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P═N Bond Formation via Incomplete N-Atom Transfer from a Ferrous Amide Precursor

Debashis Adhikari, Falguni Basuli, Hongjun Fan, John C. Huffman, Maren Pink, and Daniel J. Mindiola*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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Incomplete N-atom transfer from Fe to P is observed when the ferrous amide complex (PNP)Fe(dbabh) ($PNP^- = N[2\text{-}P(^iPr)_2\text{-}4\text{-}methylphenyl]_2$, dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene), prepared from salt metathesis of (PNP)FeCl and Li(dbabh), is thermolyzed at 70 °C over 48 h in C_6D_6. Several plausible reaction pathways resulting from the transformation of (PNP)Fe(dbabh) are discussed, including the possibility of an Fe(IV) nitride as an intermediate.

Terminal iron imides,[1] a functionality considered still rare in the context of inorganic chemistry, have recently attracted considerable interest in the bioinorganic community since this group could be implicated in nitrogenase Fe-based enzymes as well as applied to bond activation processes or group-transfer reactions.[1,2] In contrast to terminal Fe═NR linkages, the terminal iron nitride group represents an even more exotic motif, and such a functionality has been proposed en route to the much more common bridged nitride species.[2,3] Nakamoto and Wagner[4] and Wieghardt et al.[5] have reported transient iron nitrides generated via extrusion of N_2 at extremely low temperatures, while Peters and Betley reported the only thermally generated iron nitride (terminal) by anthracene elimination.[6] In the latter case, the nitride functionality was found to reductively couple engendering N≡N bond formation to afford a formally $Fe^{I,I}_2$ end-on dinitrogen species. Although the terminal iron nitride functionality has been spectroscopically observed under low-temperature matrix conditions, these examples readily decompose upon warming.[4,5] The first documented case of clean N-atom transfer involves Betley and Peters' system $[PhB(CH_2P(^iPr)_2)_3]Fe{\equiv}N$ intermediate, which subsequently undergoes an Fe(IV) to Fe(I) redox shuffle.[6] An analogous three-electron reduction process involving an Fe(VI) to Fe(III) has been also documented by Wieghardt et al.,[5d] but the fate of the nitride atom remains unknown. As a result, understanding the fate and pattern in reactivity of the terminal iron nitride functionality is seldom documented, given the inherent reactivity of such a ligand.[7] In this manuscript, we wish to report that a four-coordinate ferrous amide precursor can thermally yield a diferrous Fe_2N_2 diamond core bridged by two phosphinimide[8] pendant arms via an incomplete N-atom transfer from Fe to P (see Scheme 1). Theoretical analyses of plausible intermediates in this type of reaction hint to a putative Fe(IV) nitride being a suitable candidate along the incomplete N-atom transfer pathway.

Assembling the pincer-type framework onto Fe(II) involved the transmetalation of Li(PNP)[9] ($PNP^- = N[2\text{-}P(^iPr)_2\text{-}4\text{-}methylphenyl]_2$) with $FeCl_2(THF)_{1.5}$[10] in toluene over 6 h to afford the intense red complex (PNP)FeCl (**1**)[9] in an overall 89% isolated yield.[9] In a C_6D_6 solution, magnetic

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* Author to whom correspondence should be addressed. E-mail: mindiola@indiana.edu.

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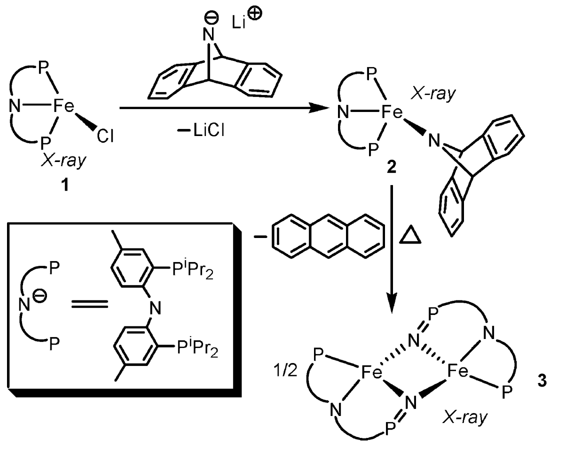
10.1021/ic800182m CCC: $40.75

Scheme 1. Synthesis of **1** and **2** and Subsequent Incomplete N-Atom Transfer to Produce **3**



