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A Low-Spin d^5 Iron Imide: Nitrene Capture by Low-Coordinate Iron(I) Provides the 4-Coordinate Fe(III) Complex $[PhB(CH_2PPh_2)_3]Fe{\equiv}N$-*p*-tolyl

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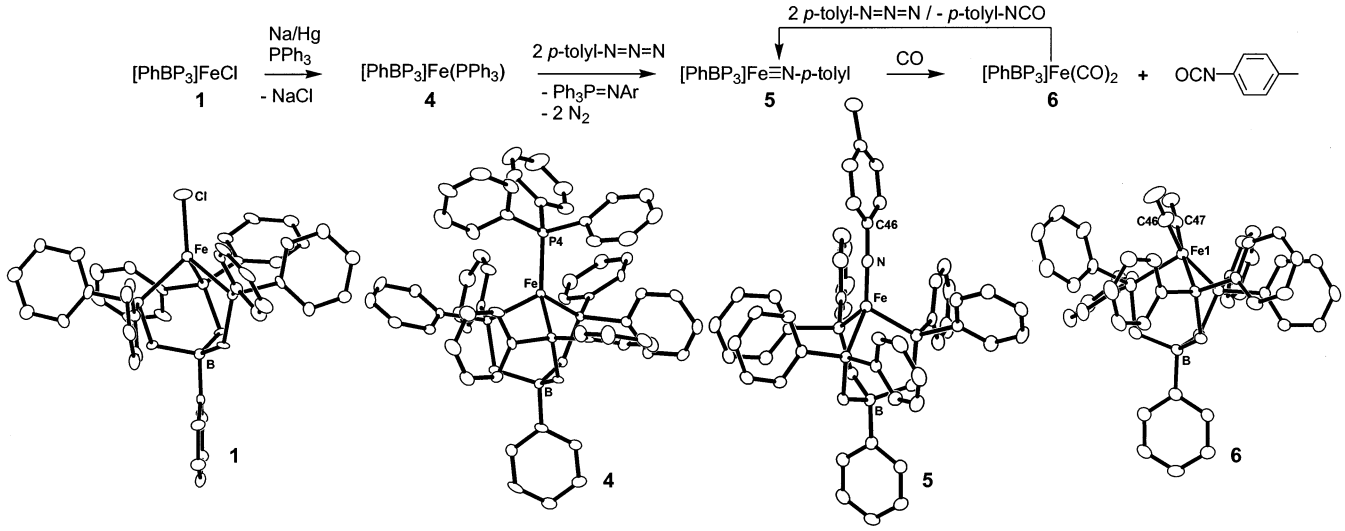
While metalloenzymes such as nitrogenases and hydrogenases are far from mechanistically well understood, it seems plausible that low-valent, sulfur-ligated Fe(II) and Fe(I) species play a critical role in their small-molecule reduction chemistry.[1] The careful preparation and study of the redox reactivity of low-coordinate Fe(I) species is therefore of concern.[2,3] Iron(I) is an unusual oxidation state whose coordination chemistry, particularly for low-coordinate examples (4-coordinate or lower), is poorly developed. This point was underscored recently in Parkin's report of the 4-coordinate Fe(I) complex $[PhTp^{But}]Fe(CO)$.[4] Knowledge of the elementary reactivity patterns of Fe(I) will guide mechanistic postulates for its possible role in biological systems.

This work describes the synthesis of a rare, 4-coordinate Fe(I) complex, $[PhBP_3]Fe(PPh_3)$ (**4**) ($[PhBP_3] = [PhB(CH_2PPh_2)_3]^-$), that serves as a synthetic surrogate to the tripodal "$[PhBP_3]Fe(I)$" subunit. Of particular interest is that this system undergoes rapid oxidation by aryl azide to produce a mononuclear, terminally bonded Fe(III) imide, $[PhBP_3]Fe(N$-*p*-tolyl) (**5**). Synthetically rare iron oxo and imide/nitrene species continue to receive intense scrutiny due to their postulated role in catalysis.[5−7] Recent work by Lee and co-workers provided important precedent for the "Fe═NR" multiple-bond linkage.[5b] However, Lee's system is synthetically ill-defined and electronically complex owing to its cluster nature, which features four magnetically coupled iron centers. The title complex reported herein provides a distinctly simple, mononuclear 4-coordinate Fe(III) imide. Its $S = 1/2$ ground-state electronic configuration is also distinct in that, to the best of our knowledge, low-spin examples of tetrahedral or pseudotetrahedral Fe(III) were previously unknown.

