

Fe-catalyzed conversion of N₂ to N(SiMe₃)₃ via an Fe-hydrazido resting state

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Supporting Information Placeholder

ABSTRACT: The catalytic conversion of N₂ to N(SiMe₃)₃ by homogenous transition metal compounds is a rapidly developing field, yet few mechanistic details have been experimentally elucidated for 3d element catalysts. Herein we show that Fe(PP)₂(N₂) (PP = R₂PCH₂CH₂PR₂; R = Me, **1**^{Me}; R = Et, **1**^{Et}) are highly effective for the catalytic production of N(SiMe₃)₃ from N₂ (using KC₈/Me₃SiCl), with the yields being the highest reported to date for Fe-based catalysts. We propose that N₂ fixation proceeds via electrophilic N_β silylation and 1e⁻ reduction to form unstable Fe^I(NN-SiMe₃) intermediates, which disproportionate to **1**^{Me/Et} and hydrazido Fe^{II}[N-N(SiMe₃)₂] species (**3**^{Me/Et}); the latter act as resting states on the catalytic cycle. Subsequent 2e⁻ reduction of **3**^{Me/Et} leads to N-N scission and formation of [N(SiMe₃)₂]⁻ and putative anionic Fe imido products. These mechanistic results are supported by both experiment and DFT calculations.

The fixation of dinitrogen is of fundamental importance to the availability of this element in both the biosphere and the chemical industry, yet it presents a significant challenge due to the stability and inertness of N₂.¹ Biological (nitrogenases)² and anthropogenic (Haber-Bosch)³ methods employ Fe-containing catalysts to execute the challenging feat of N₂ reduction. In the hope of attaining near-ambient catalytic conversion of N₂, and to gain ready mechanistic insight into such processes, much recent research has targeted the development and study of homogeneous Fe complexes;^{4,5} molecular Fe-N₂ complexes incorporating multidentate phosphine ligand frameworks have found success in this regard.⁶ For example, catalytic NH₃ production from N₂ has been reported by Peters and co-workers using P₃^EFe(N₂) complexes [P = o-(PⁱPr)₂C₆H₄; E = B, C, Si],^{7,8} and Nishibayashi *et al.* have employed diphosphine pincer Fe-N₂ species.^{9,10} Our group showed that N₂H₄ can be synthesized in high turnover directly from N₂, using Fe(depe)₂(N₂) (**1**^{Et}; depe = Et₂PCH₂CH₂PEt₂).¹¹ All these catalytic protocols use excess acid (H⁺) and reductant (e⁻), thereby mimicking the PCET-mediated route to N₂ fixation which operates in nitrogenases.¹² An alternative reduction method is the silylation of N₂ to N(SiMe₃)₃, which may be readily hydrolyzed to NH₃.^{13,14} This approach employs electrophilic [Me₃Si]⁺ sources (e.g. Me₃SiCl), in conjunction with powerful alkali-metal based reductants (Li, Na, KC₈); together these generate Me₃Si[•] radicals *in situ* which are proposed to react with ligated N₂.^{15–17}

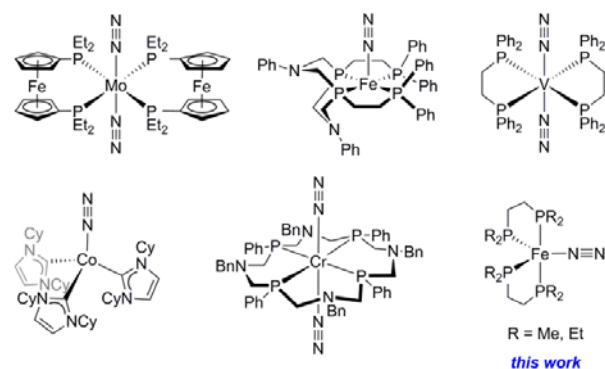


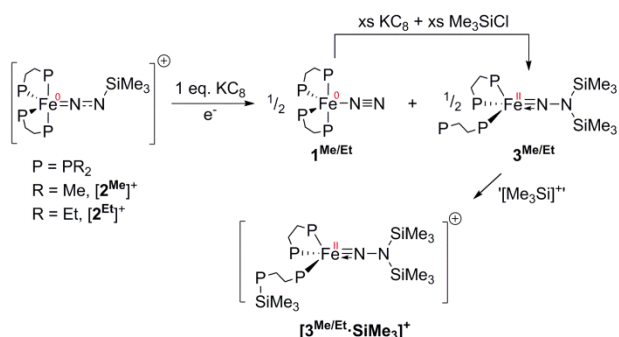
Figure 1. Examples of transition metal (TM) complexes which catalyze N₂ silylation.