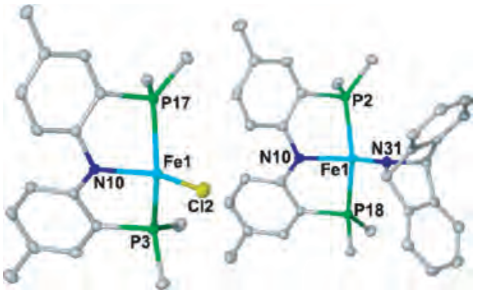


Figure 1. Molecular structures of **1** (left) and **2** depicting thermal ellipsoids at the 50% probability level. H atoms, isopropyl methyl groups on P, and the solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg) follow. For **1**: Fe1−Cl2, 2.2392(4); Fe1−N10, 1.9799(12); Fe1−P17, 2.4399(5); Fe1−P3, 2.3926(5); P17−Fe1−P3, 120.926(16); N10−Fe1−Cl2, 140.26(4); P17−Fe1−Cl2, 116.260(17); P3−Fe1−Cl2, 111.705(16); N10−Fe1−P17, 80.58(4); N10−Fe1−P3, 84.02(4). For **2**: Fe1−N31, 1.8956(16); Fe1−N10, 1.9984(16); Fe1−P18, 2.4079(6); Fe1−P2, 2.4483(6); P18−Fe1−P2, 129.86(2); N10−Fe1−N31, 139.52(7); P18−Fe1−N31, 111.36(5); P2−Fe1−N31, 111.73(5); N10−Fe1−P18, 82.84(5); N10−Fe1−P2, 80.81(5).

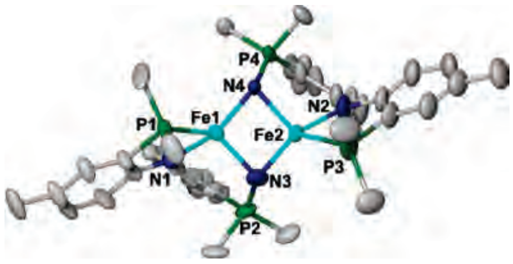


Figure 2. Molecular structures of complex **3** depicting thermal ellipsoids at the 50% probability level. H atoms, isopropyl methyl groups on P, and the solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg) follow: Fe1−N3, 2.007; Fe1−N4, 1.937; Fe2−N3, 1.934; Fe2−N4, 2.009; Fe1−Fe2, 2.570; N3−Fe2−N4, 96.74; N3−Fe1−N4, 96.72.

data for complex **1** are consistent with a high-spin ferrous system by the method of Evans ($\mu_{\mathrm{eff}} = 4.44(10)\ \mu_{\mathrm{B}}$), while solid-state magnetization data also suggest a fairly constant high-spin and monomeric system over a temperature range of 300 K (4.79 μ_{B}) to 4.7 K (4.07 μ_{B}) (Figure S1, Supporting Information).[9] The connectivity of **1** was inferred by solid-state single-crystal X-ray analysis.[9] As depicted in Figure 1, complex **1** adopts a highly distorted tetrahedral geometry, which appears to be more consistent with a cis-divacant octahedron, given the significant deviation of the chloride (~3.11 Å) from the plane defined by the atoms P_2NFe, and an angle of 69.1° originated from the Fe−Cl vector with the same plane. The geometry in **1** resembles Fryzuk et al.'s proposed geometry for the high-spin iron(II) analogue ($([Ph_2PCH_2Si(Me)_2]_2N)FeCl$).[12]

Complex **1** displays a highly cathodic and irreversible wave at −2.44 V versus $FeCp_2^{0/+}$ in 0.3 M $[Bu_4N][PF_6]$ in THF, suggesting this system to be an electron-rich Fe(II) framework amenable to serving as a reducing agent (Figure S2, Supporting Information). Surprisingly, however, treatment of **1** with the azide analogue, $Li(dbabh)(Et_2O)$,[13] yields a stable Fe(II) amide (PNP)Fe(dbabh) (**2**) in 65% yield as a red-colored material (dbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene). In contrast, using NaN_3 or $N_3Si(CH_3)_3$ with **1** results in the formation of intractable solids having very limited solubility in nonprotic media.[9] Complex **2** is a remarkably stable system containing a high-spin ferrous ion (Evans method: $\mu_{\mathrm{eff}} = 4.91(6)\ \mu_{\mathrm{B}}$). The solid-state structure of a single crystal of **2** confirms a pseudo-tetrahedral ferrous complex having a bound dbabh amide group (Fe−N, 1.8956(16) Å; Figure 1) and a gross geometry nearly identical to that of **1** and slightly shorter than a diphenylamide anologue (Fe−N distance is 1.9527(15) Å) reported by Betley and Peters.[6,9] The dbabh N atom is virtually planar, given that the angle around it is 357°, which we believe results from the weak π interaction between the nitrogen lone pair and the half-filled iron(II) d(yz) as suggested by DFT calculations.[9]

