data, ***1962****, 7, 541).*

Spectroscopic Measurements

Varian 300, 400, and 500 MHz spectrometers were used to record the ^{1}H NMR, ^{31}P NMR, and ^{15}N NMR spectra (400 or 500 MHz). ^{1}H chemical shifts were referenced to residual solvent. ^{31}P NMR chemical shifts were referenced to 85% H_3PO_4 at $\delta = 0$ ppm, and ^{15}N NMR chemical shifts were referenced to neat $C_6H_5{}^{15}NO_2$ ($\delta = 370$ ppm) in comparison to liquid ammonia (δ = 0 ppm). MestReNova (6.1.0) was used for NMR data workup, as well as for simulation of spectra. Solution magnetic moments were measured using Evans method.[1]

IR measurements were obtained with a KBr solution cell or a KBr pellet using a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Varian Resolutions Pro software set at 4 cm^{-1} resolution.

The rRaman samples were prepared by loading solutions into glass capillaries which were subsequently flame-sealed. For measurements at 77 K, samples were loaded into an NMR tube, sealed, and placed in a quartz dewar filled with liquid nitrogen for data collection. Excitation was performed at either 632.8 nm using a HeNe laser (10 mW) or at 514 nm using an Ar-ion laser. A lens collected the light that scattered at 90^o and focused it through a low-pass filter and into the entrance slit of a SPEX 750M monochromator. The dispersed light was detected by a LN/CCD array (5 cm^{-1} resolution), and the spectra recorded using Winspec (Princeton Instrument) software. Conversion from pixel to wavenumber was done by obtaining the spectrum of cyclohexane, and deriving the linear plot of pixel versus wavenumber for known vibrations. All spectra were recorded in THF (room temperature) or Me-THF (77 K), and in some instances, solvent subtraction or baseline correction was performed.

Optical spectroscopy measurements were taken on a Cary 50 UV-Vis spectrophotometer using a 1 cm two-window quartz cell sealed with standard ground-glass joints or Teflon plugs. Measurements at reduced temperatures were accomplished by using a dip-probe that was immersed into a solution of analyte in a custom-made Schlenk tube under an N_2 atmosphere.

Electrochemistry

Electrochemical measurements were carried out in a glove-box under a dinitrogen atmosphere in a one-compartment cell using a BAS model 100/W electrochemical analyzer. A glassy carbon electrode and platinum wire were used as the working and auxillary electrodes, respectively. The reference electrode was $Ag/AgNO_3$ in THF. Solutions (THF) of electrolyte (0.4 M tetra-n-butylammonium hexafluorophosphate) and analyte were also prepared in a glovebox. Experiments were conducted at room temperature, and in certain instances, in a drop freezer maintained at -35 ^{o}C. Ferrocene was subsequently added to the samples, and a CV obtained to allow for referencing versus Fc/Fc^{+}.

X-ray Crystallography Procedures

Low-temperature diffraction data were collected on either a Siemens or Bruker Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo or Cu Kα radiation ($\lambda = 0.71073$ or 1.54178 Å, respectively), performing φ- and ω-scans. The structures were solved by direct or Patterson methods using SHELXS[2] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[3] The structures were refined using established methods.[4] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except hydrogen atoms directly attached to the nitrogen atom in **5**) were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). The protons attached to the iron-bound nitrogen atom of **5** could be located in the difference Fourier synthesis and subsequently those H atoms were refined semi-freely with the help of distance restraints.

All disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. All close contacts, both inter and intramolecular, reported by the Platon validation software[5] involve at least one partner from a minor component of a disorder.

The structure of **4** suffers from total molecule disorder, with 18 % of the molecules translocated along the b-axis of the unit cell. The data was modeled assuming this disorder to obtain a satisfactory solution.

Starting Materials and Reagents

$[PhBP^{CH2Cy}{}_3]FeMe$,[6] $^{15}N_2H_4$,[7] and Me_2Mg[8] were prepared according to literature methods. $Pb(OAc)_4$ was purchased from Aldrich (99.999+%), purified as described in the literature,[9] and recrystallized from cold THF to afford a white crystalline solid. Acetic acid was dried according to literature methods.[9] All other reagents were purchased from commercial vendors and used without further purification.

Synthesis of $[PhBP^{CH2Cy}{}_3]Fe(OAc)$, 1. To a stirring solution of $[PhBP^{CH2Cy}{}_3]FeMe$ (0.2732 g, 0.3116 mmol) in 16 mL DME, neat anhydrous acetic acid (17.9 μL, 0.312 mmol) was added. The solution immediately changed color from yellow to pale grey/purple. After stirring for 24 h, the volatiles were removed. The resulting solids were collected on a frit and rinsed with pentanes to afford analytically pure material (0.2338 g, 81.5 %). A second crop can be isolated by storing the pentane extract at -35 °C for several days. ^1H NMR (THF-d_8, 400 MHz, 25 °C) δ 98.1 (s), 65 (bs), 25.2 (s), 13.9 (s), 12.8 (s), 1.9 (s), 1.2 (s), 0.6 (s), 0.1 (s), -2.6 (s), -7.3 (s), -8.2 (s), -9.0 (s), -9.7 (s), -16.5 (s), -23.2 (s). Evans Method (C_6D_6): 4.5 B.M. UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 745 (240), 392 (400). Anal. Calcd. for $C_{53}H_{92}BFeO_2P_3$: C 69.12; H 10.07; N 0. Found: C 68.77; H 9.93; N 0.

