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Conversion of Fe-NH_2 to Fe-N_2 with release of NH_3

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Abstract

Tris(phosphine)borane ligated Fe(I) centers featuring N_2H_4, NH_3, NH_2, and OH ligands are described. Conversion of Fe-NH_2 to Fe-NH_3^+ by addition of acid, and subsequent reductive release of NH_3 to generate Fe-N_2, is demonstrated. This sequence models the final steps of proposed Fe-mediated nitrogen fixation pathways. The five-coordinate trigonal bipyramidal complexes described are unusual in that they adopt $S = 3/2$ ground states and are prepared from a four-coordinate, $S = 3/2$ trigonal pyramidal precursor.

Due the structural and mechanistic complexity of biological nitrogen fixation[1] a variety of mechanisms have been proposed that invoke either Mo or Fe as the likely active site for N_2 binding and reduction. Fe-NH_2 is an intermediate common to both limiting mechanisms (i.e., distal vs. alternating) being considered for Fe-mediated N_2 fixation scenarios at the FeMo-cofactor.[2,3] Such a species could form via reductive protonation of the nitride intermediate of a distal scheme (i.e., Fe(N) → Fe(NH) → Fe(NH_2) → Fe(NH_3)), or by reductive protonation of a hydrazine intermediate of an alternating scheme (i.e., Fe(NH_2-NH_2) → Fe(NH_2) + NH_3). In the latter context, detection of an EPR active Fe-NH_2 or possibly Fe-NH_3 common intermediate has been proposed under reducing conditions at the FeMo-cofactor from substrates including N_2, N_2H_4, and MeN=NH.[3a]

One key to realizing a catalytic cycle in either limiting scenario concerns the regeneration of Fe-N_2 from Fe-NH_2 with concurrent release of NH_3.[4] While there have been recent synthetic reports demonstrating NH_3 generation from Fe(N) nitride model complexes, these studies have not provided information about the plausible downstream Fe(NH_x) (X = 1, 2, 3) intermediates en route to NH_3 release, nor have these systems illustrated the feasibility of regeneration of Fe-N_2.[5] Herein we describe a terminal, $S = 3/2$ Fe-NH_2 complex for which the stepwise conversion to Fe-NH_3, and then to Fe-N_2 along with concomitant release of NH_3, is demonstrated (eqns 1 and 2).

$$\mathrm{Fe{-}NH_2 + H^+ \rightarrow Fe{-}NH_{3^+}} \quad (1)$$

$$\mathrm{Fe{-}NH_{3^+} + e^- + N_2 \rightarrow Fe{-}N_2 + NH_3} \quad (2)$$

Addition of methyllithium to (TPB)FeBr[6] affords the corresponding methyl complex (TPB)FeMe (**1**) in high yield (Scheme 1). Protonation of **1** by $HBAr^F_4 \cdot 2Et_2O$ ($BAr^F_4{}^- =$

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ASSOCIATED CONTENT

Supporting Information. Detailed experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

$B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$) in a cold ethereal solution releases methane to yield [(TPB)Fe][BAr$^F_4$] (**2**) which serves as a useful synthon with a vacant coordination site.

XRD data were obtained for **1** and **2** (Figure 1). The geometry of **1** is pseudo trigonal bipyramidal about Fe with an Fe-C bond length of 2.083(10) Å and an Fe-B bond length of 2.522 (2) Å. In the solid state **2** possesses a four-coordinate distorted trigonal pyramidal geometry with no close contacts in the apical site trans to boron, making this complex coordinatively unsaturated. Additionally, there is one wide P-Fe-P angle of 136°. The origin of this large angle is not clear, but a possible explanation is increased back-bonding from a relatively electron rich Fe center into the phosphine ligands that would arise from this distortion.

