



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

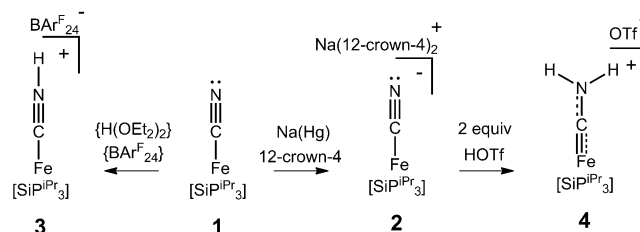
Jonathan Rittle and Jonas C. Peters*

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, $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CN})$ (where $[\text{SiP}^{\text{iPr}}_3]$ represents a tris(phosphine)-silyl ligand), on exposure to proton and electron equivalents. $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CN})$ additionally serves as a useful entry point to rare examples of terminally-bound $\text{Fe}(\text{CNH})$ and $\text{Fe}(\text{CNH}_2)$ 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 $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CNMe}_2)$ complex suggests the possibility of multiple, competing mechanisms for cyanide activation and reduction.

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 $\text{H}_2\text{C}=\text{NH}$, $\text{H}_3\text{C}-\text{NH}_2$, 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 $\text{Fe}(\text{CN})$ complex supported by a tris(phosphine)silyl ligand ($[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CN})$, **1**, Scheme 1)

Scheme 1. Synthesis of $\text{Fe}(\text{CNH}_x)$ complexes.

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 $\text{Fe}(\text{CNH})$ and $\text{Fe}(\text{CNH}_2)$ complexes that are plausible intermediates of the overall reduction process.

Entry into this CN^- reduction system was made via the reaction of $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{Cl})$ ^[9a] ($[\text{SiP}^{\text{iPr}}_3] = [(2\text{-iPr}_2\text{PC}_6\text{H}_4)_3\text{Si}]^-$) with a slight excess of either NaCN , K^{13}CN , or KC^{15}N to furnish the three isotopomers of $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CN})$ (**1**) as pink solids. Compound **1** was found to display rich electrochemical behavior (see the Supporting Information) and reduction with $\text{Na}(\text{Hg})$ in the presence of 12-crown-4 cleanly afforded the one-electron reduced salt $\{[\text{Na}(\text{12-crown-4})_2][[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CN})]\}$ (**2**) as a dark brown solid. Complexes **1** and **2** are paramagnetic with solution spin states of $S=1$ ($\mu_{\text{eff}}=2.6\ \mu_{\text{B}}$) and $S=1/2$ ($\mu_{\text{eff}}=2.0\ \mu_{\text{B}}$), 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 $[\text{SiP}^{\text{iPr}}_3]$ platform.^[9]

$\text{Fe}(\text{CN})$ **1** is readily protonated by the acid $\{\text{H}(\text{OEt}_2)_2\}\{\text{BAr}^{\text{F}}_{24}\}$ ($\text{BAr}^{\text{F}}_{24} = (3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}^-$) to afford the cationic hydrogen-isocyanide complex, $\{[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CNH})\}\{\text{BAr}^{\text{F}}_{24}\}$ (**3**) (Scheme 1). Compound **3** adopts an $S=1$ spin state in solution ($\mu_{\text{eff}}=2.6\ \mu_{\text{B}}$), 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 $\text{C}\equiv\text{N}-\text{H}$ ligand. A hydrogen bond is observed between the isocyanide proton and a co-crystallized molecule of diethyl ether ($d(\text{N}\cdots\text{O}): 2.639(3)\ \text{\AA}$, $\angle(\text{O}\cdots\text{H}-\text{N}): 173(4)^\circ$). The KBr IR spectrum of polycrystalline **3** displays very broad absorbances that span the range of 3100 to $1900\ \text{cm}^{-1}$ (Supporting Information), a feature that may arise from the coupling of

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201606366>.

