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# Proton-Coupled Reduction of an Iron Cyanide Complex to Methane and Ammonia

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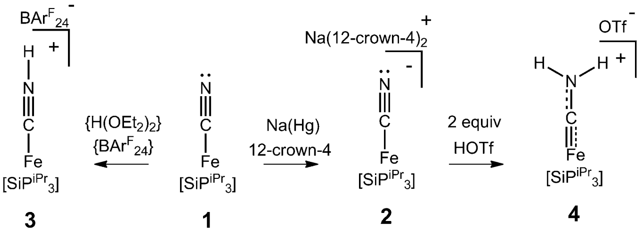
***Abstract:*** *Nitrogenase enzymes mediate the six-electron reductive cleavage of cyanide to $CH_4$ and $NH_3$. Herein we demonstrate for the first time the liberation of $CH_4$ and $NH_3$ from a well-defined iron cyanide coordination complex, $[SiP^{iPr}_3]Fe(CN)$ (where $[SiP^{iPr}_3]$ represents a tris(phosphine)-silyl ligand), on exposure to proton and electron equivalents. $[SiP^{iPr}_3]Fe(CN)$ additionally serves as a useful entry point to rare examples of terminally-bound Fe(CNH) and $Fe(CNH_2)$ species that, in accord with preliminary mechanistic studies, are plausible intermediates of the cyanide reductive protonation to generate $CH_4$ and $NH_3$. Comparative studies with a related $[SiP^{iPr}_3]Fe(CNMe_2)$ complex suggests the possibility of multiple, competing mechanisms for cyanide activation and reduction.*



*Scheme 1.* Synthesis of $Fe(CNH_x)$ complexes.

In addition to catalyzing $N_2$-to-$NH_3$ conversion under ambient conditions,[1] nitrogenase ($N_2$-ase) enzymes facilitate the multi-electron reduction of a wide range of other substrates, such as azide, acetylene, carbon dioxide, and nitrous oxide.[2] Cyanide ($CN^-$) is perhaps most noteworthy in this context as it is isoelectronic with $N_2$ and can be reduced in two-, four-, or six-electron processes to furnish $H_2C{=}NH$, $H_3C\text{-}NH_2$, or $CH_4$ and $NH_3$, respectively.[3] To date there is scant synthetic precedent for the overall reduction of $CN^-$ to $CH_4$ and $NH_3$, either stoichiometrically or catalytically, by well-defined coordination complexes; beyond $N_2$-ases, $CN^-$ conversion to $CH_4$ and $NH_3$ is thus far limited to extracted nitrogenase cofactors, or via reductive electrolysis by Ni electrodes.[4,5]

We have had an ongoing interest in the study of single-site iron complexes that mediate $N_2$-to-$NH_3$ conversion as functional inorganic models of biological nitrogen fixation at the iron rich cofactors of $N_2$-ases.[6] We naturally became interested in whether such single-site precursors might functionally model the enzymatic reduction of $CN^-$ to liberate $CH_4$ and $NH_3$. Such a process is likely to proceed through classic organometallic intermediates[7] with appreciable Fe-to-C covalency, and this possibility, in addition to the recent discovery that $N_2$-ases can also mediate Fischer–Tropsch type CO reduction,[8] motivates functional organometallic model studies.

Herein we report an Fe(CN) complex supported by a tris(phosphine)silyl ligand ($[SiP^{iPr}_3]Fe(CN)$, **1**, Scheme 1) that releases significant amounts of $NH_3$ and $CH_4$ on exposure to excess acid and reductant. We also report the isolation and structural characterization of terminal Fe(CNH) and Fe-($CNH_2$) complexes that are plausible intermediates of the overall reduction process.