High-yield (>80%) entry to the "$[PhBP_3]Fe$" system proceeded from metallation of FeX_2 salts (X = Cl, Br, I) by $Tl[PhBP_3]$ to produce the yellow, 4-coordinate high-spin ($S = 2$) halide derivatives $[PhBP_3]FeX$ (**1**−**3**, respectively).[8] The chloride derivative **1** underwent reduction by sodium/mercury amalgam (THF) in the presence of 3 equiv of PPh_3 to give the desired iron(I) precursor **4** as an orange, crystalline solid in 62% yield. Complexes **1** and **4** were each characterized by both X-ray crystallography (Scheme 1) and SQUID magnetometry (Figure 1). Their solid-state structures establish a 4-coordinate, pseudotetrahedral geometry for each case.[9] The magnetization data for **1** and **4** were rigorously temperature-independent between 10 to 310 K and provided effective moments at 290 K of 5.00 and 4.11 μ_B, respectively (See Figure 1a). These moments suggest a high spin $S = 2$ ground state in the case of chloride **1** and an $S = 3/2$ ground state for **4**. The bromide and iodide derivatives **2** and **3** are also high-spin (Evans method, 295 K).[10] Complex **4** underwent clean oxidation by *p*-toyl azide at room temperature in benzene to provide the forest-green, d^5 imido complex **5**, which could be crystallized (50% isolated) by vapor diffusion of petroleum ether into the reaction solution. The overall reaction appeared to be quantitative by ^1H and ^{31}P NMR spectroscopies: a stoichiometric equivalent of *p*-tolyl-N═PPh_3 was produced as the only detectable byproduct. Complex **5** was thoroughly characterized by X-ray diffraction (Scheme 1), SQUID magnetization (Figure 1a), EPR spectroscopy (Figure 1b), and cyclic voltammetry (Figure 1c). The Fe−N(1)−C(46) bond angle in **5** is 169.96(2)° and the Fe−N(1) bond distance of 1.6578(2) Å is much shorter than typical Fe−amido linkages and is similar to that reported by Lee.[5b] These structural data are consistent with strong π-bonding in the Fe−N(1) linkage: **5** is best represented with a triple bond as shown in Scheme 1. The axial π-interactions destabilize two orbitals of d_{xz} and d_{yz} parentage to provide the low-spin $S = 1/2$ configuration observed for **5,** as indicated from its

Scheme 1



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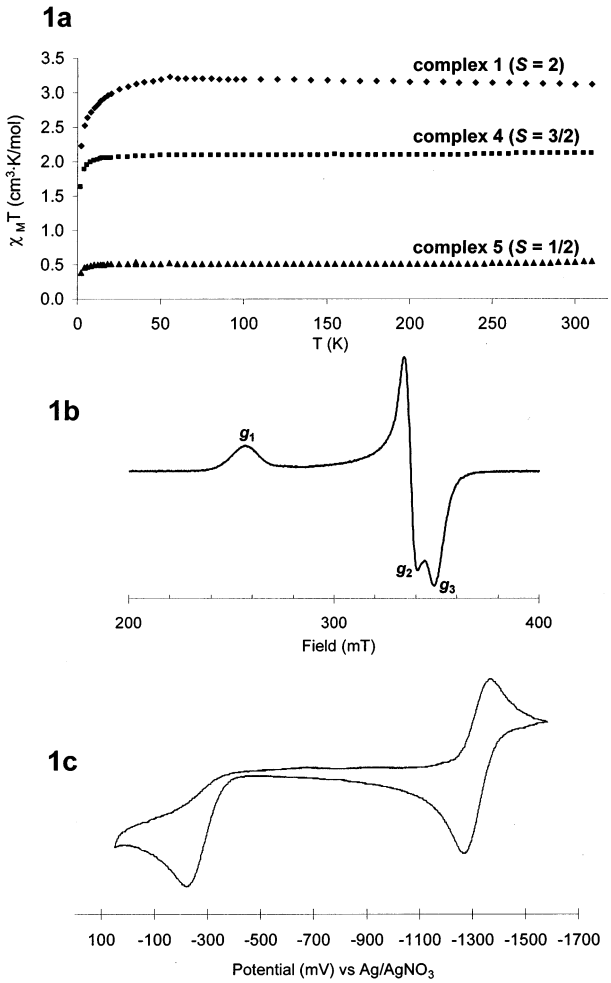

Figure 1. (a) SQUID magnetization data for complexes **1**, **4**, and **5**. (b) EPR spectrum of **5** (toluene at 30 K, X-band, 9.474 GHz). (c) Cyclic voltammetry of **5** (0.3 M [TBA][PF_6], 30 mV/s).

SQUID magnetization data. The rhombic EPR spectrum for **5** shows g_1 in the region 2.61, suggesting the unpaired spin resides in an orbital orthogonal to the Fe−N(1) vector, and g_2 and g_3 in the region 2.0. While the three components g_1, g_2, and g_3 are well resolved at 30 K, g_2 and g_3 were not resolved in a 77 K EPR spectrum. Assignment of the electronic configuration of **5** can be made cautiously by assuming approximate three-fold symmetry and placing the molecular *z*-axis along the Fe−N bond vector. Using this coordinate system we suggest that a half-filled d_{xy} orbital sits slightly above two lower-lying and filled $d_{x^2-y^2}$ and d_{z^2} orbitals to provide the ground-state configuration $(d_{z^2})^2(d_{x^2-y^2})^2(d_{xy})^1(d_{xz})^0(d_{yz})^0$.[11] This electronic model suggests that it should be possible to reduce **5** by one electron, in accord with its cyclic voltammetry. A well-behaved and fully reversible FeII/III couple is observed at −1.35 V, whereas an irreversible oxidation is observed at ∼−300 mV in the CV (Figure 1c). That **5** can be reversibly reduced to the d^6 anion "[[$PhBP_3$]Fe≡NAr]$^-$" is plausible, given the stability of its isolobal and isoelectronic d^6 relative [$PhBP_3$]Co≡NAr.[12]