The Fe-B distance in **2** (2.217(2) Å) is markedly shorter than that in (TPB)FeBr (2.459(5) Å), which is noteworthy because one might expect the loss of an anionic σ-donor ligand to reduce the Lewis basicity of the metal and thus weaken the Fe-B bond. For example, the Au-B distance in (TPB)AuCl (2.318 Å) lengthens upon chloride abstraction to 2.448 Å in [(TPB)Au]$^+$.[7] To explain this difference we note that the boron center in four-coordinate **2** is less pyramidalized (Σ(C−B−C) = 347.3°) than that in five-coordinate (TPB)FeBr (Σ(C−B−C) = 341.2°), pointing to a weak interaction despite the short distance. These observations suggest that the geometry of **2** might be best understood as derived from a planar three-coordinate Fe(I) center distorted towards a T-shaped geometry,[8] the unusually short Fe-B distance being due largely to the constraints imposed by the ligand cage structure. This interpretation is consistent with a computational model study: the DFT (B3LYP/6-31G(d)) optimized geometry of the hypothetical complex $[(Me_2PhP)_3Fe]^+$ (see SI for details) exhibits a planar geometry with P-Fe-P angles of 134.8°, 113.1°, and 111.7°, very close to those measured for [(TPB)Fe]$^+$ (137.5°, 113.2°, 109.1°).

When considering the bonding of the $(Fe\text{-}B)^7$ subunit of **2** to estimate the best oxidation state and valence assignment, two limiting scenarios present themselves: Fe(III)/B(I) and Fe(I)/B(III). The structural data and computations for **2** are suggestive of a weak Fe-B interaction and indicate that this species is better regarded as Fe(I)/B(III) rather than Fe(III)/B(I). Calculations indicate that a small amount of spin density resides on the Batom of **2** (SI) and suggest some contribution from an Fe(II)/B(II) resonance form may also be relevant. The rest of the complexes **3–6** presented herein possess significantly longer, and presumably weaker, Fe-B interactions (*vide infra*) and are hence also better classified as Fe(I) species. Additional spectroscopic studies (e.g., XAS and Mössbauer) will help to better map the Fe-B bonding interaction across the variable Fe-B distances and also the spin states of the complexes. These studies would thereby help to determine the value and limitation of classically derived oxidation/valence assignments for boratranes of these types.[9]

Solutions of **2** are orange in Et_2O and pale yellow-green in THF. Titration of THF into an ethereal solution of **2** results in a distinct change in the UV-vis spectrum consistent with weak THF binding. Addition of an excess of N_2H_4 to an ethereal solution of **2** results in a slight lightening of the orange color of the solution to afford [(TPB)Fe(N_2H_4)][BAr$^F_4$] (**3**) in 89% yield. Complex **3** shows a paramagnetically shifted ^{1}H NMR spectrum indicative of an $S = 3/2$ Fe center that is corroborated by a room temperature solution magnetic moment, μ_{eff}, of 3.5 μ_B. Crystals of **3** were obtained and XRD analysis (Figure 2A) indicates a distorted trigonal bipyramidal geometry. The Fe-N distance of 2.205(2) Å is unusually long (2.14 Å is the average quaternary N-Fe distance in the Cambridge Structural Database) reflecting its unusual quartet spin state.

Complex **3** is stable to vacuum, but solutions decompose cleanly at room temperature over hours to form the cationic ammonia complex [(TPB)Fe(NH_3)][BAr$^F_4$], **4**, which was assigned by comparison of its ^1H NMR spectrum with an independently prepared sample formed by the addition of NH_3 to the cation **2**. Analysis of additional degradation products shows only NH_3 and trace H_2 (SI). The assignment of **4** as an ammonia adduct was confirmed by XRD analysis (Figure 2B). Like **3**, complex **4** shows a long Fe-N distance of 2.280(3) Å in the solid state. The complexes **2**, **3** and **4** are unusual by virtue of their $S = 3/2$ spin states and underscore the utility of local 3-fold symmetry with respect to stabilizing high spin states at iron, even in the presence of strong-field phosphine ligands.

Addition of $NaNH_2$ to the cation **2** affords the terminal amide, (TPB)Fe-NH_2 (**5**) in ca. 85% non-isolated yield by ^1H NMR integration. The XRD structure of **5** (Figure 2C) shows an overall geometry similar to that observed in **1**, **3**, and **4**. Of interest is the short Fe-N distance of 1.918(3) Å by comparison to **4** (2.280(3) Å). The amide hydrogens were located in the difference map and indicate a nearly planar geometry about N (with the sum of the angles around N being 355°).

