



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

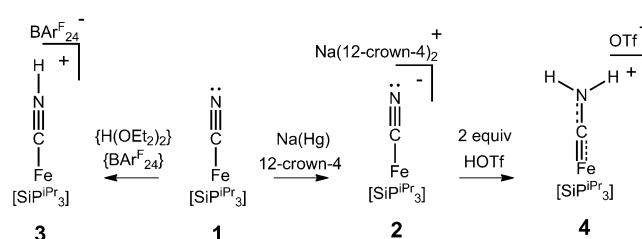
Jonathan Rittle and Jonas C. Peters*

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-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 $[SiP^{iPr}_3]Fe(CI)^{[9a]}$ ($[SiP^{iPr}_3] = [(2-iPr_2PC_6H_4)_3Si]^-$) 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 $\{Na(12-crown-4)_2\}[\{SiP^{iPr}_3\}Fe(CN)]$ (**2**) as a dark brown solid. Complexes **1** and **2** are paramagnetic with solution spin states of $S = 1$ ($\mu_{eff} = 2.6 \mu_B$)



Scheme 1. Synthesis of Fe(CNH_2) complexes.

and $S = 1/2$ ($\mu_{eff} = 2.0 \mu_B$), respectively, observed at room temperature. Anionic **2** additionally displays a quasi-axial EPR spectrum ($g_{||} = 2.23$, $g_{\perp} \approx 2.05$) 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]

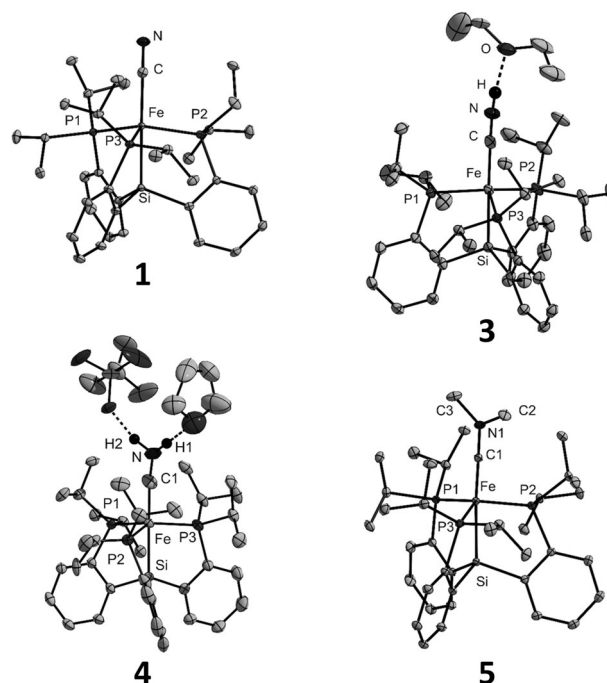


Figure 1. X-ray diffraction crystal structures of **1**, **3**, **4**, and **5** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms (excepting the N-H's), the $BArF_{24}$ counteranion of **3** and co-crystallized solvent molecules have been removed for clarity. Two independent molecules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

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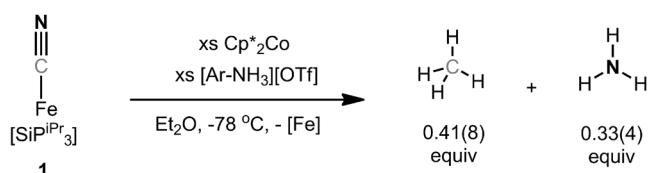
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Fe(CN) **1** is readily protonated by the acid $\{H(OEt_2)_2\}\{BAr^F_{24}\}$ ($BAr^F_{24} = (3,5-(CF_3)_2C_6H_3)_4B^-$) to afford the cationic hydrogen-isocyanide complex, $\{[SiP^{iPr}_3]Fe(CNH)\}\{BAr^F_{24}\}$ (**3**) (Scheme 1). Compound **3** adopts an $S=1$ spin state in solution ($\mu_{\text{eff}} = 2.6 \mu_B$), 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=N-H ligand. A hydrogen bond is observed between the isocyanide proton and a co-crystallized molecule of diethyl ether ($d(N\cdots O)$: 2.639(3) Å, $\angle(O\cdots H-N)$: 173(4)°). The KBr IR spectrum of polycrystalline **3** displays very broad absorptions that span the range of 3100 to 1900 cm^{-1} (Supporting Information), a feature that may arise from the coupling of 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 ($d(N\cdots O)$ 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-d₂** (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, $\{[SiP^{iPr}_3]Fe=NNH_2\}\{OTf\}$,^[6c] consistent with their similar structures. While synthetic Fe complexes have previously been shown to support terminal CNH ligands or bridging 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