Well-defined TM-N₂ complexes (Figure 1),^{13,14,16–22} and a number of N₂-free Fe pre-catalysts,^{15,23,24} have been shown to catalyze N₂ silylation. Although intermediates containing N-SiMe₃ bonds have been isolated for Mo-catalysed reactions, which were shown to participate in their respective catalytic cycle, analogous mechanistic detail for first-row TM-mediated protocols is scarce,²¹ and notably absent for Fe. Recently we reported the synthesis of the cationic silyldiazido species [Fe(PP)₂(NN-SiMe₃)]⁺ (PP = depe [**2**^{Et}]⁺ or dmpe [**2**^{Me}]⁺; dmpe = Me₂PCH₂CH₂PMe₂) via electrophilic silylation of **1**^{Et} and Fe(dmpe)₂(N₂) (**1**^{Me}) with Me₃SiCl.²⁵ Here we report the catalytic conversion of N₂ to N(SiMe₃)₃ by **1**^{Me} and **1**^{Et}, with the yields of N(SiMe₃)₃ being the highest reported for any Fe catalyst to date. Furthermore, mechanistic investigations show that catalysis proceeds via neutral disilylhydrazido intermediates Fe(κ²-PP)(κ¹-PP)(NN{SiMe₃})₂ [PP = depe (**3**^{Et}) or dmpe (**3**^{Me})], which constitute examples of Fe complexes bearing terminal hydrazido(2-) ligands (FeNNR₂) derived from N₂.²⁶ This is the first time intermediates have been isolated from an Fe-catalyzed N₂ silylation system.

Since [**2**^{Me/Et}]⁺ do not react with potent [Me₃Si]⁺ sources such as Me₃SiOTf, we envisaged that further productive derivatization of the N₂ unit might occur via electronation. Cyclic voltammograms of [**2**^{Me/Et}][BAR^F₄] (Ar^F = 3,5-[CF₃]₂C₆H₃; [nBu₄N][BAR^F₄] electrolyte, Et₂O, vs Fc⁺/Fc) each featured an irreversible reduction wave at E_{p,red} ~ -2.7 V, indicating the feasibility of chemical reduction by a strong reductant, and ensuing reactivity of the resultant species. Consequently, treatment of [**2**^{Me/Et}][BAR^F₄] with 1 eq. of KC₈ (Et₂O, 25 °C) led

to rapid consumption of starting material, with ^{31}P NMR revealing the formation of the parent $\text{Fe}(\text{o})\text{-N}_2$ compounds $\mathbf{1}^{\text{Me/Et}}$ and a new diamagnetic species ($\mathbf{1}:\mathbf{1}$), respectively.

Scheme 1. Reduction of $[\mathbf{2}^{\text{Me/Et}}]^+[\text{BAR}^{\text{F}}_4]^-$ to their $\text{Fe}\equiv\text{N}$ and $\text{Fe-NN}(\text{SiMe}_3)_2$ counterparts, and electrophilic silylation of $\mathbf{3}^{\text{Me/Et}}$. $[\text{BAR}^{\text{F}}_4]^-$ counterions omitted for clarity.



