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N₂ Functionalization at Iron Metallaboratranes

Marc-Etienne Moret and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125 (USA)

Abstract

The reactivity of the anionic dinitrogen complex [(TPB)Fe(N₂)][−] (**2**, TPB = tris-[2-(diisopropylphosphino)phenyl]borane) towards silicon electrophiles has been examined. Compound **2** reacts with trimethylsilyl chloride (TMSCl) to yield the silyldiazenido complex (TPB)Fe(NNSiMe₃) (**3**), which is reduced by Na/Hg in THF to yield the corresponding sodium-bound anion [(TPB)Fe(NNSiMe₃)]Na(THF) (**4**). The use of 1,2-bis(chlorodimethylsilyl)ethane in the presence of excess Na/Hg results in the disilylation of the bound N₂ molecule to yield the disilylhydrazido(2−) complex (TPB)Fe≡NR (**5**, R = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl). One of the phosphine arms of TPB in **5** can be substituted by CO or ^tBuNC to yield crystalline adducts (TPB)(L)Fe≡NR (**6**: L = CO; **7**: L = ^tBuNC). The N–N bond in **7** is cleaved upon standing at room temperature to yield a phosphoraniminato/disilylamido iron(II) complex (**8**). The flexibility of the Fe–B linkage is thought to play a key role in these transformations of Fe-bound dinitrogen.

Low-valent iron complexes that bind dinitrogen have attracted much interest,¹ in part due to their potential as functional models of nitrogenases.² While a relatively large number of such compounds have been prepared, examples in which the metal-bound dinitrogen molecule can be functionalized are scarce. Several phosphine-supported iron–N₂ compounds have been found to afford low yields of ammonia and/or hydrazine upon reaction with Brønsted acids,³ but little is known about the mechanism of these reactions. As part of our effort to delineate the elementary reactions accessible to iron-bound dinitrogen, our group has reported two examples of substituted diazenido compounds (BⁱPr₃)Fe–N=N–Me ((BⁱPr₃) = {PhB[CH₂P(*i*-Pr)₂]₃}[−])⁴ and (SiⁱPr₃)Fe–N=N–SiMe₃ ((SiⁱPr₃) = [2-(*i*Pr₂P)C₆H₄]₃Si)⁵ that are generated by reaction of the corresponding anionic iron(0)–N₂ complex with methyl tosylate and trimethylsilyl chloride (TMSCl), respectively.

Very recently, we have shown that ferraboratranes derived from tris-[2-(diisopropylphosphino)phenyl]borane⁶ (TPB) are able to accommodate both a π-acidic terminal N₂ ligand and a π-basic terminal imido ligand thanks to the flexibility of the Fe–B linkage.⁷ Thus, we anticipated that N₂ functionalization might be facilitated by the ability of the TPB platform to stabilize the increasing Fe–N bond order arising from population of the π*(N–N) orbitals. Here we show that the (TPB)Fe scaffold indeed mediates the conversion of dinitrogen to silyldiazenido species in two different oxidation states as well as a disilylhydrazido(2−) species with an Fe≡N triple bond.

In a first experiment, the previously characterized⁷ anion [(TPB)Fe(N₂)][−] (**2**) was generated *in situ* from (TPB)FeBr (**1**) and an excess of sodium amalgam, and treated with 1.1

*Corresponding Author: jpeters@caltech.edu.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and spectroscopic data, DFT optimized coordinates, Complete ref. 10 (ref. 5 in SI). This material is available free of charge via the Internet at <http://pubs.acs.org>.

