On the feasibility of N 2 fixation via a single-site Fe I /Fe IV cycle: Spectroscopic studies of Fe I (N 2)Fe I , Fe IV N, and related species

Supporting Information

Files in this Data Supplement:

Supporting Figure 7

Fig. 7. Mössbauer spectra of toluene solutions of 38 mM [PhBP$^{iPr}_3$]Fe(H)$_3$(PMe$_3$) (**5**) (*A*) and 40 mM [PhBP$^{i}Pr_3$]FePMe$_3$ (**6**) (*B*) at 140 K and zero applied magnetic field. The short vertical lines are the experimental data, and the solid lines are fits using the following parameters. (*A*) d= 0.01(2) mm/s and DE_Q = 0.58(2) mm/s. (*B*) d = 0.57(2) mm/s and DE_Q = 0.23(3) mm/s.

Supporting Figure 8

Fig. 8. Isofield parallel magnetization (cT, dots) for a powder sample of **4** at the magnetic fields listed on the plot. The simulations (solid lines) use: $S_A = S_B = 3/2$, $J = +4$ cm^{-1}, $D_A = D_B = -53$ cm^{-1}, $E/D_A = E/D_B = 0.10$, $g_A = g_B = 2.35$. The Brillouin curve ($D = 0$, $g = 2.0$) is for an $S = 3$ state at 0.5 T.

Supporting Figure 9

Fig. 9. EPR spectrum (solid line) and simulation (dashed line) of 46 mM [PhBP$^{i}Pr_3$]FePMe$_3$ in toluene. Simulation parameters: $S = 3/2$, $D = +20$ cm^{-1}, $E/D = 0.16$, and $g = 2.2$. Spectral parameters: microwaves, 9.65 GHz (**B$_1$^ B**), 0.2 mW, $T = 15$ K.

Table 3. Mossbauer parameters of major and minor components in the various samples

Complex	δ, mm/s	ΔE_Q, mm/s
1	0.58(2)	1.65(2)
1 minor species (18%)	0.90(4)	2.66(5)
2	0.55(3)	1.75(4)
2 minor species (18%)	0.72(5)	3.10(5)
3a	-0.34(1)	6.01(1)
3a minor species a (40%)	0.61(5)	2.05(5)
3a minor species b (18%)	0.59(5)	2.87(5)
3a minor species c (7%)	0.53(5)	0.89(5)
3b	-0.34(1)	6.01(1)
3b minor species (25%)	0.15(1)	0.89(5)
4	0.53(3)	1.65(1)
4 minor species (18%)	1.10(4)	3.50(4)
5	0.01(2)	0.58(2)
6	0.57(2)	0.23(3)

Table 4. Geometry optimized bond distances and spin densities

Complex	S	Distances (Å)				Spin densities				
		Fe-X*	Fe-P			Fe	X*	P		
1	2	2.28	2.50	2.51	2.50	3.65	0.109	0.052	0.066	0.073
2	2	1.89	2.53	2.53	2.54	3.61	0.126	0.030	0.052	0.055
3	0	1.51	2.29	2.30	2.30					
4	3/2	1.80	2.34	2.35	2.39	3.33	-0.453	0.008	0.014	0.049
	3/2	1.83	2.33	2.36	2.36	3.34	-0.452	0.006	0.024	0.039
5	0	2.21	2.41	2.42	2.44					
6	3/2	2.43	2.45	2.46	2.46	2.91	0.005	0.005	0.014	0.017

Table 5. Crystallographically determined bond distances without geometry optimization and corresponding spin densities

Complex	S	Distances (Å)				Spin densities				
		Fe-X†	Fe-P			Fe	X*	P		
1	2	2.22	2.41	2.43	2.43	3.58	0.117	0.068	0.086	0.111
2	2	1.95	2.54	2.55	2.55	3.60	0.195	0.039	0.050	0.059
4	3/2	1.81	2.34	2.35	2.39	3.07	-0.222	0.024	0.064	0.069
	3/2	1.82	2.33	2.36	2.37	2.96	-0.207	0.026	0.055	0.082
5	0	2.16	2.28	2.28	2.28					
6	3/2	2.32	2.32	2.34	2.35	2.79	0.058	0.032	0.039	0.044

†X corresponds to the axial ligand in the fourth coordination site. For **1:** Cl, **2**,**3**,**4**: N, and for **5** and **6**: P.