Synthesis of $\{[PhBP^{CH2Cy}{}_3]Fe(OAc)\}_2(\mu\text{-}N_2)$, 2. Cooling THF solutions of **1** to -35 °C affords **2**. Pink crystals of **2** suitable for diffraction were grown by cooling a saturated Et_2O solution of **1** to -35 °C in a nitrogen-filled glovebox. The bound N_2 in **2** is labile; by Toepler analysis, qualitative release of N_2 was observed when a THF solution of **2** was maintained at -78 °C. In the solid-state, the bound N_2 is also labile, as pink crystals of **2** change color to grey/purple upon exposure to vacuum. rRaman (514 nm, Me-THF, 77 K) (cm^{-1}): 2083 (NN). UV-vis (THF, -78 °C) λ_{max}, nm (ε, M^{-1} cm^{-1}): 750 (240), 532 (1200).

Samples of ^{15}N-**2** were prepared by freeze pump thawing solutions of **1**/**2** and subsequently exposing **1** to a ^{15}N atmosphere and cooling the solution to -75 °C. ^{1}H NMR (THF-d_8, 400 MHz, -75 °C) δ 7.1 (s, 4H), 6.9 (s, 4H), 6.9 (s, 2H), 0 – 2.7 (m, overlap with solvent, 168H). ^{31}P NMR (THF-d_8, 162 MHz, -75 °C) δ 53.7 (bs, 2P), 44.54 (dt, $^2J_{PP}$ = 71.1 Hz, $^2J_{PN} \approx 15$ Hz). ^{15}N NMR (THF-d_8, 40 MHz, -75 °C) δ 328.6 (d, $^2J_{PN} \approx 15$ Hz). rRaman (514 nm, Me-THF, 77 K) (cm^{-1}): 2010 (NN) (2012 cm^{-1} predicted for an NN harmonic oscillator).

Synthesis of $\{[PhBP^{CH2Cy}{}_3]Fe(OAc)\}_2(\mu\text{-}N_2H_4)$, 3. A solution of **1** (0.0356 g, 0.0393 mmol) in 1 mL THF was cooled to – 78 °C, and a solution of anhydrous hydrazine in 1 mL THF (0.68 μL, 0.02 mmol) was added dropwise. The solution changed color from pink to purple as **3** was generated. When the reaction is rigorously maintained at -78 °C, no other species are present by ^{1}H and ^{31}P NMR spectroscopy. The bound hydrazine in **3** is labile, and at -30 °C resonances ascribed to **1** are observed by ^{1}H NMR spectroscopy. At this temperature **3** is also unstable, and resonances ascribed to **4** are observed by ^{1}H NMR spectroscopy. UV-vis (THF, -78 ^{o}C) λ_{max}, nm (ε, M^{-1} cm^{-1}): 549 (650).

Samples of ^{15}N-**3** were prepared following an analogous synthetic procedure using $^{15}N_2H_4$. ^{1}H NMR (THF-*d*$_8$, 400 MHz, -75 ^{o}C) δ 7.1 (bs, 4H), 6.88 (t, *J* = 6.4 Hz, 4H), 6.71 (t, *J* = 6.1 Hz, 2H), 2.51 (d, $^1J_{NH}$ = 66.0 Hz, NH_2, 4H), 0.75 – 2.2 (m, overlap with solvent, 168H), 0.19 (bs, 4H), -0.15 (bs, 3H). ^{31}P NMR (THF-*d*$_8$, 162 MHz, -75 ^{o}C) δ 66.17 (d, $^2J_{PP}$ = 60.3 Hz), 54.51 (dt, $^2J_{PP}$ = 55.9 Hz, $^2J_{PN}$ = 8.2 Hz). ^{15}N NMR (THF-*d*$_8$, 40 MHz, gHSQCAD, -75 ^{o}C) δ 103.

Synthesis of {[PhBP^{CH2Cy}$_3$]Fe(OAc)}$_2$(μ-N$_2$H$_2$), 4. Neat anhydrous hydrazine (0.54 μL, 0.017 mmol) was added to a stirring solution of **1** (0.0300 g, 0.0335 mmol) in 1 mL benzene. The solution immediately changed color from pale grey to dark blue. After stirring for 2 h, the volatiles were removed. The solids were rinsed with Et_2O, and a midnight blue analytically pure powder of **4** was isolated (0.0236 g, 75.3 %). Crystals suitable for diffraction were grown by the vapor diffusion of pentane into a dilute benzene solution of **4**. Crystals that were grown from THF/pentane also suffered from total molecule disorder. Complex **4** is stable to vacuum at room temperature, but upon heating a toluene solution of **4** to 60 ^{o}C, transforms to **1** (and **5**) over 2 h. ^{1}H NMR (C_6D_6, 400 MHz, 25 ^{o}C) δ 17.72 (bs, 2H, N*H*), 7.98 (d, *J* = 7.2 Hz, 4H), 7.51 (t, *J* = 7.3 Hz, 4H), 7.25 (t, overlap with solvent, *J* = 6.9 Hz, 2H), 0.5 – 2.5 (m, 168H). ^{31}P NMR (C_6D_6, 162 MHz, 25 ^{o}C) δ 52.7 (d, $^2J_{PP}$ = 60.8 Hz), 34.9 (t, $^2J_{PP}$ = 60.8 Hz). UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 726 (17,700). IR (KBr) (cm^{-1}): 3244, 748, 446. rRaman (633 nm, THF) (cm^{-1}): 1299, 1232, 608. Anal. Calcd. for $C_{106}H_{186}B_2Fe_2N_2O_4P_6$: C 68.02; H 10.02; N 1.50. Found: C 68.35; H 9.81; N 1.37.

