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Ammonia and Hydrazine from coordinated Dinitrogen by Complexes of Iron(0)

Leslie D. Field,^{*[a]} Hsiu L. Li,^[a] Scott J. Dalgarno^[b] and Ruaraidh D. McIntosh^[b]

Abstract: The iron(0) dinitrogen complexes $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{R}})]$ ($\text{PP}_3^{\text{R}} = \text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_3$, $\text{R} = \text{Ph}$, ^iPr , Cy) were synthesized by reduction of the precursor chloro complexes with potassium graphite. On reaction with triflic acid, $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{R}})]$ complexes afforded ammonia and hydrazine in yields of up to 23 and 16% respectively. The complex $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ which has only been previously synthesized *in situ*, has now been isolated and fully characterized by ^{15}N NMR spectroscopy and by X-ray crystallography.

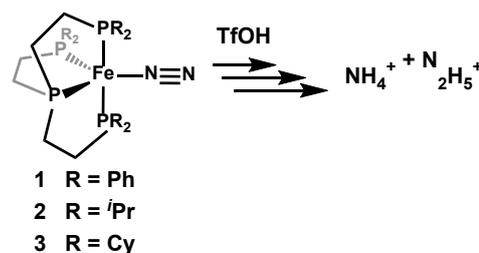
Introduction

Nitrogen fixation, where inert dinitrogen is converted to more reactive forms such as ammonia or hydrazine, is a process of fundamental importance, as the nitrogen necessary for essential biomolecules such as proteins and nucleic acids is ultimately derived from this process.^[1] While nitrogen can be fixed industrially by the Haber-Bosch process or biologically by anaerobic microorganisms such as rhizobia, there is currently interest in the development of new catalysts to convert dinitrogen to ammonia (and hydrazine) under relatively mild conditions.^[2] In particular, iron-containing catalysts are of interest given that iron is present in both the Haber-Bosch catalyst and in the enzyme nitrogenase utilized by most biological systems.^[3] Recent research by Peters,^[4] Nishibayashi,^[5] Mézailles,^[6] Shi and Deng^[7] in this area have demonstrated iron-mediated catalysis on a laboratory scale.

In this paper we report the chemistry of N_2 bound to $\text{Fe}(0)$ complexes containing the bulky tripodal tetraphosphine PP_3 ligands ($\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_3$ where $\text{R} = \text{aryl}$, alkyl). Many of the metal complexes of the PP_3 ligands are known to be catalytically active in a range of different organic transformations.^[8] The PP_3 ligands constrain the geometry of octahedral complexes such that the remaining non- PP_3 donor atoms must be in adjacent sites in the octahedral coordination sphere.^[9] Our interest lies in the iron PP_3 complexes containing dinitrogen as a ligand where little has reported on the reactivity of the dinitrogen ligand itself.^[10]

Recently, we revisited the chemistry of $\text{Fe}(0)$ dinitrogen complexes containing bidentate phosphine ligands $[\text{Fe}(\text{N}_2)(\text{PP})_2]$ ($\text{PP} = 1,2\text{-bis}(\text{diethylphosphino})\text{ethane}$ (depe), $1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$ (dmpe)) with acids. In our hands, little or no reaction at the coordinated dinitrogen ligand was observed with the main outcome being protonation at the metal center to afford metal hydride complexes. However, treatment of $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ with trimethylsilyl triflate (TMSOTf) and then triflic acid afforded NH_4^+ indicating reaction at coordinated dinitrogen.^[11] Tyler *et al.* have reported treatment of a related system $[\text{Fe}(\text{N}_2)(\text{DMeOPrPE})_2]$ ($\text{DMeOPrPE} = 1,2\text{-bis}(\text{di}(\text{methoxypropyl})\text{phosphino})\text{ethane}$) with acids such as triflic acid (TfOH), HBF_4 and HCl to give ammonium in yields of up to 17% with respect to Fe .^[12] Recently, Ashley *et al.* have reported treatment of $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ with TfOH to give hydrazine in yields of up to 9.1% while similar treatment of $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ afforded hydrazine (up to 24%) and ammonia (up to 10.5%). Treatment of the dinitrogen-bridged complex $[\text{Fe}(\text{dmpe})_2]_2(\mu\text{-N}_2)$ with TfOH afforded only low yields of hydrazine and ammonia (in 4.3 and 1.5% yield respectively).^[13]