The stability of **2** contrasts Betley and Peters' tetrahedral Fe(II) system $[PhB(CH_2P^{i}Pr_2)_3]Fe(dbabh)$ in that it is thermally robust at room temperature over several weeks. However, anthracene elimination concurrent with the formation of a new iron product can be promoted moderately cleanly (69% yield) when **2** is thermolyzed at 70 °C over 48 h in C_6D_6, as implied by ^1H NMR spectroscopy. Although the color of the reaction does not change significantly, the ^1H NMR spectrum reveals the appearance of new paramagnetically shifted resonances ranging from −3.47 to 21.4 ppm at the expense of decay for the set of resonances for **2**.[9] Moreover, the number of resonances increasing from 9 to 17 suggests that a new system of low symmetry has been generated. A single-crystal structural analysis of this new complex confirmed it to be a dimeric species, $[(PNPN)Fe]_2$ (**3**) ($PNPN^{2-}$ = N[2-P(^{i}Pr)$_2$-4-methylphenyl][2-N=P(^{i}Pr)$_2$-4-methylphenyl]), which is generated as a result of two bridging phosphinimide motifs (Figure 2). Consequently, the monoanionic PNP framework in **2** has been transformed to a dianionic PNP=N ligand, where one of the pendant phosphine groups has been oxidized by a nitrogen atom. Interestingly, both "NP" groups are on the same side of the

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(11) Reference deleted at galley stage.

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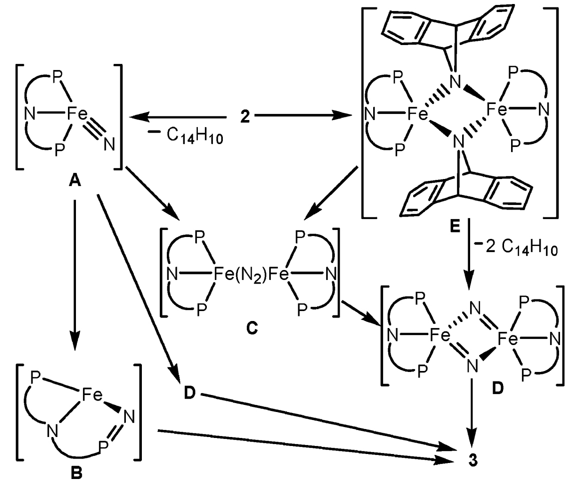
(14) Reference deleted at galley stage.

Scheme 2. Some Plausible Pathways to Formation of **3**



Fe_2N_2 mean plane.[15] A similar ligand transformation has been recently documented by Fryzuk and co-workers, whereby a transient titanium nitride, generated from N_2 activation and reduction, underwent insertion in the metal−P bond.[15] In our case, however, the formation of **3** could be transpiring via a transient Fe(IV) nitride (PNP)Fe≡N (**A**)—thermally generated from anthracene expulsion. The electrophilic nature of the nitride ligand plausibly promotes the oxidation of one of the phosphine groups to engender formation of the ferrous intermediate, "(PNP═N)Fe (**B**)", in an overall Fe(IV) → Fe(II) couple (Scheme 2). The latter intermediate would subsequently undergo dimerization to produce the $Fe_2(PN)_2$ diamond core in **3**. Alternatively, the formation of **3** can also proceed from a dinitrogen (PNP)Fe(N_2)Fe(PNP) (**C**) intermediate via reductive coupling of **A**. The dinitrogen moiety can then undergo rearrangement to a bridging nitride dimer, $[(PNP)Fe(\mu_2\text{-}N)]_2$ (**D**), then incomplete N-atom transfer to produce **3** (Scheme 2). Such a transformation has been similarly proposed in a titanium system recently reported by Fryzuk and co-workers.[16] In our case, we discard the possibility of activation and consequent cleavage of N_2 to result in the final product, as there is no precedence of N_2 splitting in iron complexes. The possibility of **A** dimerizing via **D** prior to oxidation of the phosphine group is highly unlikely given the steric constraints imposed by the encumbering PNP unit (Scheme 2). In fact, a DFT simulation fails to locate a dimer minimum, and geometry optimization using the latter species converges to the asymmetric nitride (PNP)Fe(μ_2-N)Fe(N)(PNP) thus implying that different pathways to the formation of **3** should not be overlooked.[9] Sterics also disfavor the possibility of amide bridging in **2** to form putative $[(PNP)Fe(\mu_2\text{-dbabh})]_2$ (**E**), which would then extrude anthracene to form **D** or **C**, an intermediate along the channel to **3** (Scheme 2).