Entry into this $CN^-$ reduction system was made via the reaction of $[SiP^{iPr}_3]Fe(Cl)$[9a] ($[SiP^{iPr}_3] = [(2\text{-}iPr_2PC_6H_4)_3Si]^-$) with a slight excess of either NaCN, $K^{13}CN$, or $KC^{15}N$ to furnish the three isotopomers of $[SiP^{iPr}_3]Fe(CN)$ (**1**) as pink solids. Compound **1** was found to display rich electrochemical behavior (see the Supporting Information) and reduction with Na(Hg) in the presence of 12-crown-4 cleanly afforded the one-electron reduced salt $\{Na(12\text{-}crown\text{-}4)_2\}\{[SiP^{iPr}_3]Fe(CN)\}$ (**2**) as a dark brown solid. Complexes **1** and **2** are paramagnetic with solution spin states of $S = 1$ ($\mu_{eff} = 2.6\ \mu_B$) and $S = 1/2$ ($\mu_{eff} = 2.0\ \mu_B$), respectively, observed at room temperature. Anionic **2** additionally displays a quasi-axial EPR spectrum ($g_{\parallel} = 2.23$, $g_{\perp} \approx 2.05$) in a 2-MeTHF glass at 20 K. The solid-state structures[10] reveal trigonal-bipyramidal Fe geometries ($\tau_5 = 1.02$ and 0.85 for **1** and **2**, respectively; see Figure 1 and the Supporting Information) with the CN ligand positioned *trans* to the apical Si atom. These Fe–CN complexes are nearly isostructural to the similarly-charged Fe–$N_2$ and Fe–CO complexes supported by the $[SiP^{iPr}_3]$ platform.[9]

Fe(CN) **1** is readily protonated by the acid $\{H(OEt_2)_2\}$-$\{BAr^F_{24}\}$ ($BAr^F_{24} = (3,5\text{-}(CF_3)_2C_6H_3)_4B^-$) to afford the cationic hydrogen-isocyanide complex, $\{[SiP^{iPr}_3]Fe(CNH)\}\{BAr^F_{24}\}$ (**3**) (Scheme 1). Compound **3** adopts an $S = 1$ spin state in solution ($\mu_{eff} = 2.6\ \mu_B$), complicating the assignment of the acid-derived proton by NMR techniques. Fortunately, this proton is unambiguously located in the Fourier difference map of the solid-state structure of **3** (Figure 1) as a component of a $C{\equiv}N\text{-}H$ ligand. A hydrogen bond is observed between the isocyanide proton and a co-crystallized molecule of diethyl ether ($d$(N···O): 2.639(3) Å, ∡(O···H-N): 173(4)°). The KBr IR spectrum of polycrystalline **3** displays very broad absorbances that span the range of 3100 to 1900 $cm^{-1}$ (Supporting Information), a feature that may arise from the coupling of

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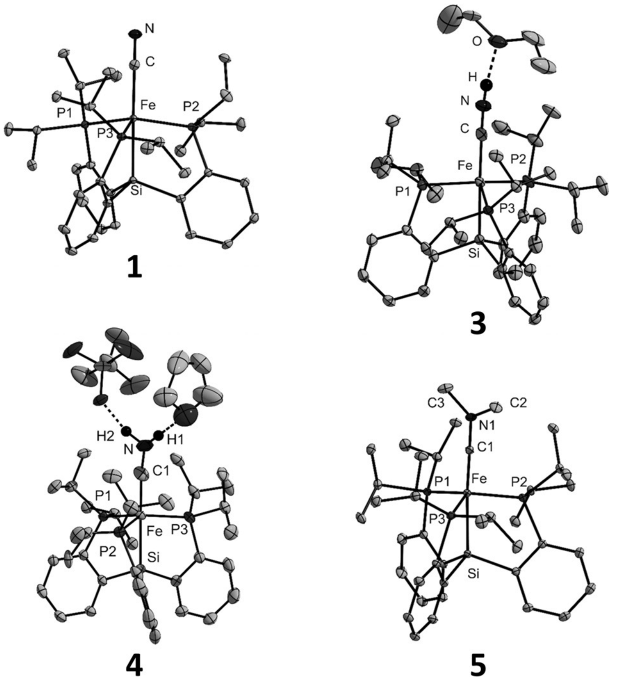
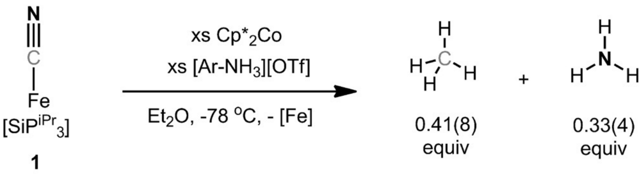


***Figure 1.*** X-ray diffraction crystal structures of **1**, **3**, **4**, and **5** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms (excepting the N-H's), the $BAr^F_{24}$ counteranion of **3** and co-crystallized solvent molecules have been removed for clarity. Two independent molecules of **4** are found in the unit cell and only one is shown.