While the XRD data set of **5** is of high quality, we were concerned about the difficulty in distinguishing an Fe-NH_2 group from a potentially disordered Fe-OH moiety. We therefore independently characterized the hydroxo complex, (TPB)Fe-OH (**6**) (Scheme 2), which possesses a geometry similar to that observed in **5** with an Fe-B distance of 2.4438(9) Å and an Fe-O distance of 1.8916(7) Å. Despite the structural similarity between **5** and **6**, different spectral signatures in both their ^1H NMR and EPR (Figure 3) spectra allow for facile distinction between them. Like **2**, **3**, and **4**, both **5** and **6** are $S = 3/2$.

Low-temperature EPR data (Figure 3) have been obtained on complexes **1–6**. All complexes show features shifted to large g-values consistent with quartet Fe species.[10] This assignment is verified by the solution magnetic moments obtained for these complexes. Variable temperature solid-state SQUID magnetic data for complexes **2–5** (SI) also establish quartet spin state assignments and display no evidence for spin-crossover phenomena. These data show a drop in magnetic moment in the range 50–70 K for all compounds studied. We propose that this effect is due to a large zero-field splitting in these species, which is consistent with Fe centers in related geometries.[11] Simulations with zero-field splitting of 10–20 cm^{-1} provide reasonable fits to the data.

Parent amide complexes of first row transition metals are rare.[12] Noteworthy precedent for related terminal M-NH_2 species includes two square planar nickel complexes[12a, d] and one octahedral and diamagnetic iron complex, $(dmpe)_2Fe(H)NH_2$.[12e] In addition to their different coordination numbers, geometries, and spin-states, $(dmpe)_2Fe(H)(NH_2)$ and **5** show a distinct difference at the Fe-NH_2 subunit. Six-coordinate $(dmpe)_2Fe(H)(NH_2)$ is an 18-electron species without **π**-donation from the amide ligand, which is pyramidalized as a result. By contrast, five-coordinate **5** accommodates **π**-bonding from the amide. This is borne out in its much shorter Fe-N distance (1.918(3) Å for **5** vs 2.068 Å for $(dmpe)_2Fe(H)(NH_2)$), and also its comparative planarity (the sum of the angles around N is 355° for **5** vs 325° for $(dmpe)_2Fe(H)(NH_2)$).

With the terminal amide **5** in hand we explored its suitability as a precursor to the previously reported N_2 complex (TPB)Fe(N_2) via release of NH_3 and hence explored reduction/protonation vs protonation/reduction sequences as a means of effecting overall H-atom transfer to the Fe-NH_2 unit. Attempts to carry out the one-electron reduction of **5** were not informative. For example, electrochemical studies of **5** in THF failed to show any reversible reduction waves, but the addition of harsh reductants (e.g., *t*BuLi) to **5** did show small amounts of (TPB)Fe(N_2) in the product profile. A more tractable conversion sequence utilized protonation followed by chemical reduction. Thus, the addition of $HBAr^F_4 \cdot 2Et_2O$ to **5** at low temperature (−35 °C) rapidly generates the cationic ammonia adduct **4**. The conversion is quantitative as determined by ^{1}H NMR spectroscopy, and **4** can be isolated in ca. 90% yield from the solution. Subsequent exposure of **4** to one equiv of KC_8 under an atmosphere of N_2 releases NH_3 and generates the (TPB)FeN_2 complex in similarly high yield.