Samples of ^{15}N-**4** were prepared following an analogous synthetic procedure using $^{15}N_2H_4$. $^{1}H\{^{31}P\}$ NMR (C_6D_6, 400 MHz, 25 °C) δ 17.72 (m, $^{1}J_{NH}$ = -71.0 Hz, $^{2}J_{NH}$ = -1.1 Hz, $^{3}J_{HH}$ = 21.0 Hz, $^{1}J_{NN}$ = 12.0 Hz, 2H, N*H*). Coupling constants were obtained by simulation of the spectrum. ^{31}P NMR (C_6D_6, 162 MHz, 25 °C) δ 52.7 (d, $^{2}J_{PP}$ = 60.8 Hz), 34.9 (dt, $^{2}J_{PP}$ = 60.8 Hz, $^{2}J_{PN} \approx$ 13 Hz). ^{15}N NMR (C_6D_6, 40 MHz, gHSQCAD, 25 °C) δ 434. IR (KBr) (cm^{-1}): 3242, 745, 438. rRaman (633 nm, THF) (cm^{-1}): 1263, 1223, 603.

Synthesis of [PhBP$^{CH2Cy}_3$]Fe(OAc)(NH_3), 5. Neat anhydrous hydrazine (0.40 μL, 0.012 mmol) was added to a stirring solution of **1** (0.0213 g, 0.0231 mmol) in 1 mL THF. The solution immediately changed color from pale grey to dark blue. Over the course of stirring for 2 h, a second color change to purple ensued. The volatiles were removed, the resulting solids extracted into Et_2O, and the Et_2O solution was concentrated to dryness. The resulting purple solids were rinsed with pentane to afford analytically pure material (0.0144 g, 66.0 %). Complex **5** is stable to vacuum at room temperature, but upon heating to 60 °C, gradually transforms to **1**. Crystals suitable for diffraction were grown by the vapor diffusion of pentane into a benzene solution of **5**. UV-vis (THF) λ_{max}, nm (ε, M^{-1} cm^{-1}): 745 (150), 550 (440), 395 (240). IR (KBr) (cm^{-1}): 3365, 3348. Anal. Calcd. for $C_{53}H_{95}BFeNO_2P_3$: C 67.87; H 10.21; N 1.49. Found: C 67.66; H 10.07; N 1.63.

Samples of ^{15}N-**5** were prepared following an analogous synthetic procedure using $^{15}N_2H_4$, or by addition of 1 atm of $^{15}NH_3$ to a THF solution of **1**. ^{1}H NMR (THF-*d*$_8$, 500 MHz, -40 °C) δ 7.12

(bs, 2H), 6.92 (bs, 2H), 6.76 (bs, 1H), 2.49 (d, ${}^{1}J_{NH}$ = 68.0 Hz, NH_3, 3H), 0.10 – 2.27 (m, 168H, overlap with solvent/${}^{15}NH_3$), -0.09 (bs, 3H). ${}^{31}P$ NMR (THF-d_8, 202 MHz, -40 °C) δ 61.89 (d, J = 56 Hz), 51.09 (t, J = 56 Hz). ${}^{15}N$ NMR (THF-d_8, 50 MHz, -40 °C) δ -21.1 (q, ${}^{1}J_{NH}$ = 68.0 Hz).

Reduction Studies of 2. In a typical experiment, **2** was massed out in the glove-box (10 – 20 mg) and transferred to a 25 mL 2-neck round bottom flask fitted with a stir bar. THF was added (ca. 5 mL), and a 180° ground glass adaptor with a Teflon plug and a rubber septum were attached. The flask was cooled in the cold-well for 30 min. (maintained at -78 °C with a dry ice/acetone bath). At this time, reductant and acid (2 or 6 equiv), reductant (1 equiv), or H-atom donors (2 or 6 equiv) were added dropwise via syringe as THF solutions (for incompatible acid/reductant combinations, these were added as separate THF solutions). The reaction was stirred for 24 h, during which time it warmed to RT. At this time, the volatiles were vac-transferred onto a frozen ethereal solution of HCl (1.0 M; 6 mL), and the residual iron-containing solids were analyzed by ${}^{31}P$ and ${}^{1}H$ NMR spectroscopy. The acidic ethereal solution was stirred for 45 min at room temperature, and the volatiles were removed. The remaining solids were analyzed by ${}^{1}H$ NMR spectroscopy (d_6-DMSO), and ammonium was quantified by integration against an internal standard of mesitylene (5.0 mM).