In this paper we report dinitrogen complexes of iron containing the bulky tetraphosphine ligands $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{R}})]$ ($\text{PP}_3^{\text{R}} = \text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_3$ ($\text{R} = \text{Ph}$ **1**, ^iPr **2**, Cy **3**) and demonstrate that these complexes produce ammonia and hydrazine on treatment with triflic acid (Scheme 1) in single batch experiments.



Scheme 1.

For most $\text{Ru}(0)$ and $\text{Fe}(0)$ phosphines containing a N_2 ligand, there are a number of competing reaction pathways (including the relatively facile substitution of N_2 , protonation at the metal centre and reaction of the coordinated N_2). The rationale for testing PP_3 -type ligands with bulky substituents on the terminal phosphorus donors was that this type of ligand partially encapsulates the metal and provides steric protection to shut down or slow down reactions at the metal centre and to direct reaction to the coordinated dinitrogen. We have recently reported the reaction of analogous $\text{Ru}(0)$ PP_3 dinitrogen complexes with acid to give mixtures of ammonia and hydrazine.^[14]

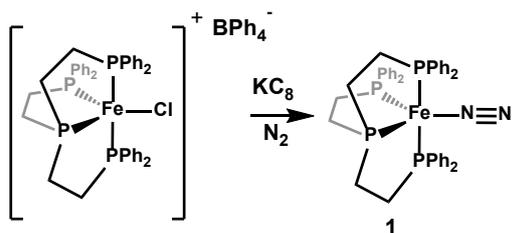
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Results and Discussion

Synthesis of dinitrogen complexes. [Fe(N₂)(PP₃^{Ph})] 1. The iron complex [Fe(N₂)(PP₃^{Ph})] **1** was synthesized by direct reduction of [FeCl(PP₃^{Ph})]⁺BPh₄⁻ in benzene or toluene with KC₈ and the complex was characterized by the usual spectroscopic methods (Scheme 2). Complex **1** has been reported previously, without isolation, by deprotonation of [FeH(N₂)(PP₃^{Ph})]⁺BPh₄⁻ with KO^tBu in tetrahydrofuran (THF).^[15]

Crystals of **1** suitable for X-ray crystallography were grown from a benzene / hexane solution (Figure 1). The geometry about the Fe center is trigonal bipyramidal with the three arms of the PP₃^{Ph} ligand being equivalent by symmetry, similar to the structure of [Fe(N₂)(PP₃^{Pr})] and [Ru(N₂)(PP₃^{Pr})].^[10a]



Scheme 2.

The N-N bond length of 1.131(11) Å is similar to the N-N bond lengths in [Fe(N₂)(PP₃^{Pr})]^[10a] and [Fe(N₂)(PP₃^{Cy})]^[10c] (1.1279(16) and 1.134(3) Å respectively) and falls within the range for other Fe complexes containing end-on bound dinitrogen (0.966–1.149 Å)^[6, 16] indicating a slight degree of activation compared to free dinitrogen (1.10 Å).^[17]

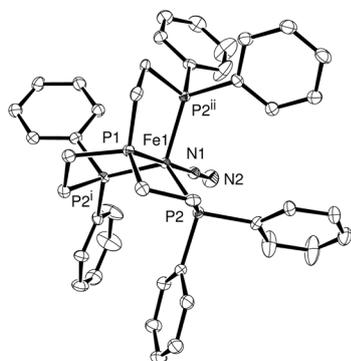


Figure 1. ORTEP plot of [Fe(N₂)(PP₃^{Ph})] **1** 50% ellipsoid probability, and hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Fe1-N1 1.826(8), Fe1-P1 2.175(2), Fe1-P2 2.2162(12), N1-N2 1.131(11), N1-Fe1-P1 180, N1-Fe1-P2 95.84(4), P1-Fe1-P2 84.16(4), P2-Fe1-P2ⁱ / P2ⁱ 118.978(15), N2-N1-Fe1 180.