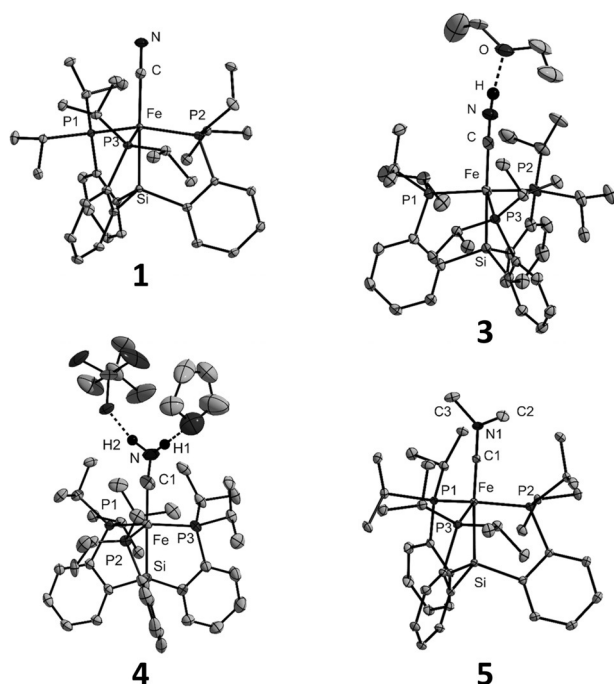


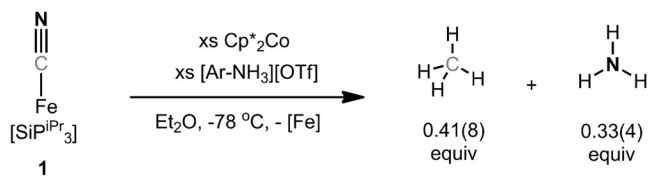
Figure 1. X-ray diffraction crystal structures of **1**, **3**, **4**, and **5** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms (excepting the N-H's), the BARF_{24}^- counteranion of **3** and co-crystallized solvent molecules have been removed for clarity. Two independent molecules 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 aminocarbene complex, $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CNH}_2)^+\{\text{OTf}\}^-$ (**4**) (Scheme 1). Aminocarbene **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 ($d(\text{N}\cdots\text{O})$ 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=NNH₂ complex, $[\text{SiP}^{\text{iPr}}_3]\text{Fe}=\text{NNH}_2\{\text{OTf}\}$,^[6c] consistent with their similar structures. While synthetic Fe complexes have previously been shown to support terminal CNH ligands or bridging CNH₂ functionalities,^[13] compound **4** is the first example of a terminal Fe(CNH₂) 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 $[\text{2,5-Cl}_2\text{-PhNH}_3][\text{OTf}]$ maintained at -78°C furnished an average of 0.33(4) equiv/Fe of NH_3 upon warming to room temperature overnight. Isotopically-enriched $[\text{N}^{15}\text{H}_4][\text{Cl}]$ 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- $\text{Cl}_2\text{-C}_6\text{H}_3$. Refer to the Supporting Information for experimental details.

