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Triphos-Fe Dinitrogen and Dinitrogen-Hydride Complexes: Relevance to Catalytic N_2 Reductions.

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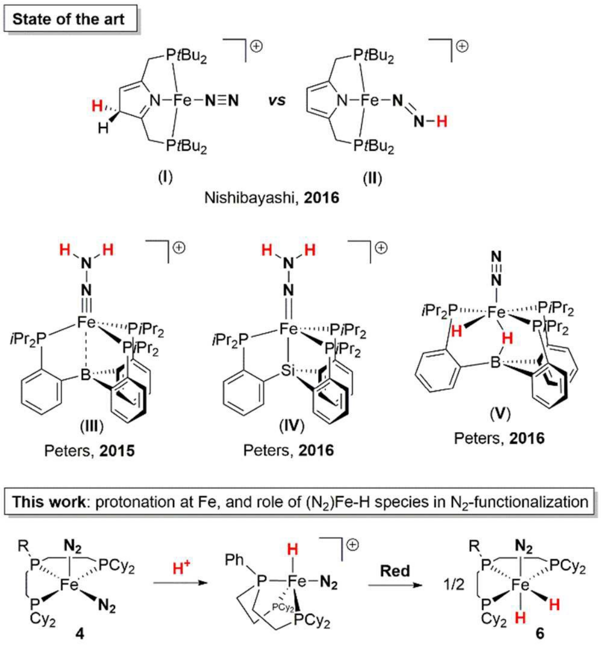
The two electron reduction of the iron complexes $[(P^RP_2^{Cy})Fe(Cl)_2]$ (R = Ph or tBu) 2a-b afforded complexes $[(P^RP_2^{Cy})Fe(N_2)_2]$ 4a-b. Protonation of 4a at the metal center and subsequent reduction to Fe(I)-H species leads to complex $[(P^{Ph}P_2^{Cy})Fe(N_2)(H)_2]$ 6a *via* spontaneous disproportionation reaction. Complex 4a behaves as one of the most efficient monometallic Fe-catalysts reported to date for the N_2-to-$N(SiMe_3)_3$ under atmospheric pressure.

Nitrogen is an essential element for our biosphere and is introduced in the living chain through ammonia. In nature, NH_3 is synthesized by a family of bacteria possessing a nitrogenase enzyme (Fe, FeV or FeMoco active center) *via* N_2 reduction involving electron and proton transfer sequences.[1] On the other hand, and only after decades of fundamental research, a handful of synthetic models capable of performing catalytic reduction of N_2 into ammonia (or hydrazine) have been developed.[2] In overwhelming majority, they rely on Mo[3-4] or Fe[5-7] complexes.[8] A closer look at the structures of the known catalysts for NH_3 formation reveals that neutral tridentate "PEP" ligands (E = N, P, C) occupy a prominent position for Mo catalysts[4],(best TON for NH_3 formation :415)[4e] whereas the tetradentate "EP_3" ligands (E = B, C) are currently the most efficient Fe systems[5] (best TON: 89).[5e] Mechanistically, the initial steps for the Mo-promoted N_2-to-NH_3 transformation have been studied for Mo dinitrogen complexes featuring bidentate, tridentate and tetradentate ligands, for which protonation at the distal N to form the Mo(N=NH) and Mo=N-NH_2 intermediates is favored.[9] In sharp contrast, there was not much information about the site of protonation for catalytically active Fe systems until very recently (Scheme 1). Nishibayashi and co-workers isolated the thermodynamic, dead-end complex **I** by protonation at the pyrrole backbone instead of the kinetically favored, catalytically-competent isomer **II**.[6] Since 2015, Peters spectroscopically identified the key intermediates **III** and **IV**, thus unequivocally providing a clear picture on the site of protonation at the distal N-atom for the "EP_3" ligated complexes.[10] Interestingly, the same group identified the hydride-borohydride $[(BP_3)(\mu\text{-}H)Fe(N_2)(H)]$ complex **V** under turnover conditions, pointing favorable protonation at the Fe center rather than at the N_2.[14] It is also the case for Fe-N_2 complexes which are not catalytically active in N_2-to-NH_3 transformation.[11] This selectivity can be switched by adding strong Lewis acid, but stoichiometric formation of NH_3 from N_2 has yet to be reported.[12] To date, studies covering protonation of low-valent Fe-N_2 species at Fe within catalytically active systems are very limited,[7] yet the evaluation of such (N_2)Fe-H species in N_2-functionalization events is critical to understanding N_2 reduction catalysis, and what may limit its efficacy.