Reaction of 4 with oxidants. Solutions of **4** in THF were typically prepared (ca. 10-20 mg in 2-5 mL THF), to which a solution (or slurry) of oxidant in THF (1 or 2 equiv) was added dropwise. The reaction stirred for 2 h, the volatiles were removed, and the resulting solids were then analyzed by ${}^{1}H$ and ${}^{31}P$ NMR spectroscopy.

For reactions that were done at -78 °C, a similar protocol was employed; the solutions were chilled for 30 min. in a cold-well in the glove-box prior to addition of oxidant to **4**, and the solutions were stirred for 30 min at -78 °C prior to warming to RT.

Disproportionation Studies of 1. A similar protocol as that described for the reduction of **2** was employed, with addition of excess hydrazine instead of reductant and acid.

Thermal Stability Studies. In a typical experiment, an NMR sample of the compound was prepared in either d_8-toluene or d_8-THF, and transferred to a re-sealable J.Young NMR tube. NMR spectra (^{31}P and ^{1}H) were obtained at room temperature, and the sample was heated for two hours to 60 °C, and the NMR spectra recorded again. Samples that did not show degradation were heated for further lengths of time, and the integrity of the sample was monitored by NMR spectroscopy.

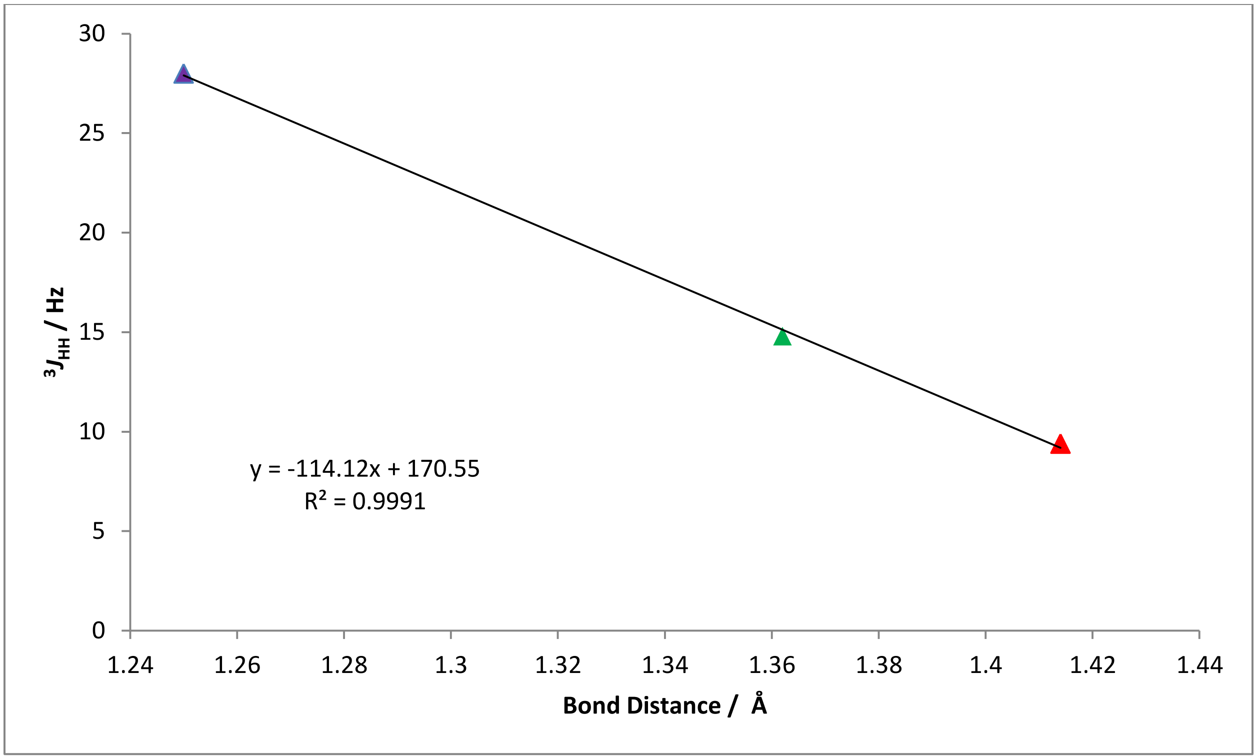

Chart S1. Plot of $^3J_{HH}$ vs. N-N bond distance in diazene-coordinated metal species. ▲= $[(CO)_5Cr]_2$(*trans*-μ-N_2H_2);[10,11] ▲= $\{[PhBP^{Ph}{}_3]Fe(CO)\}_2$(*trans*-μ-$N_2H_2$);[12] ▲= $[(\eta^5\text{-}C_5Me_4H)_2ZrI]_2$(*trans*-μ-$N_2H_2$).[13]