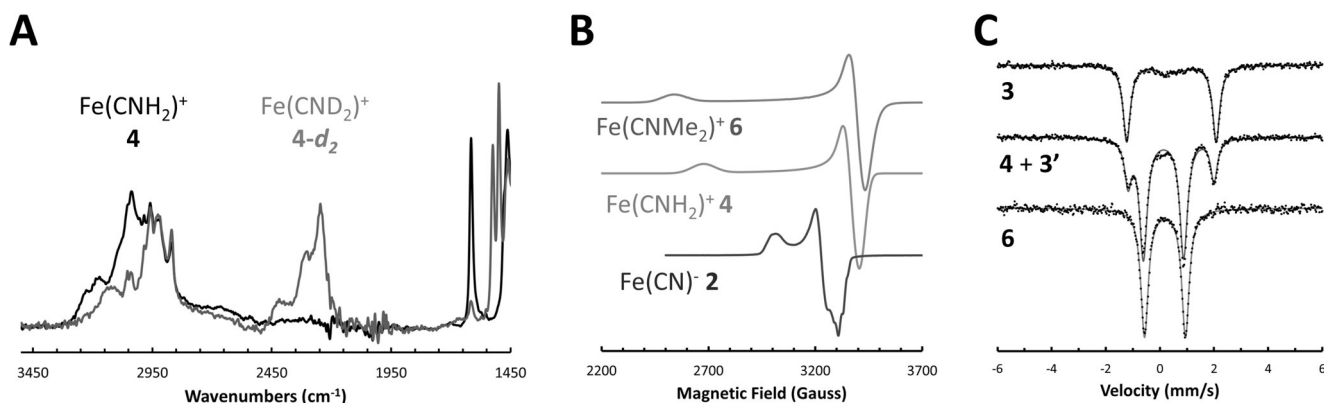


Figure 2. Pertinent spectroscopic data for Fe(CNH₂) **4** and related complexes. A) Solid IR spectra of **4** (black) and **4-d}_2** (gray). B) X-band EPR spectra of frozen 2-MeTHF solutions of **6** (top), **4** (middle) and **2** (bottom) collected at 20 K. C) Zero field, 80 K ^{57}Fe Mössbauer spectra 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 $[\text{2,5-Cl}_2\text{-PhNH}_3][\text{OTf}]$ does not increase the yield of NH_3 (0.31(2) equiv/Fe). Control reactions that replace **1** with $[\text{TBA}][\text{CN}]$ as a soluble source of $\text{CN}^{(-)}$ do not generate detectable quantities of NH_3 , implicating a likely role of the $[\text{SiP}^{\text{iPr}}_3]\text{Fe}$ 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 $^{13}\text{CH}_4$ as the dominant isotopomer detected by GC-MS (Figure 3C). Finally, replacing $[\text{2,5-Cl}_2\text{-PhNH}_3][\text{OTf}]$ 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 $[\text{TBA}][\text{CN}]$ is used in place of **1** in these reactions (Figure 2A). Taken together, these analyses indicate that the $[\text{SiP}^{\text{iPr}}_3]\text{Fe}$ 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 $\text{Fe}(\text{CNH})$ and $\text{Fe}(\text{CNH}_2)$ complexes to assess the intermediacy of these species in a cyanide cleavage process. In the absence of additional proton or electron equivalents, $\text{Fe}(\text{CNH}_2)$ **4** is unstable in solution ($\tau_{1/2}(293\text{ K}) = 24\text{ min}$), decaying to a mixture of Fe-containing products that include $[\{\text{SiP}^{\text{iPr}}_3\}\text{Fe}(\text{CNH})]\{\text{OTf}\}$ (**3'**) and $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{OTf})$ [**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, $\text{Fe}(\text{CNH})$ **3'** slowly converts to $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{OTf})$ in THF solutions ($\tau_{1/2}(298\text{ K}) = 4\text{ h}$), presumably with the loss of the CNH ligand. A similar ligand displacement reaction was observed for the hydrazine adduct, $[\{\text{SiP}^{\text{iPr}}_3\}\text{Fe}(\text{N}_2\text{H}_4)]\{\text{OTf}\}$.^[9a]

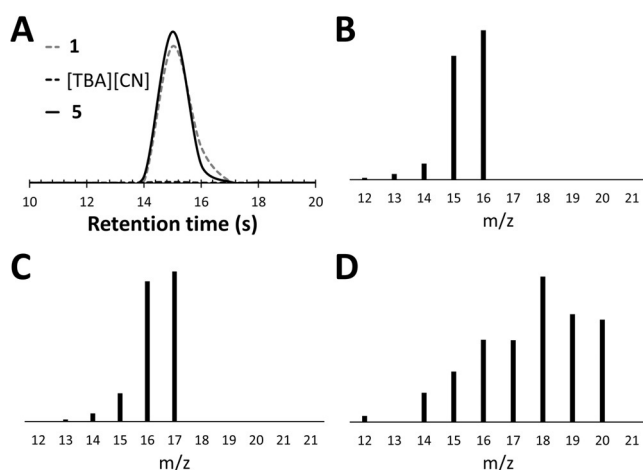


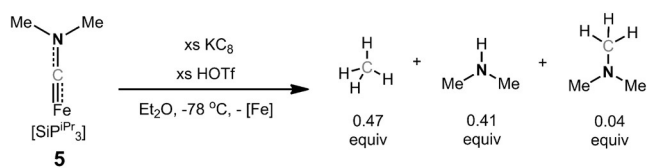
Figure 3. A) Representative GC-FID chromatograms of sampled headspaces in the reaction of (dashed gray) **1** or (dashed black) $[\text{TBA}][\text{CN}]$ with 24 equiv Cp^*_2Co and 24 equiv $[\text{2,5-Cl}_2\text{-PhNH}_3][\text{OTf}]$ in Et_2O , and (black) **5** with 10 equiv KC_8 and 10 equiv HOTf. 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 $\text{CH}_4\text{D}_{4-x}$ 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 isocyanide readily converts to hydrogen cyanide.^[7a] Non-productive decomposition of an $\text{Fe}(\text{CNH}_x)$ 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.