Scheme 2. Reductive protonolysis of Fe(CN) **1**. Ar = 2,5-Cl₂-C₆H₃. Refer to the Supporting Information for experimental details.

several conditions we found that stirred Et₂O solutions containing **1**, 24 equiv of Cp*₂Co and 24 equiv [2,5-Cl₂-PhNH₃][OTf] maintained at -78 °C furnished an average of 0.33(4) equiv/Fe of NH₃ upon warming to room temperature overnight. Isotopically-enriched [¹⁵NH₄][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 establishing that the NH₃ is derived from the cyanide N-atom. The use of 50 instead of 24 equivalents of both Cp*₂Co and [2,5-Cl₂-PhNH₃][OTf] does not increase the yield of NH₃ (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 NH₃, 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

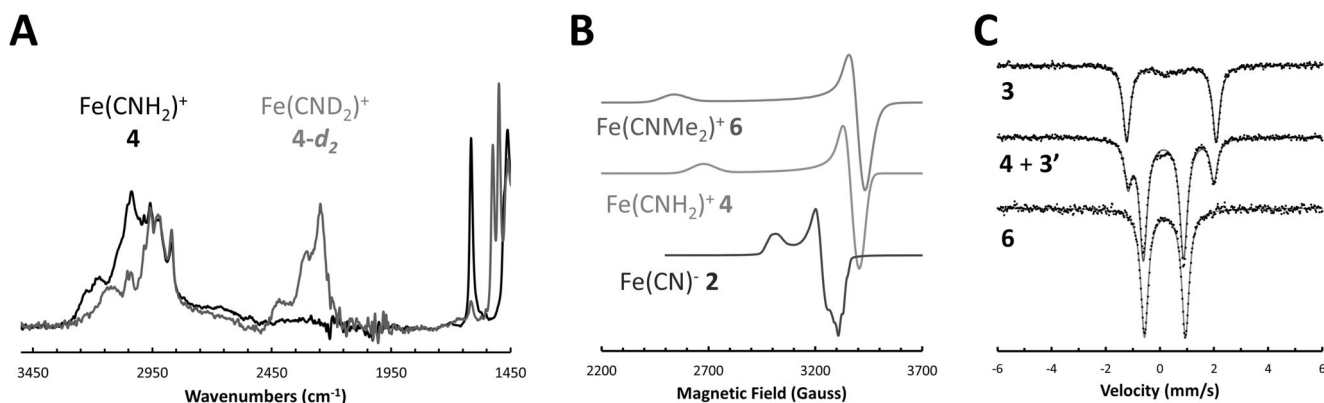


Figure 2. Pertinent spectroscopic data for Fe(CNH₂) **4** and related complexes. A) Solid IR spectra of **4** (black) and **4-d₂** (gray). B) X-band EPR spectra of frozen 2-MeTHF solutions of **6** (top), **4** (middle) and **2** (bottom) collected at 20 K. C) Zero field, 80 K ^{57}Fe Mössbauer spectra 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.