Preliminary reactivity studies with imide **5** highlight its reactive nature by comparison to its cobalt congener [$PhBP_3$]Co≡NAr, which required forcing conditions to release its "NAr" group to CO (70 °C, 12 days).[12] Complex **5** reacted immediately and at room temperature upon CO addition to quantitatively release isocyanate (O═C═N-*p*-tolyl, external integration standard) and form the golden dicarbonyl byproduct [$PhBP_3$]$Fe(CO)_2$ (**6**). Complex **6** has been structurally characterized as a distorted square pyramid (Scheme 1) and has been independently generated by reaction of **4** with excess CO. In light of the recent nickel chemistry reported by Hillhouse and Mindiola,[13] well-defined examples of nitrene transfer to CO with release of isocyanate are now established for first row systems including Fe(III), Co(III), and Ni(II). Particular to the present system is that dicarbonyl **6** is itself a precursor to imide **5**. An NMR tube experiment showed that the addition of 2 equiv of *p*-tolyl azide to **6** slowly (rt, C_6D_6, 44 h) effected its conversion back to imide **5**, along with the release of free isocyanate (80%, external standard). Efforts are underway to realize a catalytic Fe(I)/Fe(III) group transfer cycle based on **5** or **6**.

In summary, this work shows that Fe(I) supported by a strong field and tripodal phosphine donor can undergo a facile, multielectron group transfer process to accept a strongly π-donating imide ligand. The imide can be subsequently released to the acceptor substrate CO. The method of formation of imide **5**, its reactivity with CO, and its regeneration from **6** underscore the viability of a well-defined, Fe(I) → Fe(III)/Fe(III) → Fe(I) group transfer loop. Whether parallels to such group transfer processes occur in biological systems, such as the reducing FeS-clusters of certain metalloenzymes, is worth considering.

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Supporting Information Available: Detailed experimental procedures, characterization data (PDF); crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Einsle, O.; Tezcan, A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696. (b) Rees, D. C. *Annu. Rev. Biochem.* **2002**, *71*, 221. (c) Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853.

(2) (a) Seyferth, D.; Henderson, R. S.; Song, L. C. *Organometallics* **1982**, *1*, 125. (b) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Mejia-Rodriguez, R.; Chiang, C. Y.; Darensbourg, M. Y. *Inorg. Chem.* **2002**, *41*, 3917. (c) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 12518.

(3) See: Lappert, M. F.; MacQuitty, J. J.; Pye, P. L. *J. Chem. Soc., Dalton Trans*. **1998**, 1583 and references therein.

(4) Kisko, J. L.; Hascall, T.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 10561.

(5) (a) MacBeth, C. E.; Golombek, A. P.; Young, V. G., Jr.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. S. *Science* **2000**, *289*, 938. (b) Verma, A. K.; Nazif, T. N.; Achim, C.; Lee, S. C. *J. Am. Chem. Soc.* **2000**, *122*, 11013. (c) Que, L., Jr.; Chen, K.; Costas, M.; Ho, R. Y. N.; Jensen, M. P.; Rohde, J. U.; Torelli, S.; Zheng, H. *J. Inorg. Biochem.* **2001**, *86*, 88. (d) Pistorio, B. J.; Chang, C. J.; Nocera, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 7884. (e) Tshuva, E. Y.; Lee, D.; Bu, W.; Lippard, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 2416. (f) Meunier, B., Ed. *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Imperial College Press: London, 2000.

(6) Mansuy and co-workers were the first to report heme-supported [FeN-$NR_2]^+$ systems. Physical data for these systems suggests they are better represented as Fe(II) [Fe ← NNR_2] azamines than Fe(IV) [Fe═NNR_2] imides. See: Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4487. Also see refs 4 and 5 in Lee's paper (ref 5b above).

(7) Wieghardt and Meyer have provided spectroscopic evidence at 77 K for an Fe(V) nitride. See: Meyer, K.; Bill, E.; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121*, 4859.

(8) Shapiro, I. R.; Jenkins, D. M.; Thomas, J. C.; Day, M. W.; Peters, J. C. *Chem. Commun.* **2001**, 2152.

(9) Although the structure of **4** suffers from solvent disorder, the iron subunit is well-resolved. See Supporting Information.

(10) (a) Sur, S. K. *J. Magn. Reson*. **1989**, *82*, 169. (b) Evans, D. F. *J. Chem. Soc*. **1959**, 2003.

(11) Whether the predominantly d_{z^2} orbital (with admixed s and p_z character) actually lies lowest in energy is not clear. Theoretical studies to help resolve this issue are underway.

(12) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238.

(13) (a) Mindiola, D. J.; Hillhouse, G. L. *Chem. Commun.* **2002**, 1840. (b) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623.

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