Scheme 1 Protonation of low-valent Fe-N_2 complexes that are catalytically-competent in the N_2-to-NH_3 conversion.

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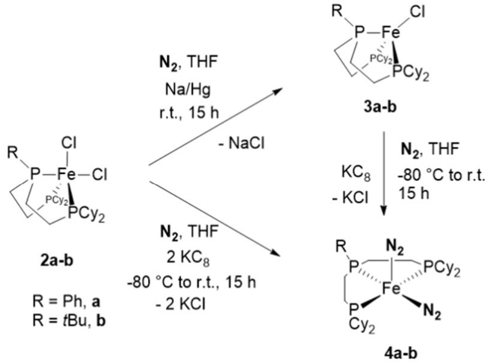
In addition to these mechanistic studies, we have evaluated the performances of our Fe complexes in the related N_2 to $N(SiMe_3)_3$ reduction process and show them to be efficient catalysts. These results are presented herein.

Our group demonstrated that the $P^{Ph}P_2^{Cy}$ ligand in conjunction with Mo promotes the stepwise functionalization of N_2 in the $[(P^{Ph}P_2^{Cy})Mo(N_2)_2]_2(\mu\text{-}N_2)$ complex by $SiMe_3Cl$ and electrons.[13] In the present work the $P^RP_2^{Cy}$ (R = Ph, *t*Bu) ligands are used for the synthesis of rare bis-N_2 species of $Fe^{(0)}$,[14] $[(P^RP_2^{Cy})Fe(N_2)_2]$ complexes **4a-b**. The $[(P^RP_2^{Cy})Fe(N_2)(H)_2]$ complexes **6a-b** were obtained upon a protonation/reduction sequence from complexes **4a-b** through a facile dismutation process from a Fe^I hydride intermediate. These complexes showed activity in the reduction of N_2 into NH_3 and **4a** emerged as one of the most efficient monometallic Fe-catalysts reported to date for the N_2 into $N(SiMe_3)_3$ functionalization.

The bulky, strongly donating alkyl ligands $P^RP_2^{Cy}$ ($P^RP_2^{Cy}$ = $RP(CH_2CH_2PCy_2)_2$, R = Ph, **1a**; tBu, **1b**) were reacted with $[FeCl_2(THF)_{1.5}]$ in THF to afford the expected Fe complexes $[(P^RP_2^{Cy})Fe(Cl)_2]$ **2a-b** (light purple for **2a**, and white powder for **2b**) in excellent isolated yields (96%[15] and 83% yield, respectively, Scheme 2). Complexes **2a-b** are paramagnetic and exhibit Mössbauer spectra with isomer shift of 0.767 $mm.s^{-1}$ and 0.730 $mm.s^{-1}$ expected for Fe^{II} in a quintuplet state (ESI). The magnetic moment of 5.2 μ_B for both **2a** and **2b** was measured in solution using the Evans' method, in agreement with the Mössbauer (4.90 μ_B is expected for a spin-only S = 2 magnetic moment).[16] X-Ray diffraction analysis of complex **2b** confirmed the trigonal bipyramid geometry at the Fe (ESI).



Scheme 2 Synthesis of the $(P^RP_2^{Cy})Fe$ complexes **3a-b** and **4a-b**.