equivalents of trimethylsilyl chloride to afford the brown silyldiazenido complex **3** (Scheme 1) in 91 % yield. Compound **3** exhibits broad ^1H NMR resonances ranging from δ -2.6 to 17.4 ppm, a solution magnetic moment of $1.7 \mu_{\text{B}}$ (Evans method), and a quasi-axial EPR signal (X-Band, toluene glass, 20 K) with $g_1 = 1.990$, $g_2 = 2.005$, $g_3 = 2.480$, consistent with an $S = 1/2$ ground state. An intense IR absorption at 1741 cm^{-1} confirms the presence of a silyldiazenido moiety similar to that in $(\text{Si}^{\text{iPr}}\text{Pr}_3)\text{Fe}-\text{N}=\text{N}-\text{SiMe}_3$ ($\nu_{\text{NN}} = 1748 \text{ cm}^{-1}$).⁵ The X-ray diffraction (XRD) crystal structure of **3** (Figure 1) exhibits a coordination environment that is intermediate between trigonal bipyramidal and pseudotetrahedral ($\Sigma(\text{P}-\text{Fe}-\text{P}) = 342.3^\circ$) with an iron-boron distance ($2.4350(9) \text{ \AA}$) significantly elongated as compared to that of $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(\text{12-crown-4})_2]$ ($2.293(3) \text{ \AA}$).

Interestingly, exposing the starting material **1** to an excess of sodium amalgam and TMSCl in a one-pot reaction in THF afforded only a small yield of **3** (17 %), with most of the material being converted to its formal one-electron reduction product $[(\text{TPB})\text{Fe}(\text{NNSiMe}_3)][\text{Na}(\text{THF})]$ (**4**) that was isolated in 74% yield as a dark brown solid. Direct reduction of **3** with Na/Hg also afforded **4**, albeit in lower yield (47%). The diamagnetic compound **4** displays three ^{31}P NMR signals at 105.1, 88.5, and 9.1 ppm, indicating an unsymmetrical structure in which one of the phosphine arms is not bound to the metal. An XRD study (Figure 1) reveals that the iron center engages in an η^3 interaction⁸ with the corresponding phenylene linker (Fe-B: $2.319(3) \text{ \AA}$, Fe-C13: $2.116(3) \text{ \AA}$, Fe-C18: $2.146(3) \text{ \AA}$), resulting in substantial dearomatization as evidenced by bond length alternation (SI). In comparison to **3**, the N-N distance increased from 1.225 to $1.260(3) \text{ \AA}$ and the N-N-Si angle decreased from ca. 164° to $131.3(2)^\circ$, likely consequences of an increase in the population of $\pi^*(\text{N}-\text{N})$ orbitals resulting in the development of a lone pair on the distal nitrogen atom N2. The sodium counterion is encapsulated by the iron-bound aromatic cycle and the silyldiazenido ligand, both η^2 -bound, and completes its coordination sphere with a THF molecule. This tight association of the cation contributes to the stability of the complex, as shown by the fact that exposing **4** to an excess of 12-crown-4 results in its rapid decomposition to $[(\text{TPB})\text{Fe}(\text{N}_2)][\text{Na}(\text{12-crown-4})_2]$ with hexamethyldisilane as the main byproduct. The coordinative flexibility of the TPB ligand in this manner affords a redox step that is not available to $(\text{Si}^{\text{iPr}}\text{Pr}_3)\text{Fe}(\text{N}_2\text{SiMe}_3)$. This fact in turn enables further N_2 functionalization in the $(\text{TPB})\text{Fe}-\text{N}_2$ system.

To illustrate this point, the reaction of **1** with 1.1 equiv of the disilylating agent 1,2-bis(chlorodimethylsilyl)ethane⁹ and an excess Na/Hg under the same conditions gave clean access to a green, diamagnetic compound that is assigned to the disilylhydrazido(2-) complex **5** (Scheme 1) on the basis of multinuclear NMR and elemental analysis. In particular, the ^{11}B (27 ppm) and ^{31}P (99.1 ppm) chemical shifts closely match those of the previously characterized iron(II) imide $(\text{TPB})\text{Fe}\equiv\text{NAr}$ ($\text{Ar} = p\text{-methoxyphenyl}$, ^{11}B : 24 ppm, ^{31}P : 102.3 ppm).⁷