$^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the latter compounds display three resonances each in a 2:1:1 ratio, with doublets ($\delta/\text{ppm} = -48.0$, $^3J_{\text{PP}} = 28$ Hz, dmpe; -17.6 , $^3J_{\text{PP}} = 22$ Hz, depe) at chemical shifts close to that of the free ligands,²⁷ which exhibit coupling to a downfield multiplet of the same relative integral; these data indicate a partially decoordinated phosphine ligand. These new species, prepared otherwise identically from isotopically labelled $[\mathbf{2}^{\text{Et-}^{15}\text{N}_2}]^+$ or $[\mathbf{2}^{\text{Me-}^{15}\text{N}_2}]^+$, each display two ^{15}N NMR resonances at $\delta \sim -30/-260$ ppm; such large differences between $\delta(\text{N}_\alpha)$ and $\delta(\text{N}_\beta)$ imply a doubly-functionalized terminal N atom in the NN fragment.^{28,29} Based on NMR data, high resolution mass spectrometry (HRMS; EI), and the structure of a derivative (*vide infra*) these new diamagnetic low-spin Fe^{II} products were assigned as neutral disilylhydrazido species $\text{Fe}(\kappa^2\text{-PP})(\kappa^1\text{-PP})(\text{NN}[\text{SiMe}_3]_2)$ ($\text{PP} = \text{dmpe}, \mathbf{3}^{\text{Me}}$; depe, $\mathbf{3}^{\text{Et}}$).³⁰ These compounds may be conveniently prepared in $> 80\%$ yield from $\mathbf{1}^{\text{Me}}$ or $\mathbf{1}^{\text{Et}}$ via reaction with excess $\text{Me}_3\text{SiCl}/\text{KC}_8$, and isolated as $\mathbf{3}^{\text{Me}}$ (red) or $\mathbf{3}^{\text{Et}}$ (purple) oils, respectively, which are highly soluble in common organic solvents.

In order to facilitate solid-state characterization of $\mathbf{3}^{\text{Me/Et}}$, we envisaged that electrophilic quaternization of the dangling phosphine would promote isolation of an ionic salt, which would display more favorable solubility characteristics. Thus, silylation was achieved via reaction of $\mathbf{3}^{\text{Me}}$ or $\mathbf{3}^{\text{Et}}$ with the powerful silylating mixture $\text{Me}_3\text{SiOTf}/\text{KBAR}^{\text{F}}_4$ in Et_2O (Scheme 1), which led to a large downfield shift of the corresponding ^{31}P NMR resonance as the only significant spectral change; virtually identical ^{15}N resonances indicate an unperturbed $\text{Fe}(\text{NN}[\text{SiMe}_3]_2)$ moiety. Addition of pentane precipitated dark red or purple crystalline solids, which characterized as the disilylhydrazido derivatives $[\mathbf{3}^{\text{Me}}\cdot\text{SiMe}_3][\text{BAR}^{\text{F}}_4]$ and $[\mathbf{3}^{\text{Et}}\cdot\text{SiMe}_3][\text{BAR}^{\text{F}}_4]$, respectively. Single crystal X-ray diffraction (XRD) data for $[\mathbf{3}^{\text{Et}}\cdot\text{SiMe}_3][\text{BAR}^{\text{F}}_4]$ ³¹ were collected and solved (see Fig. 2), which reveals a pseudotetrahedral Fe center with a very short Fe-N distance indicative of an $\text{Fe}\equiv\text{N}$ triple bond, as noted for the few previously reported Fe-NNR_2 species.^{28,29} The linear disilylhydrazido fragment features a very long N-N bond distance, suggesting a highly activated N_2 unit. Indeed,

$[\mathbf{3}^{\text{Et}}\cdot\text{SiMe}_3][\text{BAR}^{\text{F}}_4]$ contains the longest N-N bond of all Fe-NNR_2 complexes structurally characterized to date.

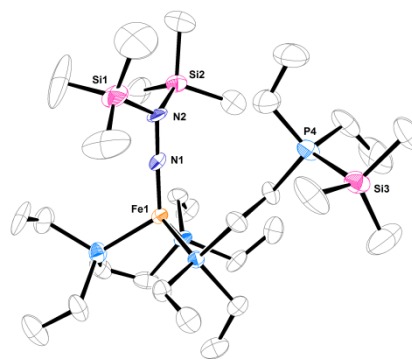


Figure 2. ORTEP diagram of the Fe-containing fragment in $[\mathbf{3}^{\text{Et}}\cdot\text{SiMe}_3]^+[\text{BAR}^{\text{F}}_4]^-$. Thermal ellipsoids set at 50% probability. C atoms grey, Fe orange, P light blue, N dark blue, and Si pink. H atoms and $[\text{BAR}^{\text{F}}_4]^-$ counterion omitted for clarity. Selected bond distances (Å)/angles (°): Fe(1)-N(1) 1.642(6); N(1)-N(2) 1.382(2); P(4)-Si(3) 2.283(3); Fe(1)-N(1)-N(2) 177.7(5).