Supporting Materials and Methods

Materials and General Procedures. All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. All manipulations were carried out by using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Nonhalogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran to confirm effective oxygen and moisture removal. Deuterated THF and benzene were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and dried over fine alumina (THF) or activated 3-Å molecular sieves (benzene) before use. The compounds H(dbabh),(1) Li(dbabh),(2) [PhBP$^{i}Pr_3$]FeCl (**1**),(3) [PhBP$^{CH2Cy}_3$]FeCl,(4) [PhBP$^{i}Pr_3$]Fe(dbabh) (**2**),(2) [PhBP$^{i}Pr_3$]Fe^{o}N (**3a**),(2), {[PhBP$^{i}Pr_3$]Fe}$_2$(m-N$_2$) (**4**),(2) [PhBP$^{i}Pr_3$]Fe(H)$_3$(PMe$_3$),(5) and [PhBP$^{i}Pr_3$]FePMe$_3$(5) were generated according to reported procedures.

[PhBP$^{CH2Cy}_3$]Fe^{o}N (3b). [PhBP$^{CH2Cy}_3$]FeCl (47.1 mg, 52.5 mmol) was dissolved in 0.5 ml of THF and chilled at -90°C. Li(dbabh) (13.4 mg, 67.3 mmol) was dissolved in 0.5 ml of THF and chilled with a stir bar at -90°C. The frozen solution of [PhBP$^{CH2Cy}_3$]FeCl was thawed, immediately added to Li(dbabh) at -90°C, and rinsed with 0.5 ml of chilled THF. The reaction mixture was then warmed to -50°C (octane/dry ice bath) and stirred at this temperature for 4-5 h. The solution of [PhBP$^{CH2Cy}_3$]Fe^{o}N is stable at -50°C for 8 h but shows modest decomposition at -40°C within 2 h. An ^{15}N-labeled sample, [PhBP$^{CH2Cy}_3$]Fe^{o15}N, also was prepared by the published method for the generation of [PhBP$^{i}Pr_3$]Fe^{o15}N. ^{1}H NMR (THF-d_8, 202 MHz, -50°C) d 6.94 (br, 2H), 6.88 (t, J = 6.5 Hz, 2H), 6.74 (t, J = 6.5 Hz, 1H), 2.14-1.67 (m, 42H), 1.40-1.12 (m, 30H), 0.92 - 0.78 (m, 12H). ^{31}P{^{1}H} NMR (THF, 202 MHz, -50°C) d 52.29. ^{15}N{^{1}H} NMR (THF, 51 MHz, -50°C) d 929.4.

Physical Methods. A Varian Mercury 300 NMR spectrometer was used to record ^{1}H NMR and ^{31}P NMR spectra at ambient temperature. ^{1}H chemical shifts were referenced to residual solvent, and ^{31}P chemical shifts were referenced to 85% H_3PO_4 at d 0 ppm. ^{15}N NMR data were acquired on an Inova 500-MHz spectrometer, and chemical shifts were referenced to CH_3NO_2 (380.23 ppm relative to liquid ammonia at 0 ppm). Mössbauer and EPR samples were loaded under nitrogen into Delrin Mössbauer cups and quartz tubes, respectively, and shipped in a liquid-nitrogen-chilled transport dewar from Caltech to Carnegie Mellon for analysis.

In several cases, minor components in the samples are observed, suggesting varying degrees of sample degradation, presumably via oxidation. All of the complexes described here are extremely oxygen- and moisture-sensitive. The spectroscopic parameters collected for each sample at Caltech before shipment were indicative of authentic samples. Because the highly sensitive solution samples were prepared at Caltech but then transferred and stored at Carnegie Mellon before EPR and Mössbauer data acquisition, and because the impurities are highly sample-dependent and unique to each sample, a degree of sample degradation clearly is evident in most cases. Worth noting is that exposure of a solution of **1** to air results in facile phosphine oxidation processes similar to those described for related [PhBP$^{i}Pr_3$]CoX systems(3). Future work might include examination of solid-state Mössbauer samples for those complexes that can be obtained as solids. The nitride **3a** can only be observed in solution, however, as it exists as its dimer **4** in the solid state.