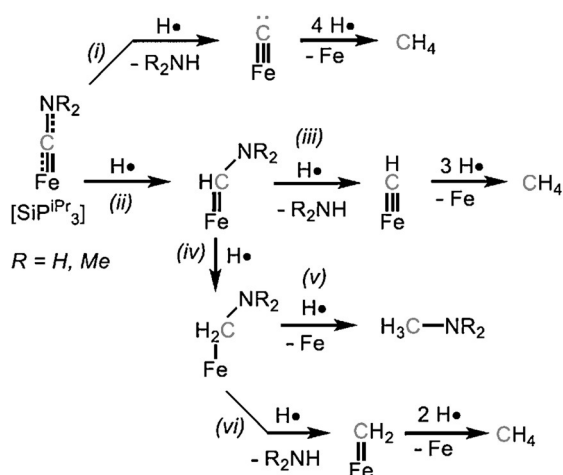
Given the challenges arising from the thermal instability of **4** and **3'** in solution, we pursued more robust $\text{Fe}(\text{CNR}_2)$ species to model the intermediacy of a terminal Fe carbyne complex in the reductive C–N bond cleavage described above. The neutral and diamagnetic dialkylaminocarbyne complex $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{CNMe}_2)$ (**5**), can be prepared in a one pot reaction via the sequential addition of $\text{Na}(\text{Hg})$ and MeOTf to solutions of **1** (82% yield) (Figure 1). $\text{Fe}(\text{CNMe}_2)$ **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 down-field resonance ($\delta = 279.6\text{ ppm}$) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum assigned to the carbyne carbon. Complex **5** is readily oxidized by $\{\text{Cp}_2\text{Fe}\}\{\text{BAR}^{\text{F}}_{24}\}$ to afford $[\{\text{SiP}^{\text{iPr}}_3\}\text{Fe}(\text{CNMe}_2)]\{\text{BAR}^{\text{F}}_{24}\}$ (**6**). The salient spectroscopic features of $\text{Fe}(\text{CNMe}_2)^+$ **6** closely match those of the isoelectronic $\text{Fe}(\text{CNH}_2)^+$ **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.

$\text{Fe}(\text{CNMe}_2)$ **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 $\text{Fe}(\text{CN})$ **1** is reduced to CH_4 and NH_3 with Cp^*_2Co and $[\text{2,5-Cl}_2\text{-PhNH}_3][\text{OTf}]$ (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 $^{13}\text{CH}_4$ 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 $[\text{H}^{15}\text{NMe}_3][\text{Cl}]$ and $[\text{H}_2^{15}\text{NMe}_2][\text{Cl}]$ 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 ^1H nuclei. Comparison of the features present in the ^1H , ^{13}C , and ^{15}N NMR spectra to authentic samples of these ammonium salts solidifies their assignments. $[\text{SiP}^{\text{iPr}}_3]\text{Fe}(\text{OTf})$ 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 $\text{Fe}(\text{CNMe}_2)$ **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 $\text{Fe}(\text{CNMe}_2)$ **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 $\text{C}\equiv\text{N}$ 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 methyldiene 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 $\text{Fe}(\text{CNMe}_2)$ **5** and $\text{Fe}(\text{CN})$ **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 $\text{Fe}(\text{CN})$ species whose $\text{C}\equiv\text{N}$ bond is cleaved upon exposure to proton and electron equivalents. An unusual $\text{Fe}(\text{CNH}_2)$ 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 $\text{C}\equiv\text{N}$ 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.

Acknowledgements

This work was supported by the NIH (grant number GM 070757) and the NSF (GRFP to J.R.). We thank Lawrence Henling and Michael Takase for assistance with XRD studies, and Kathryn Perez and Nathan Dalleska for assistance with GC experiments.

Keywords: carbyne ligands · cyanide cleavage · iron complexes · nitrogenase · nitrogen fixation

How to cite: *Angew. Chem. Int. Ed.* **2016**, 55, 12262–12265
Angew. Chem. **2016**, 128, 12450–12453

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Received: June 30, 2016

Published online: September 8, 2016