Reduction of **2a-b** to form Fe-N_2 complexes was then studied. Reduction by one electron using Na/Hg lead to the formation of the corresponding $[(P^RP_2^{Cy})Fe(Cl)]$ complexes **3a-b** in excellent isolated yield (92% and 85%, respectively). Complexes **3a-b** are paramagnetic, and **3a** exhibits a Mössbauer spectrum with isomer shift of 0.697 $mm.s^{-1}$ expected for Fe^I in a quartet state (ESI).[10a] Identical magnetic moment of 4.1 μ_B was measured in solution for **3a** and **3b** using the Evans' method (3.87 μ_B is expected for a spin-only S = 3/2 magnetic moment).[16] IR spectra of complexes **3a-b** showed that N_2 does not coordinate at the Fe^I center, which was confirmed by a X-ray diffraction study of complex **3a** (ESI).

Reduction to Fe^0 was thus studied. It can be achieved, either from **2a-b** or **3a-b** at –80 °C with the stoichiometric amount of KC_8, followed by slow warming up to room temperature over 15 h (Scheme 2). Complexes **4a** (**4b** resp.), formed quantitatively *vs* internal standard, are characterized by a triplet at 120.1 ppm (J_{P-P} = 69.2 Hz) (150.5 ppm, J_{P-P} = 48.0 Hz resp.) and a doublet at 102.4 ppm (J_{P-P} = 69.2 Hz) (97.0 ppm, J_{P-P} = 48.0 Hz resp.) in the $^{31}P\{^1H\}$ NMR spectrum (ESI), as well as by two NN stretching bands in the IR spectrum at 2047 and 1982 cm^{-1} (2048 and 1981 cm^{-1} resp.). Together, this data suggested the formation of the expected $[(P^RP_2^{Cy})Fe(N_2)_2]$ complexes. Isolation of these complexes proved difficult as loss of N_2 appeared to be a facile process under vacuum and complexes are thereby stored in THF solutions of known concentration at –30 °C for further reactivity. Nonetheless, slow evaporation of THF to dryness *via* N_2 bubbling and extraction of the complexes into pentane allowed crystallization of complex **4b** (Fig. 1). The X-ray study confirmed the formation of **4a-b** as rare examples of Fe bis-N_2 complexes.[14] $[(P^{tBu}P_2^{Cy})Fe(N_2)_2]$ features a square based pyramid geometry at Fe, with the three P-atoms located at equatorial positions. As a consequence, the two N_2-ligands occupy the remaining equatorial position and one apical position. In particular, the N–N bond lengths of 1.118(3) and 1.128(3) Å indicate weak back-donation from the Fe center to the dinitrogen ligands, in accord to previous reports.[14a]

The catalytic performance of complexes **4a-b** in the N_2-to-NH_3 transformation was then addressed. The reactions were performed using 200 equiv. of KC_8 and 200 equiv. of $HBAr^F_4$ ($HBAr^F_4$ = $[H(Et_2O)_2][BAr^F_4]$; BAr^F_4 = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate) at –80°C in Et_2O for 1 h.[14] Complexes **4a** and **4b** lead to 3.6±0.3 and 3.3±0.4 equiv. of NH_3, while negligible amounts of NH_3 were achieved in absence of reducing agent (less than 0.1 equiv.), in accord with literature precedence.[17] These observations indicate that, although the performance is rather limited, the reaction occurs *via* a catalytic process and not only *via* stoichiometric protonation of the two N_2 coordinated to the Fe center. It was thus of importance to understand the initial stages of the functionalization of coordinated N_2 along with the factors influencing catalytic turnover. In the more efficient catalytic systems, the possible formation of an anionic Fe complex (either formally Fe^0 or Fe^{-I}) has been shown.[5a,6] Cyclic voltammetry studies showed that no reduction wave corresponding for the Fe^0/Fe^{-I} couple was observed down to –3.0 V *vs* Fc/Fc^+ for complex **4a**. Confirmation was experimentally obtained as no reaction occurred between complexes **4a-b** with excess KC_8 at low temperature. The first step under catalytic conditions has thus to imply protonation of the Fe^0 species. Reaction between complex **4a** and one equivalent of $HBAr^F_4$ was therefore performed (–78°C or R.T., THF). It resulted in the formation of a paramagnetic complex characterized by a single ν_{NN} stretch at 2092 cm^{-1}, only consistent with protonation at Fe and not at the distal N, as previously observed,[17] leading to a $Fe^{II}(H)(N_2)^+$ complex **5a**. DFT calculations were carried out to probe the preferred site for protonation of the $Fe(N_2)_2$ complex **4a** (ESI). Solvent effects were taken into account using the pcm method (solvent = THF), and $HBArF_4$ was modeled as $H(OEt_2)_2^+$. The desirable