Disilylhydrazido species such as $\mathbf{3}^{\text{Me/Et}}$ have been invoked as intermediates in the Fe-catalyzed conversion of N_2 to $\text{N}(\text{SiMe}_3)_3$,¹³ and during their syntheses (under N_2) formation of $\text{N}(\text{SiMe}_3)_3$ was observed by ^1H NMR, suggesting $\mathbf{1}^{\text{Me/Et}}$ could catalyze N_2 silylation. Accordingly, treating catalytic quantities of either $\mathbf{1}^{\text{Me}}$ or $\mathbf{1}^{\text{Et}}$ with excess Me_3SiCl and KC_8 under 1 atm. of N_2 generated 42 and 47 eq. of $\text{N}(\text{SiMe}_3)_3$ per Fe atom respectively (Table 1, entries 1 and 2).

Table 1. Results of catalytic N_2 silylation reactions with $\text{Fe}(\text{pp})_2$ -based catalysts.^a

$$\text{N}_2 + \text{xs. KC}_8 + \text{xs. Me}_3\text{SiCl} \xrightarrow[\text{Et}_2\text{O}]{\text{Cat.}} 2 \text{N}(\text{SiMe}_3)_3$$

Entry	Catalyst	Me_3SiCl , KC_8 (eq.)	$\text{N}(\text{SiMe}_3)_3$ (eq.) ^b	e^- yield (%) ^c
1 ^d	$\mathbf{1}^{\text{Me}}$	1000	47	14
2 ^d	$\mathbf{1}^{\text{Et}}$	1000	42	12
3 ^{d,e}	$\mathbf{1}^{\text{Me}}$	1000	86	26
4 ^{d,e}	$\mathbf{1}^{\text{Et}}$	1000	70	21
5 ^{d,e}	$\mathbf{1}^{\text{Me}}$	1500	121	24
6 ^{d,e}	$\mathbf{1}^{\text{Et}}$	1500	103	21
7 ^d	$\mathbf{3}^{\text{Me}}$	1000	56	17
8 ^d	$\mathbf{3}^{\text{Et}}$	1000	41	12
9	$[\mathbf{3}^{\text{Me}}\cdot\text{SiMe}_3][\text{BAR}^{\text{F}}_4]$	1000	52	16
10	$[\mathbf{3}^{\text{Et}}\cdot\text{SiMe}_3][\text{BAR}^{\text{F}}_4]$	1000	40	12
11 ^f	-	1000	0	0

^aExperiments performed over 72 h using 0.005 mmol catalyst at 25 °C under 1 atm. N_2 , unless otherwise stated; eq. = equivalents. ^bDetermined by acid hydrolysis to NH_4^+ and quantified using ^1H NMR (see SI); yield per mol Fe. ^cYield calculated as the proportion of available e^- used in produc-

tive formation of $\text{N}(\text{SiMe}_3)_3$ (see SI for details). ^dAverage of 2 runs. ^ePerformed under 4 atm. N_2 . ^fControl experiment with no catalyst added.