N–H and C≡N vibrational modes and a continuum of hydrogen bonding interactions in the polycrystalline state.[11] Overall, the bond metrics of the {Fe(CNH)} unit compare well to those of the few previously characterized examples.[7a,12] By comparison, we have to date been unable to directly characterize related {Fe(NNH)} species supported by either tris(phosphino)silyl or tris(phosphino)borane ligands despite their presumed intermediacy in $N_2$-to-$NH_3$ conversion reactions.[6]

Further activation of the CN ligand was achieved via double protonation of the anionic Fe(CN) **2**. Combining solutions of **2** with 2.5 equivalents of trifluoromethanesulfonic acid (HOTf) in thawing 2-MeTHF affords the cationic iron aminocarbyne complex, $\{[SiP^{iPr}_3]Fe(CNH_2)\}\{OTf\}$ (**4**) (Scheme 1). Aminocarbyne **4** displays averaged 3-fold symmetry in THF solution, as judged by its $^1H$ NMR spectrum at 193 K; its EPR spectrum is quasi-axial ($g_\parallel = 2.51$, $g_\perp \approx 1.98$, Figure 2B) with a larger observed g-anisotropy than that of Fe(CN) **2**. The solid-state structure of **4** reveals a shortened Fe–C bond (1.800(4) Å) relative to those found in compounds **1**–**3** (1.97–1.91 Å) and is indicative of significant Fe-to-C multiple bond character. While the $CNH_2$ hydrogen atoms were not directly located in the Fourier difference map, their presence is indicated by close contacts between the CN-derived N atom, the triflate counteranion and a co-crystallized molecule of THF (d(N···O) range from 2.68 Å–3.20 Å). Solid IR spectra of **4** (Figure 2A) also reveal strong absorptions near 3100 cm$^{-1}$ that shift to 2300 cm$^{-1}$ in ***4-d*₂** (prepared from **2** and DOTf) which are assigned to N-H(D) stretching frequencies engaged in strong hydrogen bonding interactions.[11] Similar features are noted in the recently-described terminal $Fe{=}NNH_2$ complex, $\{[SiP^{iPr}_3]Fe{=}NNH_2\}\{OTf\}$,[6c] consistent with their similar structures. While synthetic Fe complexes have previously been shown to support terminal CNH ligands or bridging $CNH_2$ functionalities,[13] compound **4** is the first example of a terminal $Fe(CNH_2)$ complex.[14]

We next examined reductive cleavage of the coordinated cyanide unit from Fe(CN) **1** (Scheme 2). After canvassing several conditions we found that stirred $Et_2O$ solutions containing **1**, 24 equiv of $Cp^*_2Co$ and 24 equiv $[2,5\text{-}Cl_2\text{-}PhNH_3][OTf]$ maintained at −78 °C furnished an average of 0.33(4) equiv/Fe of $NH_3$ upon warming to room temperature overnight. Isotopically-enriched $[^{15}NH_4][Cl]$ is the sole nitrogen-containing product detected by $^1H$ and $^{15}N$ NMR spectroscopy when **$^{15}$N-1** is subjected to these conditions, hence



***Scheme 2.*** Reductive protonolysis of Fe(CN) **1**. Ar = $2,5\text{-}Cl_2\text{-}C_6H_3$. Refer to the Supporting Information for experimental details.