The infrared stretching frequency, $\nu(\text{N}\equiv\text{N})$, is 2020 cm⁻¹ which matches that previously reported for the complex.^[15] The ³¹P{¹H} NMR spectrum of **1** exhibits a quartet (²J_{PP} 42 Hz) at 177.8 ppm for the central phosphorus atom and a doublet at 85.9 ppm for the terminal phosphorus atoms.^[18] The ¹⁵N-labeled analogue [Fe(¹⁵N₂)(PP₃^{Ph})] **1-¹⁵N** was synthesized by placing an

atmosphere of ¹⁵N₂ gas over a degassed solution of [Fe(N₂)(PP₃^{Ph})] **1** in THF-*d*₈ and then allowing exchange to take place over six days. Additional coupling was evident in the ³¹P{¹H} NMR spectrum due to coupling with the ¹⁵N-labeled dinitrogen ligand. The metal bound nitrogen, N_α, (δ -31.5) exhibits larger ¹⁵N-³¹P coupling (²J_{P(trans)-N_α} = 9 Hz, ²J_{P(cis)-N_α} = 5 Hz) compared to coupling to the terminal nitrogen, N_β, (δ -3.5) (²J_{P(trans)-N_β} = 2 Hz). There is an additional ¹⁵N-¹⁵N coupling (¹J_{N_α-N_β}) of 5 Hz. The ¹⁵N chemical shifts for both N_β, and N_α (Figure 2), and are within the range reported for other Fe(0) dinitrogen complexes (δ 18.1 to -49.1).^[10a, 10b, 11, 19]

[Fe(N₂)(PP₃^{Pr})] 2. The iron(0) dinitrogen complex [Fe(N₂)(PP₃^{Pr})] **2** was synthesized by KC₈ reduction of the chloro complex [FeCl(PP₃^{Pr})]⁺BPh₄⁻ in THF under an atmosphere of nitrogen.^[10a] The dihydrido complex [FeH₂(PP₃^{Pr})] **4** was a persistent minor byproduct in the synthesis of **2**.

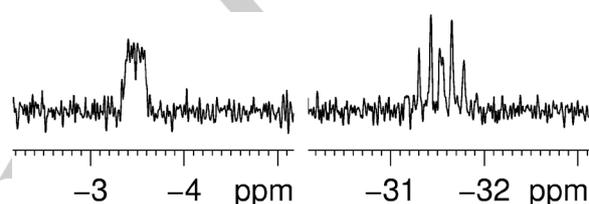
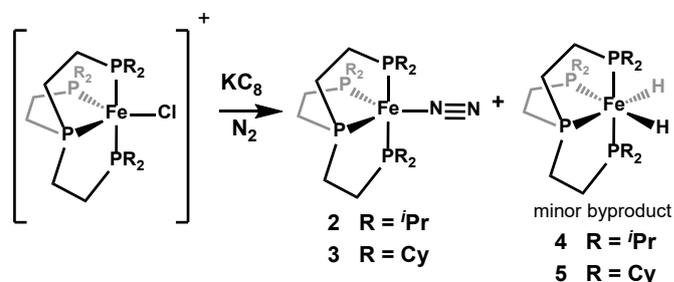


Figure 2. ¹⁵N NMR spectrum of [Fe(¹⁵N₂)(PP₃^{Ph})] **1-¹⁵N** (THF-*d*₈, 41 MHz).