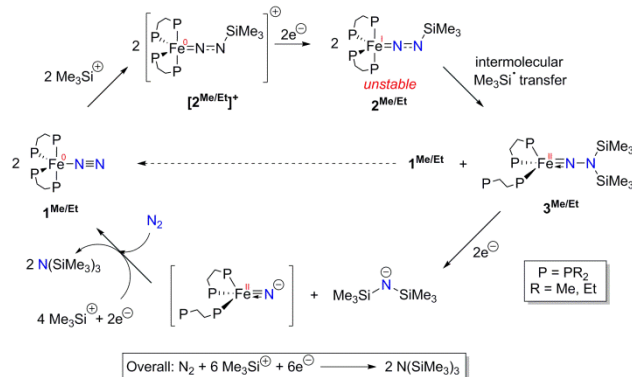
Mock *et al.* recently obtained improved yields of $\text{N}(\text{SiMe}_3)_3$ from N_2 using an $\text{Fe}(\text{o})$ -tetraphosphine catalyst at high pressures of N_2 (100 atm);³ gratifyingly we observed a significant increase in the efficiency of our system when catalysis was conducted at modestly elevated pressure (4 atm. N_2 ; Table 1, entries 3 and 4), with maximum yields of 121 and 103 eq. $\text{N}(\text{SiMe}_3)_3$ achieved for $\mathbf{1}^{\text{Me}}$ and $\mathbf{1}^{\text{Et}}$, respectively (Table 1, entries 5 and 6). These not only represent the highest yields of $\text{N}(\text{SiMe}_3)_3$ to date for Fe-catalyzed N_2 silylation, but are also among the most electron-efficient of such conversions. Only $^{15}\text{N}(\text{SiMe}_3)_3$ was formed when catalysis was run under $^{15}\text{N}_2$,³² confirming the reaction atmosphere to be the nitrogen source in the product. Aliquots taken throughout catalytic reactions reveal $\mathbf{3}^{\text{Me}}$ or $\mathbf{3}^{\text{Et}}$ as the only diamagnetic Fe-containing species in the ^{31}P NMR spectra (accounting for > 90 % starting $\mathbf{1}^{\text{Me/Et}}$), suggesting their intermediacy in the catalytic cycle. In support of this conclusion is the very similar catalytic activity displayed by both $\mathbf{3}^{\text{Me}}$ and $\mathbf{3}^{\text{Et}}$ (Table 1, entries 7 and 8) compared with $\mathbf{1}^{\text{Me}}$ and $\mathbf{1}^{\text{Et}}$, which implies that the disilylhydrazidos are on-cycle resting states.³³

In all catalytic reactions, formation of $\text{Me}_3\text{SiSiMe}_3$ is the major side-product, likely formed by radical recombination of *in situ* generated $\text{Me}_3\text{Si}^\cdot$ from reaction of KC_8 and Me_3SiCl , alongside minor amounts of Me_3SiOEt , presumably from $\text{Me}_3\text{Si}^\cdot$ -mediated solvent attack.¹⁵ Since prior examples of N_2 silylation using Fe, Co and Mo catalysts have invoked $\text{Me}_3\text{Si}^\cdot$ as active species in N-SiMe₃ bond forming events in their cycles,¹⁵⁻¹⁷ we decided to test this hypothesis using $\text{Hg}(\text{SiMe}_3)_2$ as a well-documented source of $\text{Me}_3\text{Si}^\cdot$ radicals; this has been previously used to reductively activate coordinated N_2 on Mo centers.³⁴ Treatment of either $\mathbf{1}^{\text{Me/Et}}$, $[\mathbf{2}^{\text{Me/Et}}][\text{BAR}^{\text{F}}_4]$, or $\mathbf{3}^{\text{Me/Et}}$ with excess $\text{Hg}(\text{SiMe}_3)_2$ (under photochemical or thermal conditions), however, led to no reaction of the Fe complexes; only formation of $\text{Me}_3\text{SiSiMe}_3$ and Hg^0 was evident. This supports $\text{Me}_3\text{Si}^\cdot$ formation and recombination, albeit suggesting a lack of their involvement in productive N_2 reduction. An alternative mechanism for the formation of $\mathbf{1}^{\text{Et}}/\mathbf{1}^{\text{Me}}$ and $\mathbf{3}^{\text{Et}}/\mathbf{3}^{\text{Me}}$ may be accounted for by 1e^- reduction of $[\mathbf{2}^{\text{Me/Et}}]^+$ to form the neutral, formally Fe^{I} congeners $\mathbf{2}^{\text{Me/Et}}$, followed by disproportionation of the latter via intermolecular Me_3Si transfer to furnish $\text{Fe}^0(\text{PP})_2\text{N}_2$ and $\text{Fe}^{\text{II}}(\kappa^2\text{-PP})(\kappa^1\text{-PP})(\text{NN}[\text{SiMe}_3]_2)$ (Scheme 2).³⁵ Analogous reactivity has been previously observed for the transiently formed diazenido species $\text{P}_3\text{SiFe}(\text{NN-R})$ ($\text{R} = \text{H}, \text{Me}$).^{36,37}