In summary, an unusual series of $S = 3/2$ iron complexes featuring terminally bonded N_2H_4, NH_3, NH_2, and OH functionalities has been thoroughly characterized. These complexes are supported by a tris(phosphine)borane ligand and are best described as Fe(I) species that feature weak Fe-B bonding, though other resonance contributions to the bonding scheme warrant additional consideration. The Fe-NH_2 species faithfully models the reductive replacement of the terminal NH_2 group by N_2 with concomitant release of NH_3, lending credence to such a pathway as mechanistically feasible in Fe-mediated N_2 reduction schemes. Because spectroscopic detection of a common Fe-NH_2 or Fe-NH_3 intermediate under reductive turnover of the FeMo-cofactor has been recently proposed,[3] EPR active model complexes of the types described here should prove useful for comparative purposes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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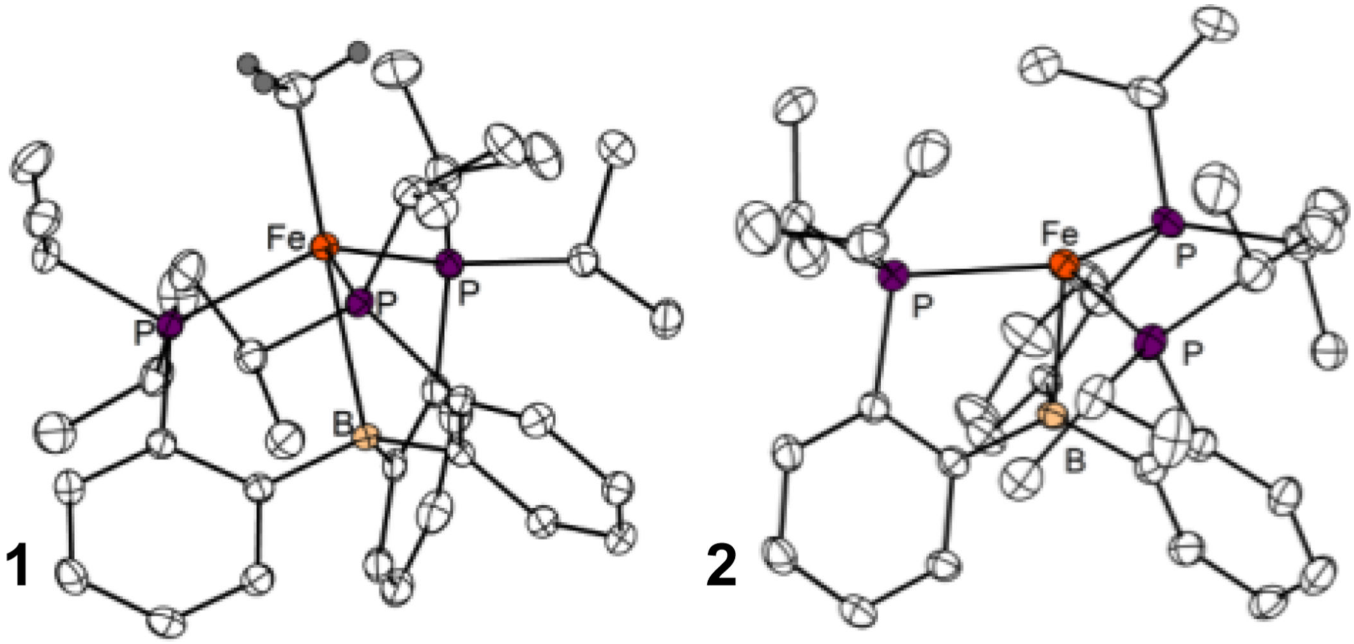


Figure 1.

X-Ray Diffraction (XRD) structures of complexes **1** (A) and **2** (B) with hydrogen atoms and counterion (for B) omitted for clarity. See Table 1 for selected bond lengths and angles.