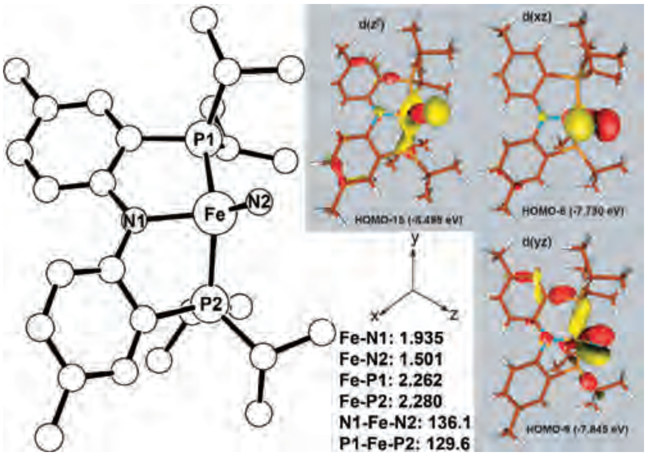


Figure 3. Computed structure for **A** at the PBE/6-31G** level of theory. The three orbitals forming the Fe≡N ligand are also depicted with an isodensity of 0.05 au.

Given both the electronic and structural interest of terminal iron nitrides,[2,4–6] we resorted to high-level DFT analyses to address some of the salient features in putative **A**. As we were interested to investigate the ground spin state of the putative nitride intermediate **A**, we chose the PBE functional instead of B3LYP since the latter tends to overestimate the exchange energy, thence resulting in artificial inclination toward the high spin state. Accordingly, complex **A** is found to possess a singlet ground state with a small singlet−triplet gap of 4.77 kcal/mol at the PBE/cc-pVTZ(-f)//PBE/6-31G** level of theory.[9] As indicated in Figure 3, complex **A** adopts a highly distorted tetrahedral geometry analogous to **1**, **2**, and a Ru(IV) nitride reported by Caulton and co-workers.[17] The Fe≡N linkage is computed to be 1.501 Å, and natural bond order calculations suggest this system to have a bond order of 2.64 by utilizing the Fe d(z^2), d(xz), and d(yz) orbitals to generate the σ and 2π bonds, respectively.[2,5–7,9,18] As anticipated, the Fe−$N_{nitride}$ functionality is shorter than the Fe−N_{amide} group composing the PNP unit (1.935 Å).

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Supporting Information Available: Complete X-ray data and characterization of **1**−**3**, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for $\mathbf{3}\cdot 0.5C_6H_{14}$: Orthorhombic, space group *Pccn*, a = 39.4630(7) Å, b = 15.8829(3) Å, c = 19.1251(4) Å, V = 1987.4(4) Å^3, Z = 8, μ(Mo Kα) = 0.626 mm^{-1}, D_c = 1.152 mg/mm^3, GOF on F^2 = 1.179, R_1 = 10.42%, and wR_2 = 26.94% (F^2, all data). Data/restraints/parameters: 10 627/267/728. Out of a total of 66 852 reflections collected, 10 627 were unique (R_{int} = 9.71%) and 9244 were observed with $I > 2\sigma I$ (brown block, 0.22 × 0.17 × 0.15 mm, 25.07° ≥ θ ≥ 1.38°). The structure showed extensive disorder of the ligands and solvent, which was refined with a strong set of restraints and constraints to achieve convergence. The solvent carbon atoms remained isotropic. The structure was of marginal quality and should be understood as proof of connectivity only. A number of systematically weak reflections and considerable TDS were observed in the diffraction pattern. A larger cell that includes the weak reflections can be indexed, which might be in super-subcell relation with the chosen cell.

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