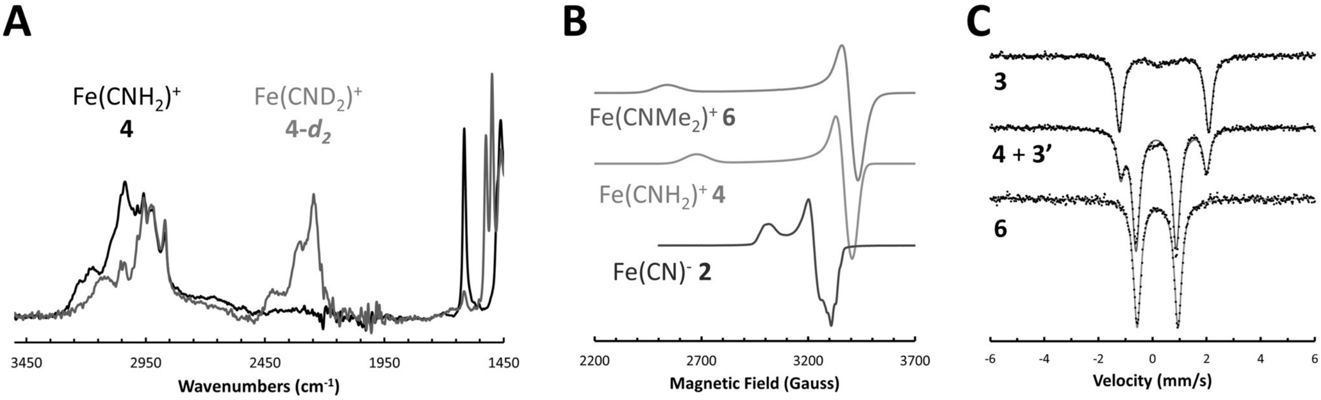


***Figure 2.*** Pertinent spectroscopic data for $Fe(CNH_2)$ **4** and related complexes. A) Solid IR spectra of **4** (black) and ***4-d*₂** (gray). B) X-band EPR spectra of frozen 2-MeTHF solutions of **6** (top), **4** (middle) and **2** (bottom) collected at 20 K. C) Zero field, 80 K $^{57}Fe$ Mössbauer spectra of solid **3** (top), $^{57}Fe$-enriched **4** contaminated with 24% **3′** collected as a frozen 2-MeTHF solution (middle) and $^{57}Fe$-enriched **6** (bottom) collected as a frozen 2-MeTHF solution.

establishing that the $NH_3$ is derived from the cyanide *N*-atom. The use of 50 instead of 24 equivalents of both $Cp^*_2Co$ and $[2,5\text{-}Cl_2\text{-}PhNH_3][OTf]$ does not increase the yield of $NH_3$ (0.31(2) equiv/Fe). Control reactions that replace **1** with [TBA][CN] as a soluble source of $CN^{(-)}$ do not generate detectable quantities of $NH_3$, implicating a likely role of the $[SiP^{iPr}_3]Fe$ platform in the activation of cyanide towards cleavage.

To ascertain the C-containing product(s) of these reactions, the headspaces were analyzed by gas chromatography (Figure 3) and found to contain 0.41(8) equiv/Fe of $CH_4$. Exposure of **$^{13}$C-1** to these reaction conditions furnishes $^{13}CH_4$ as the dominant isotopomer detected by GC-MS (Figure 3C). Finally, replacing $[2,5\text{-}Cl_2\text{-}PhNH_3][OTf]$ with partially-enriched DOTf as the proton source furnishes a mixture of deuterated methane products with masses up to and including 20 (Figure 2D) as is expected for $CD_4$. Very little $CH_4$ is detected (0.007 equiv) when [TBA][CN] is used in place of **1** in these reactions (Figure 2A). Taken together, these analyses indicate that the $[SiP_3^{iPr}]Fe$ fragment facilitates the proton-coupled six-electron reduction of coordinated cyanide to $CH_4$ and $NH_3$ in moderate overall yields.

We also studied the stoichiometric reactivity of the Fe(CNH) and $Fe(CNH_2)$ complexes to assess the intermediacy of these species in a cyanide cleavage process. In the absence of additional proton or electron equivalents, $Fe(CNH_2)$ **4** is unstable in solution ($\tau_{1/2\,(293\,K)} = 24$ min), decaying to a mixture of Fe-containing products that include $\{[SiP^{iPr}_3]Fe(CNH)\}\{OTf\}$ (**3′**) and $[SiP^{iPr}_3]Fe(OTf)$[6c] as readily-identified species. Independent reactions reveal that both $NH_3$ (0.09(2) equiv/Fe) and $H_2$ (0.24 equiv/Fe) are released on leaving solutions of **4** to stand overnight. Furthermore, Fe(CNH) **3′** slowly converts to $[SiP^{iPr}_3]Fe(OTf)$ in THF solutions ($\tau_{1/2\,(298\,K)} = 4$ h), presumably with the loss of the CNH ligand. A similar ligand displacement reaction was observed for the hydrazine adduct, $\{[SiP^{iPr}_3]Fe(N_2H_4)\}\{OTf\}$.[9a]