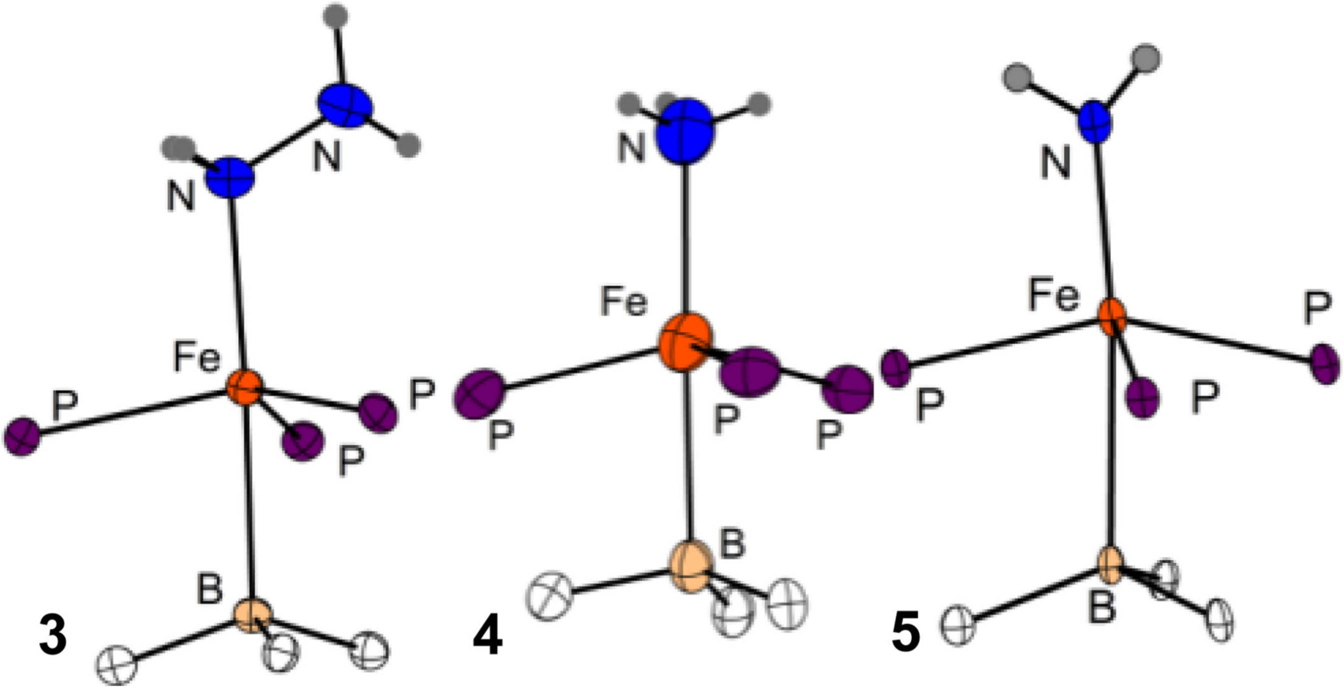


Figure 2.
XRD structures of the cores of complexes **3** (A), **4** (B), and **5** (C). See Table 1 for selected distances and angles.