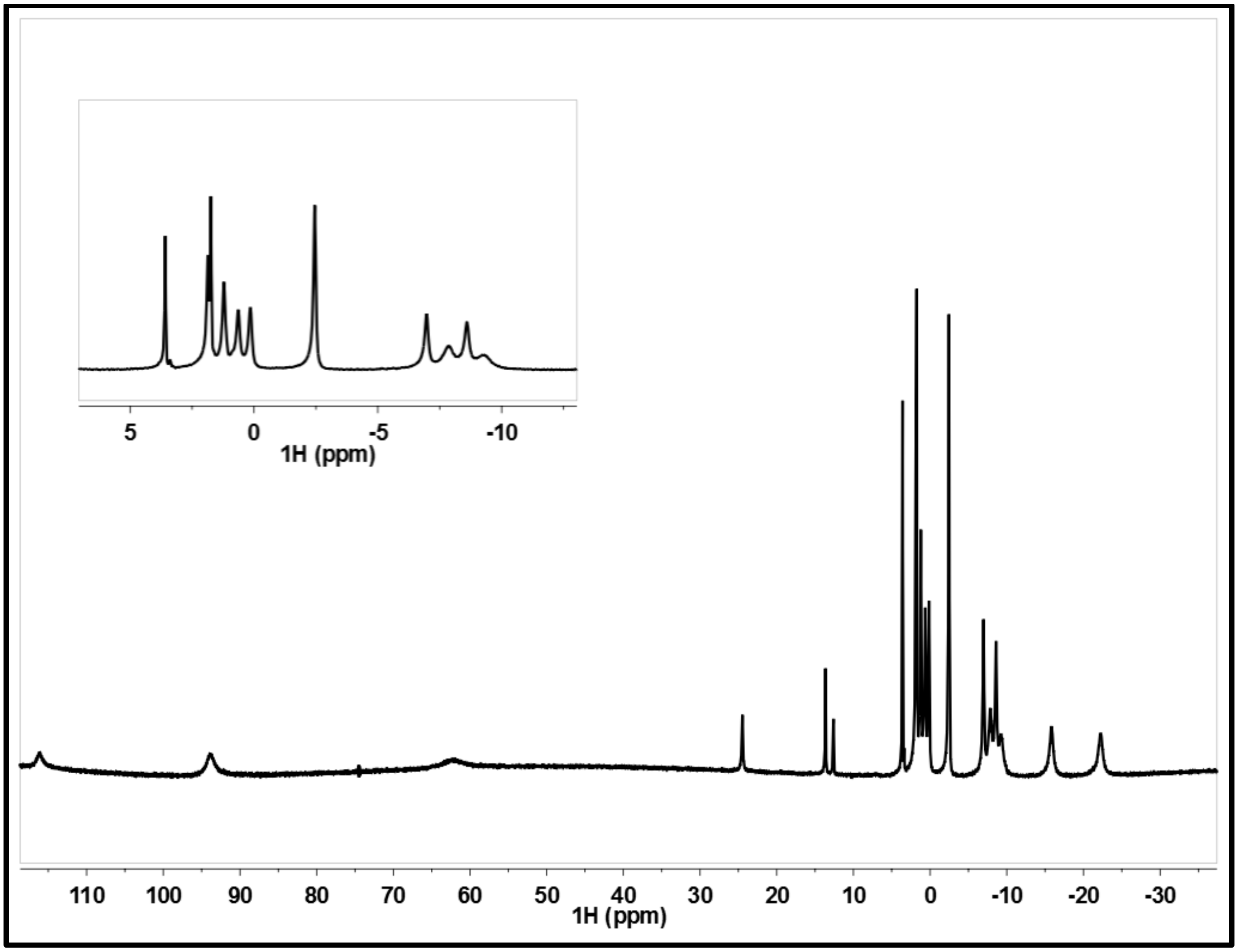

Figure S1. ^{1}H NMR spectrum of **1** (THF-*d*$_8$, 25 ^{o}C), with the inset indicating the peaks between -10 and 5 ppm.