X-band (9 GHz) EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an Oxford ESR 910 cryostat for low-temperature measurements and a Bruker bimodal cavity. All experimental data were collected under nonsaturating microwave conditions. The microwave frequency was calibrated with a frequency counter, and the magnetic field was calibrated with an NMR gaussmeter. The temperature was calibrated with resistors (CGR-1-1,000) from LakeShore. A modulation frequency of 100 kHz and amplitude 1 mT$_{pp}$ was used for all spectra unless otherwise noted. Simulations of EPR spectra used the standard spin Hamiltonian:

$$H = -2J S_A \cdot S_B + \sum_{i = A,B}[S_i \cdot D_i \cdot S_i + \beta B \cdot g_i \cdot S_i + h S_i \cdot A_i \cdot I_i] . \quad [1]$$

The simulations were calculated from diagonalization of Eq. **1**, and the nuclear term is treated with second-order perturbation theory. All intensity factors, both theoretical and experimental, are considered in the calculation, thereby allowing direct comparison of simulated spectra to the absolute intensity scale of the experimental spectrum having a known sample concentration. The only unknown factor relating the spin concentration to signal intensity is an instrumental factor that depends on the microwave detection system. This factor was determined by the spin standard, CuEDTA, for which the copper concentration was accurately determined from plasma emission spectroscopy. The Windows software package (SpinCount) is available by contacting the authors (M.P.H.).

Mössbauer spectra were recorded on a constant acceleration instrument with an available temperature range of 1.5 to 200 K. An applied magnetic field of 45 mT was applied to the samples. Isomer shifts are reported relative to Fe metal at 298 K. The low-temperature Mössbauer spectra of [PhBP$^{iPr}_3$]FePMe$_3$ (**5**) was fit with Eq. **1**, without the terms for the

second spin, plus the nuclear terms:

$$H_n = -g_{nb n}\mathbf{B}\cdot\mathbf{I} + (eQV_{zz}/12)\ [3\mathbf{I_z}^2 - I(I+1) + h(\mathbf{I_x}^2 - \mathbf{I_y}^2)]\ .\ \textbf{[2]}$$

Least-square fitting of the spectra was performed with the WMOSS software package (WEB Research, Edina, MN).

Magnetic measurements were recorded using a Quantum Designs SQUID magnetometer at Caltech's Beckman Institute running Magnetic Property Measurement System Rev. 2 software. The sample was suspended in the magnetometer in a plastic straw sealed under nitrogen with Lilly No. 4 gel caps. Loaded samples were centered within the magnetometer by using the DC centering scan at 35 K and 5,000 G. Data were acquired at 4-30 K (one data point every 2 K) and 30-300 K (one data point every 5 K). The magnetic susceptibility was adjusted for diamagnetic contributions by using the constitutive corrections of Pascal's constants. Least-square simulations of the data were calculated from Eq. **1** using the SpinCount software package.

$$m_{eff} = (7.997c_m T)^{1/2}\ .\ \textbf{[3]}$$

Computational Methods. Mössbauer spectroscopy is particularly suited for determining the composition and oxidation state of iron containing samples, but it has not generally allowed for structural characterization of iron centers. Recently it was shown that density-functional methods are capable of determining Mössbauer parameters with good accuracy. In general, quadrupole splittings, DE_Q, can be obtained to within 0.3 mm/s (6), although errors on the order of 0.3-0.5 mm/s are not uncommon (7). Isomer shifts, d, are usually predicted to within 0.1 mm/s (8). The accuracy with which these parameters can be determined suggests that theoretical methods can be used to obtain structural information from Mössbauer experiments. All calculations were performed with Gaussian 03 using the B3LYP functional (9). Geometry optimizations were performed with the 6-311G basis set. The electron density at the Fe nucleus was determined by using the Atoms in Molecules (AIM) option in Gaussian 03. Quadrupole splittings, the asymmetry parameter, h, and [57]Fe hyperfine couplings were determined at the optimized geometries using the 6-311G basis set. Isomer shifts were determined at the optimized geometries using Neese's core properties (CP) basis set (8). For this basis set, an integration grid containing 199 radial shells with 590 angular points per shell was used. The electron density at the Fe nucleus was determined by using the Atoms In Molecules (AIM) option in Gaussian 03.

1. Carpino LA, Padykula RE, Barr DE, Hall FH, Krause JG, Dufresne RF, Thoman CJ (1988) *J Org Chem* 53:2565-2572.

2. Betley TA, Peters JC (2004) *J Am Chem Soc* 126:6252-6254.

3. Betley TA, Peters JC (2003) *Inorg Chem* 42:5074-5084.

4. Lu C, Peters JC (2006) *Am Chem Soc*, in press.

5. Daida EJ, Peters JC (2004) *Inorg Chem* 43:7474-7485.

6. Zhang Y, Mao JH, Godbout N, Oldfield E (2002) *J Am Chem Soc* 124:13921-13930.

7. Neese F (2003) *Curr Opin Chem Biol* 7:125-135.

8. Neese F (2002) *Inorg Chim Acta* 337:181-192.

9. Frisch MJ, *et al.* (2004) *Gaussian 03* (Gaussian, Wallingford, CT).