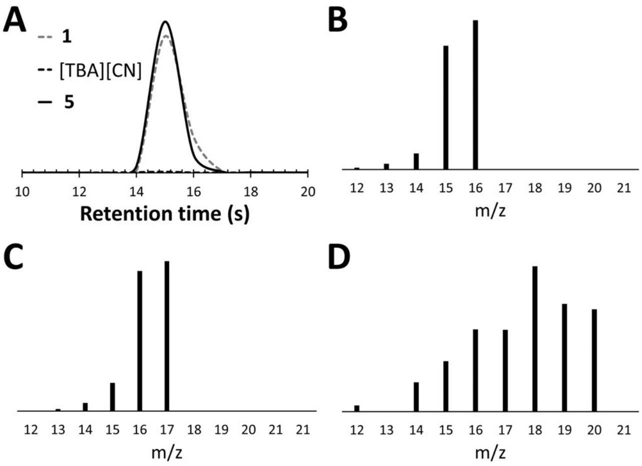


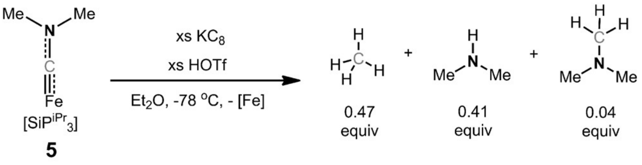
***Figure 3.*** A) Representative GC-FID chromatograms of sampled headspaces in the reaction of (dashed gray) **1** or (dashed black) [TBA][CN] with 24 equiv $Cp^*_2Co$ and 24 equiv $[2,5\text{-}Cl_2\text{-}PhNH_3][OTf]$ in $Et_2O$, and (black) **5** with 10 equiv $KC_8$ and 10 equiv HOTf. B) Mass spectrum of $CH_4$ produced from **1**. C) Mass spectrum of $CH_4$ produced from compound **$^{13}$C-1**. D) Mass spectrum of $CH_xD_{4-x}$ produced from **1**, 24 equiv $Cp^*_2Co$ and 24 equiv partially-enriched DOTf.

This ligand exchange is likely irreversible under the relevant reaction conditions as free hydrogen *iso*cyanide readily converts to hydrogen cyanide.[7a] Non-productive decomposition of an $Fe(CNH_x)$ complex may therefore partially account for the moderate yields (< 41 %) of $CH_4$ and $NH_3$ formed upon exposure of **1** to excess proton and electron equivalents.

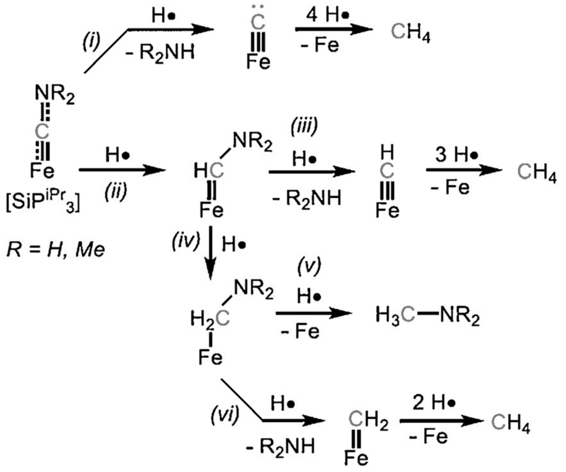
Given the challenges arising from the thermal instability of **4** and **3′** in solution, we pursued more robust $Fe(CNR_2)$ species to model the intermediacy of a terminal Fe carbyne complex in the reductive C–N bond cleavage described above. The neutral and diamagnetic dialkylaminocarbyne complex $[SiP^{iPr}_3]Fe(CNMe_2)$ (**5**), can be prepared in a one pot reaction via the sequential addition of Na(Hg) and MeOTf to solutions of **1** (82 % yield) (Figure 1). $Fe(CNMe_2)$ **5** is isoelectronic to the previously reported iron siloxycarbyne complex[9b] and accordingly displays a short Fe-C distance (1.710(1) Å), a long C-N distance (1.328(1) Å), and a downfield resonance ($\delta = 279.6$ ppm) in the $^{13}C\{^1H\}$ NMR spectrum assigned to the carbyne carbon. Complex **5** is readily oxidized by $\{Cp_2Fe\}\{BAr^F_{24}\}$ to afford $\{[SiP^{iPr}_3]Fe(CNMe_2)\}\{BAr^F_{24}\}$ (**6**). The salient spectroscopic features of $Fe(CNMe_2)^+$ **6** closely match those of the isoelectronic $Fe(CNH_2)^+$ **4** (Figure 2). Compounds **5** and **6** are very stable in solution and in the solid state when stored at room temperature under an inert atmosphere.