Crystals of **5** suffered from severe disorder that precluded an unambiguous structure determination by XRD. Thus, we performed a geometry optimization of the model compound **5-Me** at the B3LYP/6-31G(d) level, in which the isopropyl substituents of the TPB ligand have been replaced by methyl groups.^{10,11} The obtained structure (Figure 2) displays a short Fe-N distance ($1.629 \text{ \AA}$) indicative of $\text{Fe}\equiv\text{N}$ triple bond character, as well as a very long Fe-B distance ($2.785 \text{ \AA}$) pointing to a very weak interaction. The calculated frontier orbitals (Figure 2) exhibit three occupied orbitals of d parentage, while the LUMO is boron-centered and the LUMO+1 and LUMO+2 are of $\pi^*(\text{Fe}-\text{N})$ character, supporting the description of **5** as a d^6 Fe(II) compound with an $\text{Fe}\equiv\text{N}$ triple bond akin to the previously reported $(\text{TPB})\text{Fe}\equiv\text{NAr}$ ($\text{Ar} = p\text{-methoxyphenyl}$).⁷

Crystalline derivatives of **5** featuring the intact disilylhydrazido ligand were obtained by treatment with CO and ^tBuNC (Scheme 1), affording good yields of adducts **6** and **7** that display intense IR absorptions at 1856 and 1992 cm⁻¹, respectively. The ³¹P NMR spectrum of **7** displays a sharp resonance at -0.11 ppm and two broad ones at 91.3 and 89.4 ppm, indicating that coordination of an additional ligand results in the dissociation of one phosphine arm of TPB. This is additionally confirmed by the observation of the Fe-C≡NR carbon as a sharp triplet (²J_{C-P} = 16 Hz) at 183.8 ppm in the ¹³C NMR spectrum. A broad ¹¹B resonance at 49 ppm suggests that the Fe-B interaction is even weaker than in **5**.^{6b} Compound **6** exhibits similar NMR data with an additional set of slightly shifted resonances that are tentatively attributed to a minor isomer (ca 15 %). The XRD structures of **6** (Figure 1) and **7** (SI) confirm the connectivities inferred from NMR data and show very long Fe-B distances (**6**: 2.943 Å, **7**: 2.863 Å) indicating the absence of strong interactions. The short distances between the iron centers and the PPN plane (ca 0.2 Å) guide us to describe the geometry at iron as derived from trigonal pyramidal, a rarely observed geometry for iron(II).¹²

Complexes **5-7** represent rare examples of iron-bound disubstituted hydrazido(2-) ligands, the only other structurally characterized example being the formally iron(IV) complex (TPP^{Cl})Fe(NNC₉H₁₈) (TPP^{Cl} = *meso*-tetra-*p*-chlorophenylporphyrinato, NNC₉H₁₈=(2,2,6,6-tetramethylpiperid-1-yl)imido).¹³ The planarity of the distal nitrogen in the disilylhydrazido(2-) ligand indicate sp² hybridization resulting in partial N-N double bond character, as was found in a series of tungsten complexes incorporating the same ligand.⁹

Benzene solutions of compound **7** were found to slowly decompose at room temperature to a mixture of products from which the major component was isolated as colorless needles (46 % yield) and identified crystallographically (Figure 1) as compound **8** (Scheme 2), in which the N-N bond has been cleaved. Complex **8** is best described as a trigonal planar iron(II) complex featuring an unusual heterocyclic ligand that can be described as phosphoraniminato ligand interacting with a borane Lewis acid.¹⁴ ¹H NMR resonances ranging from -91.6 to 163 ppm and a solution magnetic moment of 5.7 μ_B (Evans method) indicate a high spin configuration with a significant orbital contribution to the effective magnetic moment, consistent with reported observations on related 3-coordinate Fe(II) compounds.¹⁵ A possible mechanism for the formation of **8** (Scheme 2, dashed arrows) consists of initial insertion of the disilylhydrazido(2-) ligand in a P-Fe bond of **7** to form iron(0) phosphazine complex (**A**) followed by oxidative addition of the N-N bond and isocyanide release from intermediate **B**. The reaction sequence **1** → **5** → **7** → **8** represents an overall series of synthetic transformations of iron-bound N₂ that results in full scission of the N≡N bond.