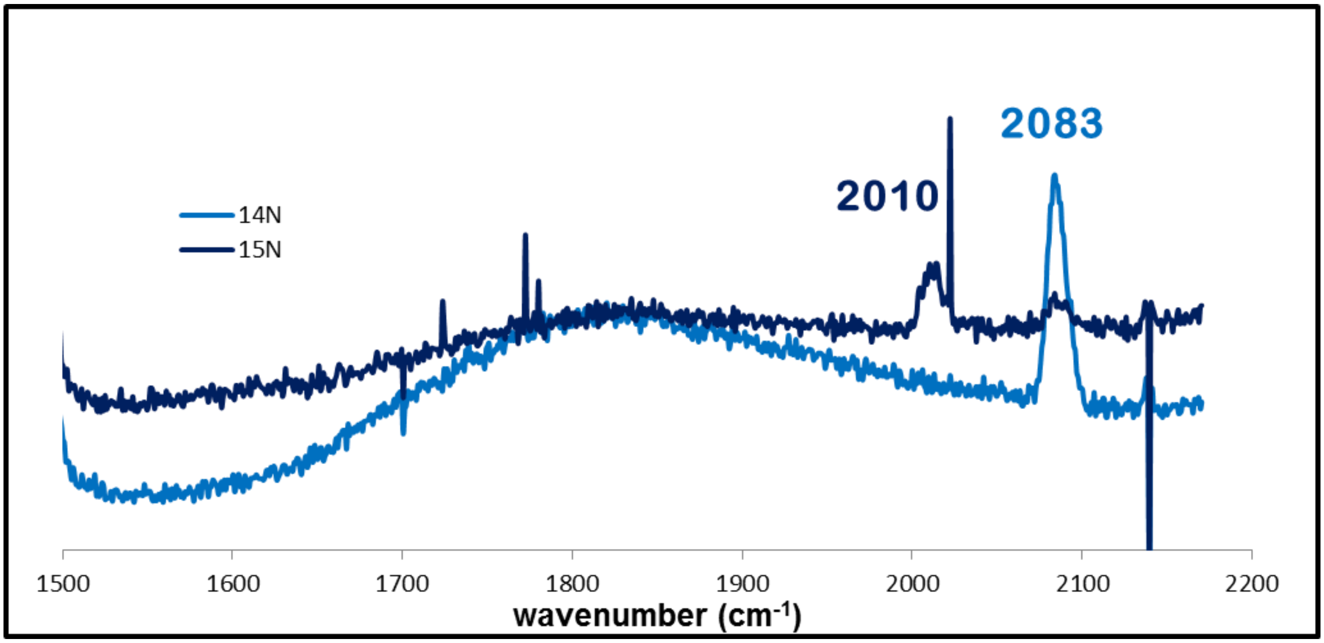

Figure S2. Overlay of rRaman spectra of ^{14}N-**2** and ^{15}N-**2** (514 nm excitation, 77K, MeTHF glass).

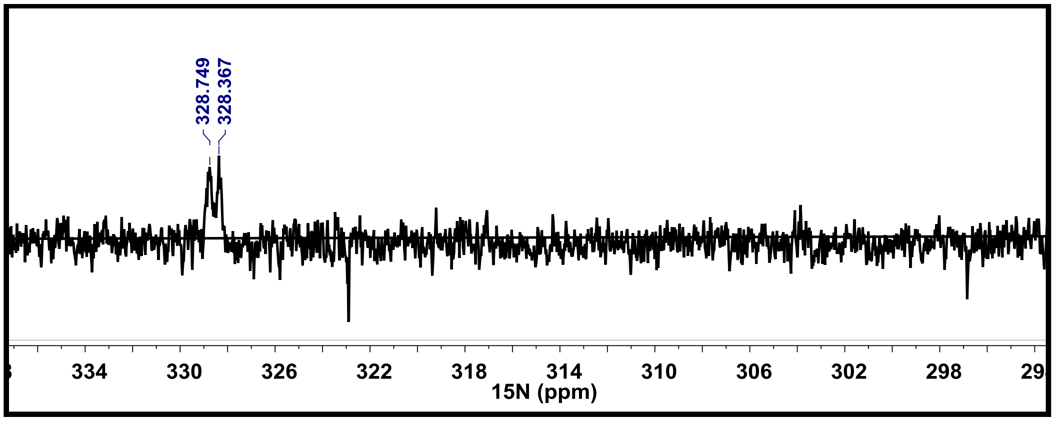

Figure S3. ^{15}N NMR spectrum (d_8-THF, -75 ^{o}C) of **2**.

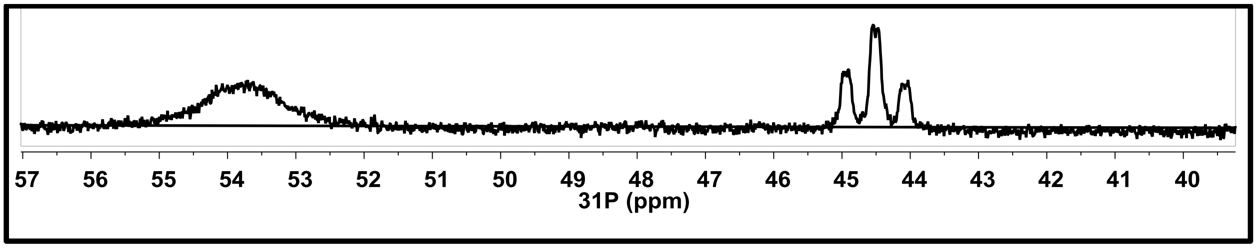

Figure S4. ^{31}P NMR spectrum (d_8-THF, -75 ^{o}C) of **2**.