An authentic sample of the dihydrido complex **4** was synthesized independently and the complex was characterized spectroscopically (see Supplementary Material). While we have not studied the mechanism of formation of the metal dihydride, it probably arises from the reaction of the reduced iron species with H₂ formed by reaction of KC₈ with adventitious water^[20] or with THF.^[21]

[Fe(N₂)(PP₃^{Cy})] 3. [Fe(N₂)(PP₃^{Cy})] **3** was synthesized by reduction of the chloro complex [FeCl(PP₃^{Cy})]⁺BPh₄⁻ with KC₈. The synthesis of [Fe(N₂)(PP₃^{Cy})] by a similar method has been previously reported, however the dihydrido complex [FeH₂(PP₃^{Cy})] **5** was formed concurrently as a byproduct in variable amounts and the dinitrogen compound was isolated by fractional crystallization.^[10c] By employing short reaction times (40 mins) and using THF as the solvent or a solvent mixture of pentane and THF (4:1), the dihydrido complex was formed only as a minor byproduct (Scheme 3).



Scheme 3.

Formation of ammonia and hydrazine from dinitrogen complexes of Fe.

Reaction of [Fe(N₂)(PP₃^{Ph})] **1 with Acids.** Treatment of [Fe(N₂)(PP₃^{Ph})] **1** with TfOH in pentane afforded NH₄⁺ and N₂H₅⁺ in 23 and 1% yield respectively (Table 1). Our method of choice for quantification of both NH₃ and N₂H₄ is GC-MS. NH₃ can be detected directly by GCMS and N₂H₄ can be analyzed by GCMS after derivatization with acetone to form acetone azine (Me₂C=N-N=CMe₂; 2-(1-methylethylidene)hydrazone 2--propanone).^[22]

Table 1. Yields of ammonia and hydrazine from reactions of [Fe(N₂)(PP₃^R)] (R = Ph (**1**), ⁱPr (**2**), Cy (**3**)) with acids.

Complex	Solvent, Conditions	% yield of NH ₄ ⁺ ^[a]	% yield of N ₂ H ₅ ⁺ ^[a]	% N ₂ converted ^[b]
1	Pentane, TfOH	23	1	12
1	Benzene, TfOH	8	1	5
1	Pentane, TfOH, Cp* ₂ Co	12	1	7
1	Benzene / Et ₂ O, HCl	0	<1	<1
1	Benzene, [H(OEt ₂) ₂][B(C ₆ F ₅) ₄]	14	1	8
1	Et ₂ O, [H(OEt ₂) ₂][B(C ₆ F ₅) ₄]	5	0	3
1	Pentane, [H(OEt ₂) ₂][B(C ₆ F ₅) ₄]	<1	0	<1
1	Benzene, [H(OEt ₂) ₂][B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄]	0	0	0
1	Et ₂ O, [H(OEt ₂) ₂][B(C ₆ H ₃ -3,5-(CF ₃) ₂) ₄]	0	<1	<1
2 ^[c]	Pentane, TfOH	17	16	24
2 ^[c]	Benzene, TfOH	13	7	13
2 ^[c]	Pentane, TfOH, Cp* ₂ Co	28	3	17
3 ^[d]	Pentane, TfOH	14	4	11
3 ^[d]	Benzene, TfOH	6	3	6
3 ^[d]	Pentane, TfOH, Cp* ₂ Co	19	3	12

[a] Yield calculation based on 1:1 ratio of metal complex:ammonium or hydrazinium as quantified by GC. [b] Percentage of complexed dinitrogen from the starting material which ends up as NH₄⁺ or N₂H₅⁺ (calculated as half % yield NH₄⁺ + % yield of N₂H₅⁺). [c] Contained up to 14% [FeH₂(PP₃^{Pr})]. [d] Contained up to 8% [FeH₂(PP₃^{Cy})].