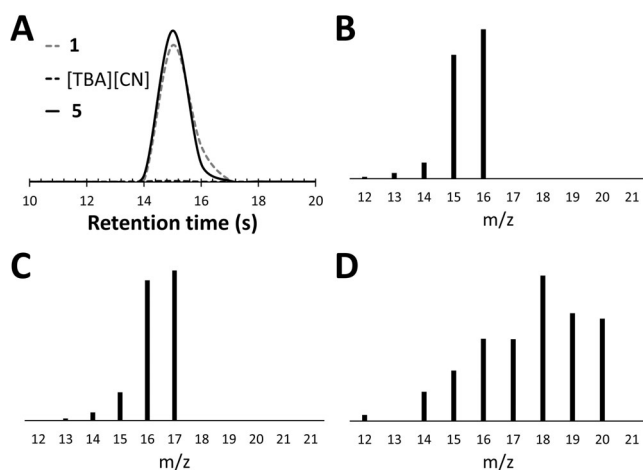


Figure 3. A) Representative GC-FID chromatograms of sampled head-spaces in the reaction of (dashed gray) **1** or (dashed black) [TBA][CN] with 24 equiv Cp^*Co and 24 equiv [2,5- $\text{Cl}_2\text{-PhNH}_3$][OTf] in Et_2O , and (black) **5** with 10 equiv KC_8 and 10 equiv HOTf. B) Mass spectrum of CH_4 produced from **1**. C) Mass spectrum of CH_4 produced from compound $^{13}\text{C-1}$. D) Mass spectrum of $\text{CH}_4\text{D}_{4-x}$ produced from **1**, 24 equiv Cp^*Co and 24 equiv partially-enriched DOTf.

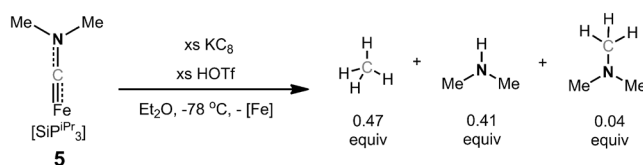
(Figure 3) and found to contain 0.41(8) equiv/Fe of CH_4 . Exposure of $^{13}\text{C-1}$ to these reaction conditions furnishes $^{13}\text{CH}_4$ as the dominant isotopomer detected by GC-MS (Figure 3C). Finally, replacing [2,5- $\text{Cl}_2\text{-PhNH}_3$][OTf] with partially-enriched DOTf as the proton 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 $[\text{SiP}^{\text{IPr}}_3]\text{Fe}$ 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 ($\tau_{1/2(293\text{ K})} = 24$ 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 ($\tau_{1/2(298\text{ K})} = 4$ 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] 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 downfield resonance ($\delta = 279.6$ 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.

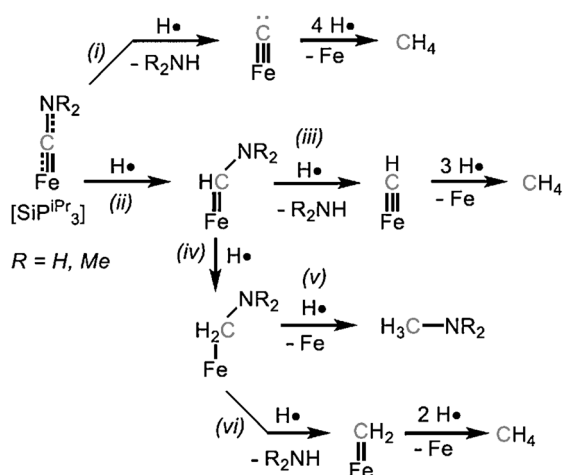
$\text{Fe}(\text{CNMe}_2)$ **5** was found to react with proton and electron equivalents to afford a mixture of CH_4 , Me_2NH and small amounts of Me_3N . Whereas $\text{Fe}(\text{CN})$ **1** is reduced to CH_4 and NH_3 with Cp^*Co and [2,5- $\text{Cl}_2\text{-PhNH}_3$][OTf] (vide supra), exposure of 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 $^{13}\text{C-5}$ generate $^{13}\text{CH}_4$ as



Scheme 3. Reductive protonolysis of $\text{Fe}(\text{CNMe}_2)$ **5**. Refer to the Supporting Information for experimental details.

the predominant isotopomer, confirming the carbyne carbon as the source of this hydrocarbon. Analysis of the reaction volatiles obtained when $^{15}\text{N-5}$ 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. 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



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

intermediates [path (i)] or terminal methyldiyne 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

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

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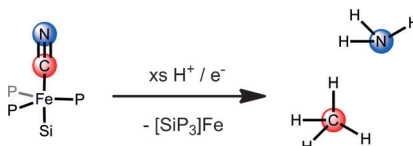
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Communications



Nitrogen Fixation

J. Rittle, J. C. Peters* ——— ■■■■-■■■■

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

Reductive cleavage of cyanide : A trigonal bipyramidal iron cyanide complex is shown to evolve methane and ammonia upon exposure to proton and electron equivalents at low temperature (see picture). Terminally bound Fe(CNH) and Fe(CNH₂) complexes are characterized as possible intermediates in this CN⁻ cleavage reaction.