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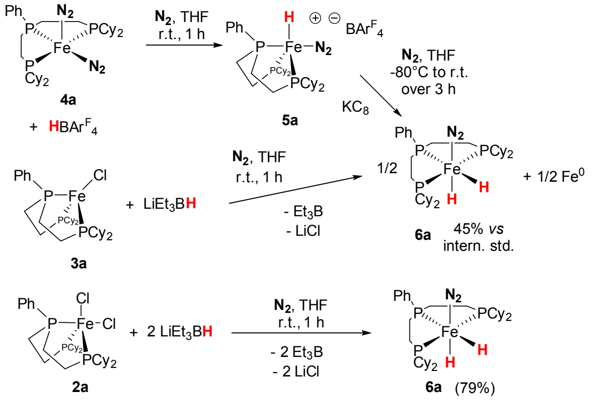
protonation at a distal N to form $[(PP_2)Fe(N_2)(N_2H)]^+$ (triplet state) is only marginally exergonic (–2.1 kcal/mol) because of the entropic gain generated by the liberation of two Et_2O molecules from $H(OEt_2)_2^+$. Indeed, the reaction is calculated to be endothermic (ΔH = +10.7 kcal/mol), and at best protonation at terminal N would be in equilibrium with starting material. On the other hand, protonation at Fe is both exothermic (ΔH = –1.6 kcal/mol) and strongly exergonic (–24.9 kcal/mol), leading to the formation of the $[(PP_2)Fe^{II}(H)(N_2)]^+$ complex (triplet state), *via* spontaneous elimination of the N_2 ligand *trans* to the incoming H ligand. Accordingly, further experimental evidence of the protonation at Fe was given by the subsequent reduction by one equivalent of KC_8 starting at low temperature. Instead of forming the expected $[(P^{Ph}P_2^{Cy})Fe^{I}(H)(N_2)]$ complex (paramagnetic, doublet state), a novel diamagnetic complex was formed in *ca* 50% (*vs* internal standard). This species is characterized by a broad triplet at 120.2 ppm (J_{P-P} = 6.7 Hz) and a doublet at 111.1 ppm (J_{P-P} = 6.7 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. Two highly coupled hydride signals resonate at –9.8 ppm and –20.9 ppm in the ^1H NMR spectrum (ESI) and a ν_{NN} stretch at 2051 cm^{-1} was measured by IR spectroscopy. Together, this data pointed to the formation of the Fe^{II} complex $[(P^{Ph}P_2^{Cy})Fe(N_2)(H)_2]$ complex **6a** (Scheme 3).



Scheme 3 Multiple synthetic routes of access to the complex $(N_2)Fe(H)_2$ **6a**.