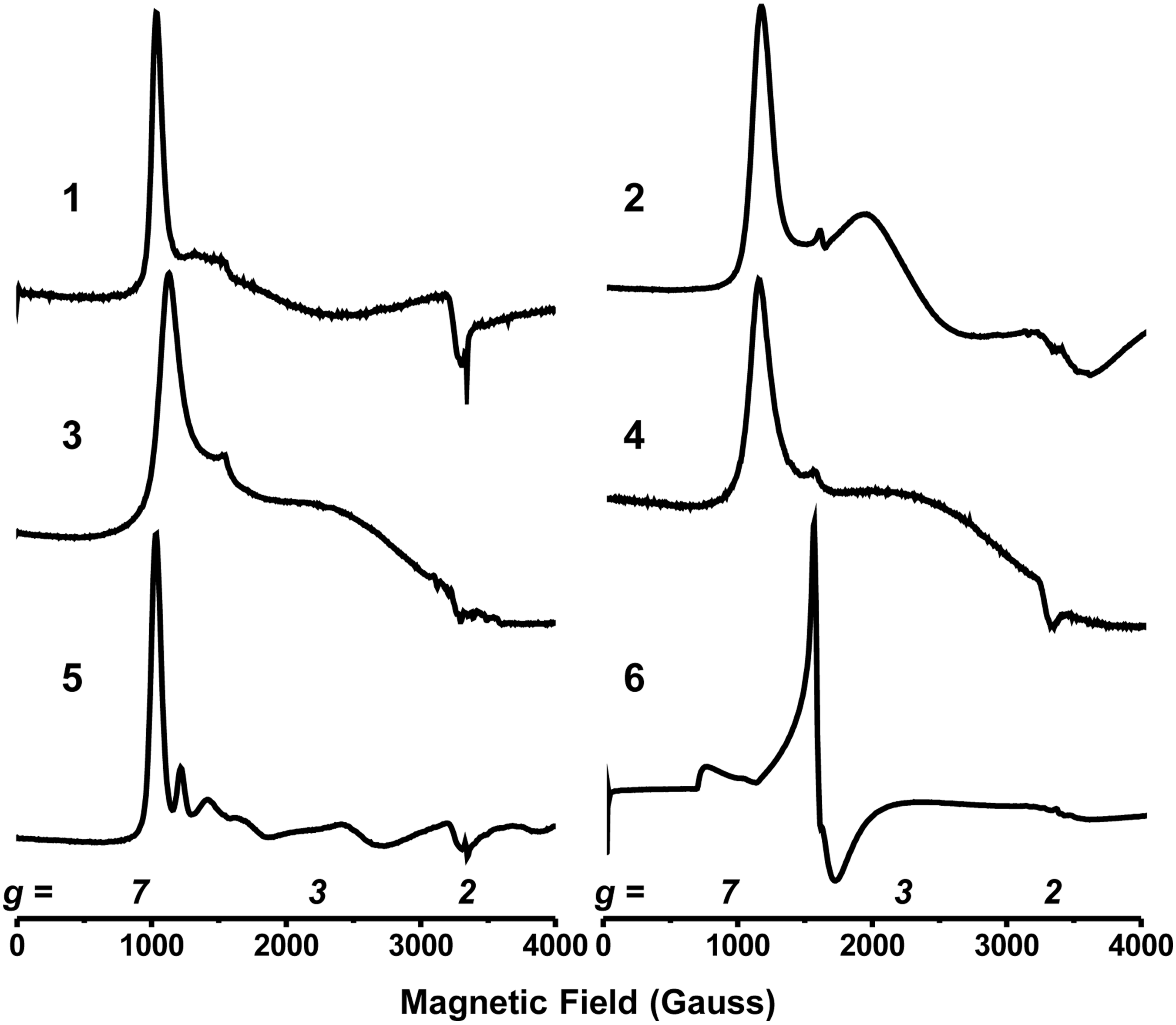
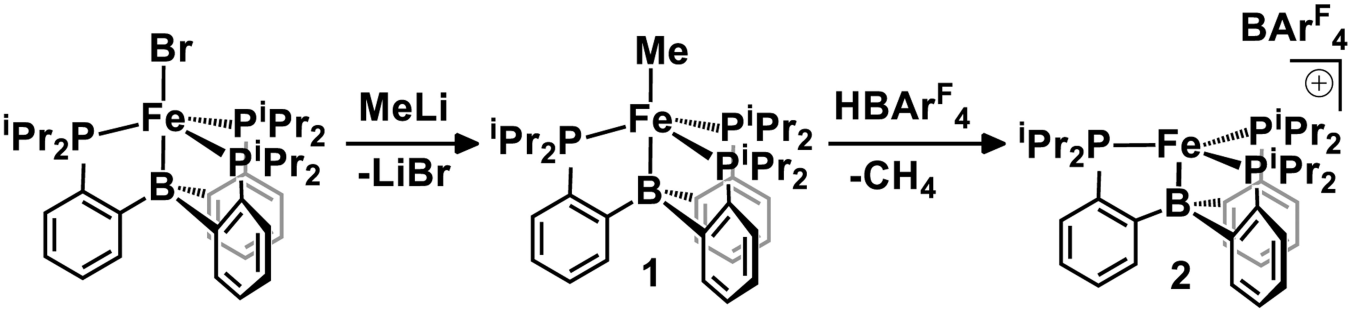
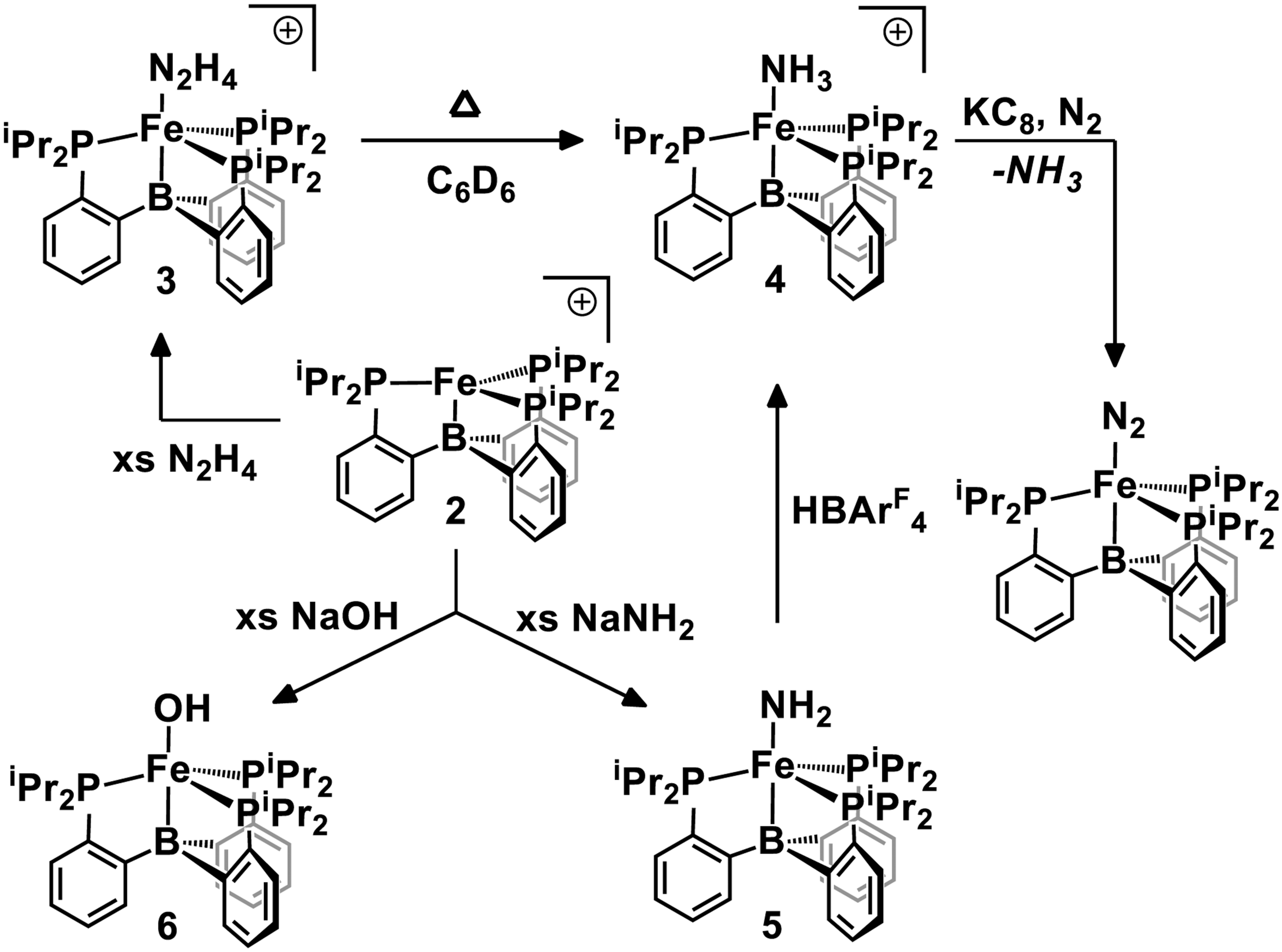


Figure 3.
X-Band EPR spectra for complexes **1–6**. Conditions for **1**: Toluene, 8 K; **2**: 2:1 Toluene:Et_2O, 10 K **3**: 2-MeTHF, 10 K; **4**: 2-MeTHF, 10 K; **5**: 2-MeTHF, 10 K; **6**: Toluene, 10 K.



SCHEME 1.


3
4
2
6
5
Δ
C_6D_6
KC_8, N_2
$-NH_3$
xs N_2H_4
$HBAr^F_4$
xs NaOH
xs $NaNH_2$
N_2H_4
NH_3
N_2
OH
NH_2
Fe
B
$^iPr_2P$
P^iPr_2

SCHEME 2.

Table 1

Selected Metrics for Complexes 1–6

	Fe-X (Å)	Fe-B (Å)	Avg. Fe-P (Å)	Σ P-Fe-P	Σ C-B-C
1	2.083(10)	2.523(2)	2.40	339°	341°
2	-	2.217(2)	2.38	359°	347°
3	2.205(2)	2.392(2)	2.44	350°	339°
4	2.280(3)	2.433(3)	2.44	349°	341°
5	1.918(3)	2.449(4)	2.39	343°	339°
6	1.8916(7)	2.4438(9)	2.39	348°	337°