The series of compounds **2**, **3**, **4**, and **5** can be viewed to crudely mimic the first stages of an iron-based Chatt cycle (Fe-N≡N → Fe-N=NH → Fe≡N-NH₂) for nitrogen fixation,^{16,17} silylium cations being seen as reductively stable proton surrogates. Relevant crystallographic parameters are compiled in Table 1, complemented with DFT values where XRD data is unavailable. The gradual lengthening of the N-N bond from 1.131 Å in (TPB)Fe(N₂) to 1.349 Å in **5-Me**, coupled to the shortening of the Fe-N linkage from 1.881 Å to 1.629 Å, are consistent with an increasing population of the π*(N-N) orbitals. Wiberg bond indexes (Figure 3) computed in the natural atomic orbitals (NAO) basis¹⁸ corroborate this interpretation, the N-N bond index monotonically decreasing to 1.2 in **5-Me** while the Fe-N index increases to 1.9.

The formation of hydrazido(2-) moieties from a metal bound N₂ molecule is a well documented process for group 6 metals,^{9,19} where these ligands are thought to be

intermediates en route to ammonia or substituted amines. Such reactions had been unknown so far for later transition metals, presumably due to the historical difficulty to stabilize metal-ligand multiple bonds at high *d*-electron counts. Here we show that the TPB-iron platform featuring a hemilabile Lewis-acidic site in the apical position possesses enough flexibility to stabilize both Fe–N₂ and Fe≡N–NR₂ linkages as well as intermediate structures, providing some support to the potential feasibility of an iron-based Chatt-type cycle. We have suggested elsewhere that a similar hemi-labile role may be played by the interstitial light X-atom of the FeMo-cofactor, enabling a high degree of conformational and redox flexibility at a single iron N₂ binding site.²⁰ In this regard the central X-atom could act like a spring as the iron site coordinates various reduced nitrogenous ligands during turnover. This scenario would allow the iron center to modulate its local geometry by varying its degree of interaction with the light X-atom under crude local three-fold symmetry, possibly sampling trigonal bipyramidal, trigonal pyramidal, and/or pseudotetrahedral geometries as a function of the nature of the state of reduction of the nitrogenous ligand.²¹ The iron metallaboratrane featured herein offers a crude inorganic model to help consider this hypothesis, with the Fe–B interaction serving the function of the spring. Furthermore, in view of the well-documented role of iron imide complexes as intermediates in nitrene transfer reactions to substrates such as isocyanides,^{22a,b} olefins,^{22c,d} or C–H bonds,^{22d} the formation of imide-type structure 5 from dinitrogen opens up the intriguing possibility that N₂ might be incorporated as an N-atom source in a group transfer cycle. Studies in this direction are underway in our laboratories.

Supplementary Material

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Acknowledgments

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Figure 1.

Solid state structures of **3**, **4**, **6** and **8**. Thermal ellipsoids set at 50%. For clarity, hydrogen atoms, unbound solvent, as well as the minor component of the disordered unbound diisopropylphosphino moiety in structure **6** are omitted. The minor component (49%) of the disordered NNTMS moiety in structure **3** is indicated by dashed bonds.

Figure 2. Structure (left) and frontier molecular orbitals (right) of 5-Me calculated at the B3LYP/6-31G(d) level. Bond lengths in Å, energies in eV.

Figure 3.

N-N (red) and Fe-N (blue) Wiberg bond indexes computed from NBO analyses of the electron densities obtained from DFT calculations at the B3LYP/6-311+G(d,p)//6-31G(d) level.

Scheme 1.

Scheme 2.

Table 1

Bond lengths and angles

Cpnd	Fe–B [Å]	Fe–N [Å]	N–N [Å]	Fe–N–N [°]
N ₂	-	-	1.097	-
(TPB)Fe(N ₂)	2.222 ^a	1.881 ^a	1.131 ^a	177.9 ^a
2	2.293(3)	1.776(2)	1.149(2)	175.9(2)
3	2.4350(9)	1.6960(8)	1.225 ^b	164 ^b
4	2.319(3)	1.673(3)	1.260(3)	169.8(2)
5-Me	2.785 ^a	1.629 ^a	1.349 ^a	176.8 ^a
6	2.943	1.6438(5)	1.3273(7)	160.37(5)
7	2.863	1.640(2)	1.351(3)	162.6(2)

^aFrom geometry optimization at the B3LYP/6-31G(d) level.^bAverage from two equally populated disorder positions.