To gain further insight into the mechanism, DFT calculations were performed using the ADF program suite³⁸ (details in SI). Geometry optimisation of $\mathbf{3}^{\text{Et}}$ was attempted by binding an additional Me_3Si group to N_β of $\mathbf{2}^{\text{Et}}$. During the course of the optimization a P atom decoordinated to give the spectroscopically observed $(\kappa^2\text{-PP}, \kappa^1\text{-PP})$ structure. This decoordination may be induced by the strongly π -donating NNR_2 moiety to the Fe center, which is reminiscent of the flexible Fe-B bonding exhibited by Peters' $\text{P}_3\text{R}_3\text{Fe}$ systems when accommodating π -donating vs π -acid N_xR_y ligands ($x = 1, 2$; $\text{R} = \text{alkyl}, \text{H}$; $y = 0-4$).³⁹⁻⁴¹ The calculated short Fe- N_α distance (1.645 Å) indeed suggests that the *bissilylhydrazido* ligand acts as a 4e^- (LX_2) donor to Fe, resulting in an 18 valence-electron configuration for $\mathbf{3}^{\text{Et}}$.⁴² Modeling the mechanism for the proposed bimolecular disproportionation of $\mathbf{2}^{\text{Et}}$ to $\mathbf{1}^{\text{Et}}$ and

$\mathbf{3}^{\text{Et}}$, using the less computationally demanding *dmpe* system, gave a possible transition state involving an $\text{S}_{\text{N}}2$ -type reaction between N_β of one $\mathbf{2}^{\text{Me}}$ molecule with the Me_3Si group of another ($\text{Si-N}_\beta \cdots \text{Si}$ distance = 3.20 Å). The free energy of the disproportionation reaction was calculated to be highly favorable ($\Delta_r G = -179 \text{ kJ mol}^{-1}$), and displayed a feasible activation energy (76 kJ mol^{-1}).

Scheme 2. Proposed mechanism for the reductive silylation of N_2 catalyzed by $\mathbf{1}^{\text{Me/Et}}$ and $\mathbf{3}^{\text{Me/Et}}$.



Having established a plausible pathway for the conversion of $\mathbf{1}^{\text{Me/Et}}$ to $\mathbf{3}^{\text{Me/Et}}$, we attempted to elucidate later stages of the catalytic cycle. Electrophilic silylation of $\mathbf{3}^{\text{Me/Et}}$ was shown to occur on the pendant phosphine rather than the NNR_2 fragment (*vide supra*), precluding this as a productive step. Instead, electronation may follow formation of disilylhydrazido intermediates, as has been demonstrated for a Mo-based N_2 silylation system,¹⁹ and this possibility was investigated via DFT calculations upon $\mathbf{3}^{\text{Me}}$. Optimization of the singly-reduced derivative $[\mathbf{3}^{\text{Me}}]^-$ revealed lengthened Fe-N and N-N bonds (1.71 and 1.39 Å; cf. $\mathbf{3}^{\text{Me}}$: 1.64 vs. 1.36 Å, respectively) resulting from increased population of an orbital that is anti-bonding with respect to both partners. Double reduction of $\mathbf{3}^{\text{Me}}$ to $[\mathbf{3}^{\text{Me}}]^{2-}$ followed by optimization led to cleavage of the N-N bond and concomitant generation of $[\text{N}(\text{SiMe}_3)_2]^-$ and an anionic imide complex $[\text{Fe}(\kappa^1\text{-dmpe})(\kappa^2\text{-dmpe})\text{N}]^-$ (see SI for further details). Indeed, ^1H NMR spectra of $\mathbf{3}^{\text{Me/Et}}$ stirred with excess KC_8 or K(s)^{43} (Et_2O , 36 h) displayed a resonance attributable to $\text{KN}(\text{SiMe}_3)_2$, which was corroborated by comparison with an authentic sample in Et_2O .^{44,45} Subsequent addition of Me_3SiCl to these solutions instantaneously produces $\text{N}(\text{SiMe}_3)_3$ (^1H NMR), which was similarly generated when commercial samples of $\text{KN}(\text{SiMe}_3)_2$ and Me_3SiCl were mixed in Et_2O , thus verifying that any $\text{KN}(\text{SiMe}_3)_2$ formed during catalysis is rapidly consumed to form $\text{N}(\text{SiMe}_3)_3$.