Alternatively, this complex can be synthesized in a selective manner from the reaction between complex **2a** and two equivalents of $LiBEt_3H$. Unlike complexes **4a-b**, **6a** does not release coordinated N_2 under vacuum, and was crystallized in a very good 79% yield. The solid state Mössbauer spectrum gives rise to a quadrupole doublet for a Fe^{II} S = 0 species (δ = 0.063 $mm.s^{-1}$ and ΔE_Q = 0.673 $mm.s^{-1}$; see ESI). The X-ray structure of the complex corroborated the NMR data, and confirmed the two different hydride environments, one being *trans* to the central P atom and the second *trans* to N_2.[18] The N–N bond distance of 1.085(2) Å in **6a** is comparable to the one found for **4b** despite a less electron rich Fe center (Fe^{II} *vs* Fe^0), this observation being attributed to the strong *trans* influence of the hydride ligand. The reactivity we observed from either Fe^{II} or Fe^{I} is in sharp contrast with the most recent report by Peters and co-workers who obtained the Fe^{I} complex $[P_2^{P'Ph}Fe(H)]_2(\mu\text{-}N_2)$ ($P_2^{P'Ph}$ = $PhP(2\text{-}(iPr_2P)C_6H_4)_2$) from the hydride reduction of the $Fe^{II}X_2$ precursor featuring a tridentate phosphine ligand.[7] In the present case, formation of complex **6a** from **5a** appears to involve reduction to the $Fe^{I}(N_2)(H)$ intermediate which is not stable toward dismutation. In order to verify this assumption, the reaction between Fe^{I} complex **3a** and one equivalent of $LiBEt_3H$ was conducted under N_2 and followed by $^{31}P\{^1H\}$ NMR spectroscopy. Within minutes of mixing, a mixture of diamagnetic complexes was observed, among which complex **6a**. After 2 h at room temperature, complex **6a** is formed in *ca* 50% yield, confirming the favorable dismutation reaction of the Fe^{I} intermediate. The thermodynamic stability of the hydride-dinitrogen complexes of Fe^{I} *vs* Fe^{II} in this series therefore depends to the highest extent on the tridentate neutral phosphine ligand.

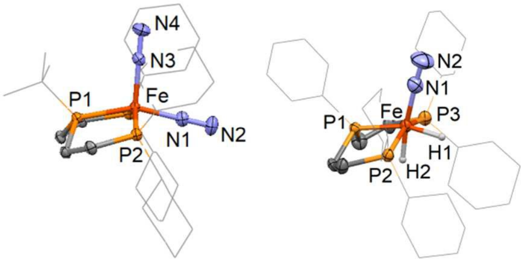


Fig. 1 Molecular structure of **4b** (left) and **6a** (right). Hydrogen atoms (except metallic hydrides) and solvent molecules are omitted for clarity; thermal ellipsoids are drawn with 50% probability.

The $[(P^{Ph}P_2^{Cy})Fe(N_2)(H)_2]$ complex **6a** was then subjected to the model catalytic conditions (*i.e.* 200 equiv. of KC_8 and 200 equiv. of $HBAr^F_4$ at –80°C in Et_2O for 1h), leading to the formation of 2.7±0.3 equiv. of NH_3. One should note that this result is almost identical to the one obtained by Peters and co-workers with their $[(P_2^{P'Ph})Fe(N_2)(H)_2]$ complex (2.6±0.1 equiv. NH_3).

The aforementioned mechanistic aspects derived from the protonation of the low-valent Fe-N_2 complex **4a** indicate that addition of electrophiles at the distal N-atom is of utmost importance to reach good turnover numbers when dealing with Fe-catalyzed N_2 functionalization. Given the high affinity of Si moieties for N_2 ligands bonded to transition metals, we turned our attention toward the N_2-silylation with $ClSiMe_3$.[2,19] To date, the most efficient catalytic systems are based on Mo (best TON : 220)[19a] and Co (best TON: 195).[19i] Concerning Fe, several Fe-hydride clusters have been shown to be very active (TON: 160 for a Fe_4 cluster, *i.e.* 40 per Fe center; 183 for Fe_6 cluster, *i.e.* 31 per Fe center)[19e] while the most efficient monometallic Fe complex was reported while our work was under evaluation (TON: 121).[19h] Having in hands several Fe-N_2 complexes, **4a**, **4b** and **6a**, their efficiency in this process was tested. Optimization of the model reaction conditions was done with complex **4a**. As often observed, THF appears critical, as well as the use of 600 equiv. of K as reducing agent.[13,19f] Under these conditions, complex **4a** provides a TON of 32.0±0.8 in the range of the more efficient monometallic Fe catalysts for the synthesis of silylamines from N_2 .[20] It corresponds to an efficiency in the formation of the N-Si bond of 16% (17%, ref 19f, 15.5% and 20%, ref 19e; 24% ref 19h). Complex **4b** performs slightly less with a TON of 27.0±0.5,