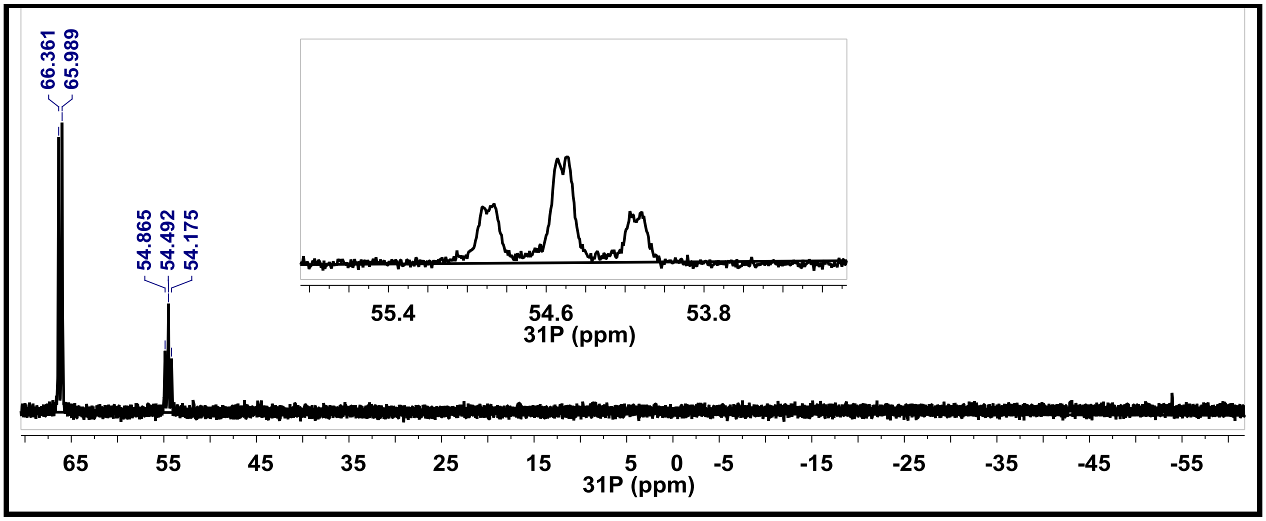

Figure S5. ^{31}P NMR spectrum (d_8-THF, -75 °C) of **3**.

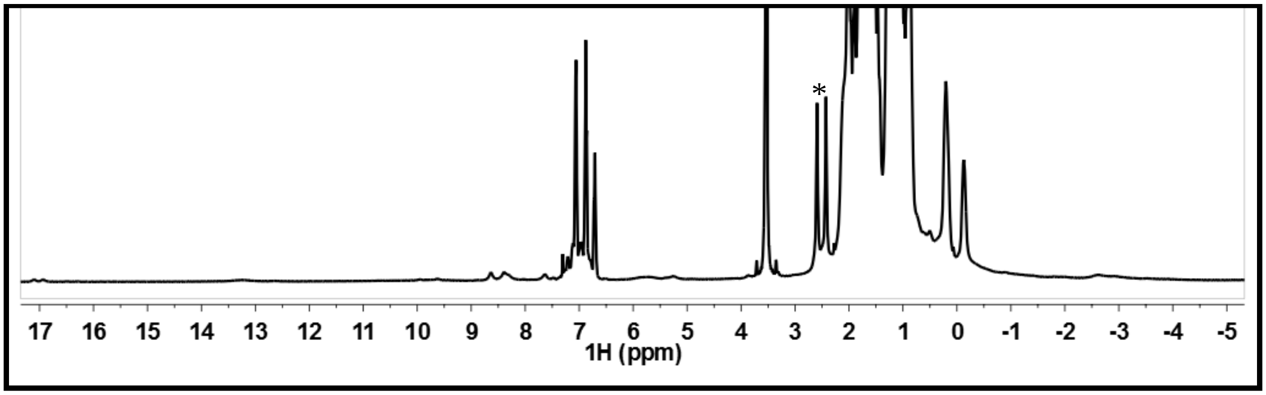

Figure S6. ^{1}H NMR spectrum (d_8-THF, -75 °C) of ^{15}N-**3**. The doublet marked with an asterix corresponds to the hydrazine protons.