In conclusion we have demonstrated the ability of $\text{Fe}(\text{PP})_2(\text{N}_2)$ to catalyze the conversion of N_2 to $\text{N}(\text{SiMe}_3)_3$, with higher yields of $\text{N}(\text{SiMe}_3)_3$ achieved than for any other Fe catalyst to date. Additionally, we have shown that catalysis involves *bissilylhydrazido* $\text{Fe}(\kappa^1\text{-PP})(\kappa^2\text{-PP})(\text{NN}[\text{SiMe}_3]_2)$ species as resting states, and represent the first isolated intermediates of Fe-catalyzed N_2 silylation. Further investigations into the N_2 -fixation reactivity of Fe-phosphine dinitrogen complexes, and the mechanisms of their catalytic transformations, are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental methods and spectra (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interests.

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- Low-spin Fe^{II} compounds in tetrahedral or pseudotetrahedral ligand fields are extremely rare. For an example see: Brown, S. D.; Peters, J. C., *J. Am. Chem. Soc.*, **2005**, *127*, 1913.
- Single crystals of both species were grown by slow diffusion of pentane into an Et₂O solution; unfortunately those of [3^{Me/Et}-SiMe₃][BAR^F₄] suffered from severe disorder, which precluded structural characterization by single crystal XRD analysis.
- Using ¹⁵N₂-labeled **1**^{Me} or **1**^{Et}.
- The N₂ silylation activity of [3^{Me/Et}-SiMe₃][BAR^F₄] was found to mirror that of 3^{Me/Et}, respectively. This may be rationalized by reactions of [3^{Me/Et}-SiMe₃][BAR^F₄] with KC₈, which instantly produce Me₃SiSiMe₃ and 3^{Me/Et}, hence [3^{Me/Et}-SiMe₃][BAR^F₄] act merely as precursors for the latter compounds, under reaction conditions for catalysis.
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- Unfortunately ESR experiments (CW X-band, Et₂O, 150 K) performed upon the KC₈ reduction of [2^{Me/Et}][BAR^F₄] did not resolve any signals (other than for KC₈), presumably due to slow reaction kinetics at these low temperatures. Conversely upon warming to room temperature, very broad and mechanistically uninformative resonances were transiently observed.
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- An increase in the production of disilane was observed in the presence of **1**^{Me} (73 %) and **1**^{Et} (40 %) over the background reaction of KC₈/Me₃SiCl/Et₂O, under otherwise identical conditions. This suggests that **1**^{Me/Et} also act as catalysts for Me₃Si-SiMe₃ formation, analogous to the production of H-H when N₂ is catalytically reduced by H⁺/e⁻ sources. See Matson, B. D.; Peters, J. C., *ACS Catal.*, **2018**, *8*, 1448.
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- The calculated Fe-N and N-N distances (N-N = 1.36 Å) are in good agreement with those crystallographically determined for [3^{Et}-SiMe₃][BAR^F₄]. See SI for details.
- K metal was used in this reaction due to its more rapid reduction kinetics vs KC₈. However, in catalytic runs this was found to be a substantially inferior reductant to KC₈, likely due to its faster rate of reaction with Me₃SiCl, vs electronation of Fe-based intermediates in the catalytic cycle.
- Computational calculations suggest [Fe(dmpe)₂N]⁻ to be a low-spin species. Unfortunately we have not yet been able to obtain spectroscopic (NMR, MS) evidence for the postulated [Fe(PP)₂N]⁻K⁺ products, which may be due to their decomposition in the absence of a trapping agent (e.g. Me₃SiCl); when Me₃SiCl and KC₈ are both present, we propose that

these imido species undergo rapid silylation and electronation to $\text{N}(\text{SiMe}_3)_3$, prior to uptake of N_2 at Fe in order to close the catalytic cycle. The final steps are the subject of ongoing experimental and computational investigations.

45 The presence of $\text{KN}(\text{SiMe}_3)_2$ from the reaction of $\mathbf{3}^{\text{Me}}$ and $\mathbf{3}^{\text{Et}}$ and $\text{K}_{(\text{s})}$ was confirmed via a ^1H - ^{29}Si NMR correlation (HMBC) experiment. While a previous attempt to directly observe a ^{29}Si NMR resonance for an authentic sample of $\text{KN}(\text{SiMe}_3)_2$ was not possible (see ref. 19), we were able to detect an identical ^1H - ^{29}Si NMR correlation between the ^1H NMR resonance ($\delta = -0.11$ ppm) and a signal at $\delta = -20$ ppm in the ^{29}Si NMR domain.

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