$Fe(CNMe_2)$ **5** was found to react with proton and electron equivalents to afford a mixture of $CH_4$, $Me_2NH$ and small amounts of $Me_3N$. Whereas Fe(CN) **1** is reduced to $CH_4$ and $NH_3$ with $Cp^*_2Co$ and $[2,5\text{-}Cl_2\text{-}PhNH_3][OTf]$ (vide supra), exposure of $Et_2O$ solutions of **5** to these reagents only furnishes small quantities of $CH_4$ (ca. 0.01 equiv/Fe). Apparently, more reactive proton and electron sources are required for C–N bond scission in the case of **5**, and 0.47 equiv of $CH_4$ are detected when **5** is exposed to 10 equiv of $KC_8$ and HOTf (Scheme 3). Reactions that employ **$^{13}$C-5** generate $^{13}CH_4$ as the predominant isotopomer, confirming the carbyne carbon as the source of this hydrocarbon. Analysis of the reaction volatiles obtained when **$^{15}$N-5** is exposed to these conditions reveals two detectable $^{15}$N-containing products (see the Supporting Information). Resonances assigned to the N-H protons of $[H^{15}NMe_3][Cl]$ and $[H_2{}^{15}NMe_2][Cl]$ are present at $\delta = 10.84$ and 9.05 ppm, respectively, in the $^1H$ NMR spectrum and display well-resolved coupling to adjacent $^{15}$N- and $^1$H nuclei. Comparison of the features present in the $^1$H, $^{13}$C, and $^{15}$N NMR spectra to authentic samples of these ammonium salts solidifies their assignments. $[SiP^{iPr}_3]Fe(OTf)$ was identified as the major Fe-containing product of these reactions (see the Supporting Information).

The organic products of these reactions lend some insight into possible pathways for Fe-mediated cyanide reduction.



***Scheme 3.*** Reductive protonolysis of $Fe(CNMe_2)$ **5**. Refer to the Supporting Information for experimental details.



*Scheme 4.* Possible routes to the formation of $CH_4$ and amine products.

Upon exposure of Fe(CNMe$_2$) **5** to proton and electron equivalents, dimethylamine is found to be the dominant (90 %) *N*-containing product. Its formation is consistent with a mechanism whereby an early cleavage of the cyanide-derived $C\equiv N$ bond occurs and is followed by the formation of $CH_4$. Scheme 4 outlines scenarios by which such a process might in principle proceed, invoking unusual terminal carbide intermediates [path (i)] or terminal methylidyne intermediates [path (ii)-to-(iii)]. Such pathways are conceptually related to the distal pathway of $N_2$ reduction.[1b] While only observed as a minor product, the $NMe_3$ product cannot be derived from a distal pathway, and may indicate a competing pathway wherein H-atom equivalents are delivered to the Fe-bound carbyne carbon of **5** without C−N bond rupture [Scheme 4, paths (iv) and (v)]. Conceptually related crossover distal-to-alternating mechanisms have been proposed for Fe-mediated $N_2$ activation,[6c] and these scenarios will warrant further consideration in the present context of cyanide reduction. The fact that different reaction conditions/reagents are required for the activation of the cyanide-derived C−N bond in Fe(CNMe$_2$) **5** and Fe(CN) **1** necessitates caution in mechanistically relating the reaction profile of **5** to generate $CH_4$ and $HNMe_2$ (or $NMe_3$) with that of **1** to generate $CH_4$ and $NH_3$. Nonetheless, reactions pathways that bypass C−N bond cleavage, such as that represented by *(v)* of Scheme 4, do not appear to be competent in the case of the proton-coupled reduction of **1** as $MeNH_2$ is not observed.

In conclusion, we have disclosed the synthesis of a trigonal bipyramidal Fe(CN) species whose $C\equiv N$ bond is cleaved upon exposure to proton and electron equivalents. An unusual Fe(CNH$_2$) complex has been characterized and may serve as a plausible intermediate en route to the $CH_4$ and $NH_3$ products derived from this 6-electron/proton $C\equiv N$ cleavage reaction. This work lends indirect support to the notion that one (or more) Fe centers within the FeMoco (or FeVco) can serve to activate myriad substrates, including $N_2$, CO and cyanide. The catalytic reduction of cyanide by a synthetic molecular system remains a worthwhile challenge, and the complexes described here serve as promising starting points.

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