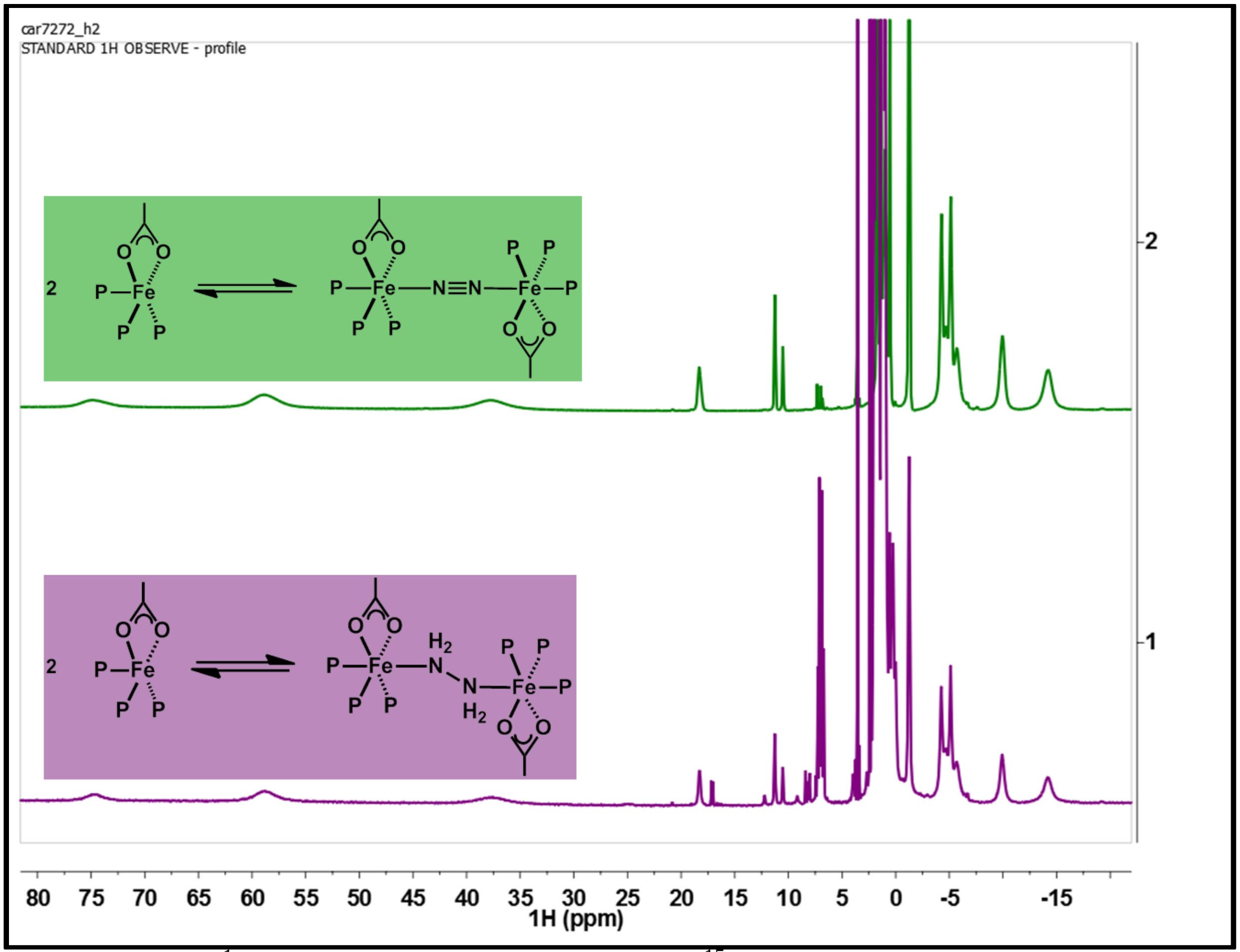

Figure S7. (top) ^{1}H NMR spectrum (d_8-THF, 0 ^{o}C) of ^{15}N-**2** and **1**, indicating the equilibrium between the two species, and (bottom) ^{1}H NMR spectrum (d_8-THF, 0 ^{o}C) of ^{15}N-**3** and **1**, indicating the equilibrium between the two species. The additional diamagnetic resonances are ascribed to **4** and **5**, which forms at this temperature.

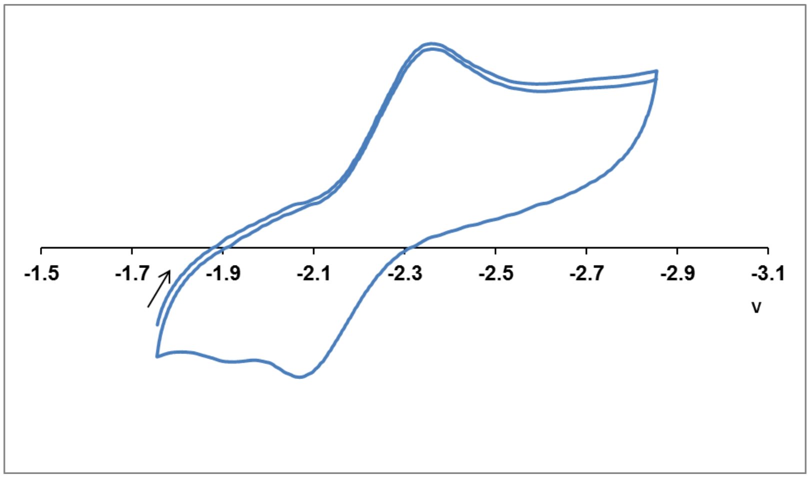

Figure S8. CV of **2** recorded at -35 ^{o}C, externally referenced vs. Fc/Fc^{+}. Scan rate of 100 mV/s, with 0.4 M TBA.PF$_6$ in THF. See general considerations for experimental details.

References:

(1) Schubert, E. M., *J. Chem. Educ.* **1992**, *69*, 62.
(2) Sheldrick, G. M., *Acta Cryst.* **1990**, *A46*.
(3) Sheldrick, G. M., *Acta Cryst.* **2008**, *A64*.
(4) Müller, P.; Herbst-Irmer, R.; Spek, A. L.; Schneider, T. R.; Sawaya, M. R., *Crystal Structure Refinement: A Crystallographer's Guide to SHELXL*. Oxford University Press: Oxford, 2006.
(5) Spek, A. L., L. PLATON A Multipurpose Crystallographic Tool. Utrecht University: Utrecht, Holland, 2008.
(6) Saouma, C. T.; Müller, P.; Peters, J. C., *J. Am. Chem. Soc.* **2009**, *131*, 10358.
(7) Schrock, R. R.; Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payack, J. F., *Inorg. Chem.* **1988**, *27*, 3574.
(8) Tang, H.; Richey, H. G., *Organometallics* **2001**, *20*, 1569.
(9) Armarego, W. L. F.; Chai, C. L. L., *Purification of Laboratory Chemicals*. 5 ed.; Butterworth-Heinmann: London, 2002.
(10) Smith, M. R.; Cheng, T. Y.; Hillhouse, G. L., *J. Am. Chem. Soc.* **1993**, *115*, 8638.
(11) Huttner, G.; Gartzke, W.; Allinger, K., *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 822.
(12) Saouma, C. T.; Kinney, R. A.; Hoffman, B. M.; Peters, J. C., *Angew. Chem. Int. Ed.* **2011**, *50*, 3446.
(13) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J., *J. Am. Chem. Soc.* **2005**, *127*, 7901.