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whereas the dihydride complex **6a** is about half as efficient (entry 7, TON 14.5).

Table 1. Catalytic investigations.

$$\underset{\text{600 equiv.}}{\text{TMSCl}} + \underset{\text{600 equiv.}}{\text{Red.}} \xrightarrow[\text{solvent, } \mathbf{N_2}\text{, r.t., 2 days}]{\text{Cat. (0.01 mmol)}} \text{N(TMS)}_3$$

observed by ^{29}Si NMR
quantified *via* indophenol
method after hydrolysis

Entry[a]	Cat.	Solvent	Red.	Equiv. **N(TMS)$_3$**
1	**4a**	THF	Na	15.8
2	**4a**	THF	K	**32.0±0.8**[b]
3	**4a**	1,4-dioxane	K	7.7
4	**4a**	2-MeTHF	K	6.5
5	**4a**	Et_2O	K	< 2.0
6	**4b**	THF	K	**27.0±1.0**[b]
7	**6a**	THF	K	**14.5**

[a]Equiv. **N(TMS)$_3$** = equiv. amine/**Cat.** [b]: done in duplicate

In conclusion, we show here that the tridentate ligand $P^RP^{Cy}{}_2$ is able to stabilize rare Fe^0 *bis*-N_2 complexes **4a-b**. These complexes expand the small field of iron species able to perform N_2 reduction into NH_3 under mild conditions in homogeneous phase. Their weak activity can be explained by kinetically favored protonation at the metallic center rather than at a nitrogen atom as well as the *in situ* formation of the Fe^{II} species $[(P^{Ph}P_2{}^{Cy})Fe(N_2)(H)_2]$ **6a** from transient $Fe^I(H)(N_2)$ species. The use of the bulkier, softer electrophile $ClSiMe_3$ precluded such a reactivity at the Fe center and thereby complex **4a** rises up as one of the most competent catalysts for $N(TMS)_3$ production from N_2. These results provide further guidance toward the development of more efficient Fe complexes in the N_2 catalyzed reduction.

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Conflicts of interest

There are no conflicts to declare.

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20 A $(P_2P_2)Fe(N_2)$ complex is reported to give 5.4 equiv. of $N(SiMe_3)_3$ under 1 atm of N_2, and 65 equiv. under 100 atm.: D. E. Prokopchuk, E. S. Wiedner, E. D. Walter, C. V. Popescu, N. A Piro, W. S. Kassel, R. M. Bullock, M. T. Mock *J. Am. Chem. Soc.,* 2017, **139**, 9291.

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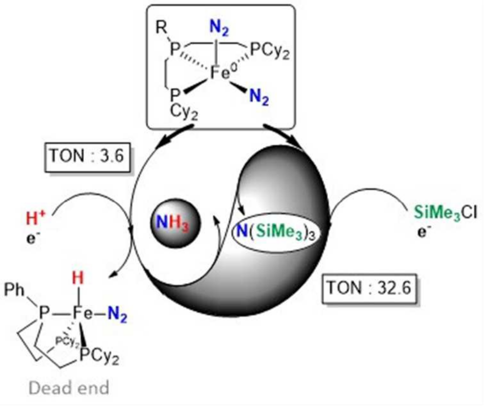

Mechanistic investigations of the catalyzed reduction of N_2 with a rare (tridentate phosphine)Fe(0) bis dinitrogen complex.