The combined yields of NH₄⁺ and N₂H₅⁺ are best expressed as “% N₂ converted” which reflects the percentage of complexed dinitrogen from the starting material which ends up as NH₄⁺ or

as N₂H₅⁺.^[13] “% N₂ converted” is a raw measure of the amount of coordinated N₂ that is converted to reduced products. We note that this measure of % N₂ converted takes no account of the source of electrons required to fuel the production of NH₃ and N₂H₄ products. In batch reactions (with no added reducing agents), all of the required electrons must derive from Fe(0) in the starting complexes. If all of the starting Fe(0)-N₂ complex was converted to NH₃, and all Fe(0) was oxidized to Fe(II) then 3 equivalents of the Fe(0) complex would be required to supply the electrons required to completely reduce N₂ and the maximum possible yield would be 33%. In the reaction of complex **1** with TfOH in pentane as the solvent, the % N₂ converted was 12%.

Lower yields of NH₄⁺ were obtained when the reactions were carried out in benzene (8%) and also only a low yield of N₂H₅⁺ (1%) giving rise to a % N₂ converted of 5% (Table 1). The ability of complex **1** to mediate the formation of NH₄⁺ and N₂H₅⁺ is interesting as it contrasts directly with the results from the analogous Ru complex [Ru(N₂)(PP₃^{Ph})] **6**, where no NH₄⁺ or N₂H₅⁺ was formed at all.^[14] There is a significant difference in the IR stretching frequency ν(N≡N) for compound **1** (2020 cm⁻¹) compared with its Ru analogue **6** (2080 cm⁻¹),^[23] and the greater activation of the N₂ ligand in the Fe complex may contribute to the better conversion of coordinated N₂ to reduced products on treatment with acid.

No NH₄⁺ was observed when HCl was used as the acid although a trace amount of N₂H₅⁺ was detected. Use of the oxonium acid containing a BAR^F anion [H(OEt₂)₂][B(C₆F₅)₄] afforded NH₄⁺ in 14% yield when the reaction was carried out in benzene, although only 5% when in diethyl ether and very little NH₄⁺ was formed when the reaction was carried out in pentane.

The analogous oxonium acid containing a different BAR^F anion [H(OEt₂)₂][B(C₆H₃-3,5-(CF₃)₂)₄] did not afford NH₄⁺ in either benzene or diethyl ether and very little N₂H₅⁺. In all cases of the reaction of complex **1** with acids, only a trace amount of N₂H₅⁺ was formed (<1%).

For complex **1**, triflic acid was the most effective acid in producing reduced products from coordinated dinitrogen, [H(OEt₂)₂][B(C₆F₅)₄] triggered nitrogen reduction but was less effective than triflic acid under the reaction conditions. We observed only traces of reduction products when [H(OEt₂)₂][B(C₆H₃-3,5-(CF₃)₂)₄] was used as the acid however this may reflect, the fact that the oxonium acids are less soluble than triflic acid in the reaction solvents. Weaker acids were ineffective in producing ammonia or hydrazine from complex **1**.

There was no increase in % N₂ converted on addition of 6 equivalents of a strong external reductant (Cp*₂Co) (Table 1) however this probably reflects the fact that Cp*₂Co would react rapidly with the strong acid in the reaction mixture.

Reaction of [Fe(N₂)(PP₃^{Pr})] **2 with TfOH.** Treatment of the iron complex [Fe(N₂)(PP₃^{Pr})] **2** with TfOH in pentane afforded NH₄⁺ and N₂H₅⁺ in 17 and 16% yield respectively (Table 1). Yields of NH₄⁺ and N₂H₅⁺ were slightly lower when the reaction was conducted in benzene as the solvent.

The formation of ammonia and hydrazine in this reaction contrasts strongly with the previously reported work on [Fe(N₂)(dmpe)₂] where no ammonium was formed on treatment

with various acids.^[11] It is, however, more in line with reports by Tyler and Ashley where they observed N₂ reduction with [Fe(N₂)(DMeOPrPE)₂] or [Fe(N₂)(depe)₂] with TfOH and this may be due to the greater steric bulk of the various phosphine ligands compared to dmpe.^[12-13]

When [Fe(N₂)(PP₃^{Pr})] **2** was reacted with TfOH in pentane with an added 6 equivalents of Cp*₂Co, the proportion of NH₄⁺ formed was increased and the amount of N₂H₅⁺ decreased however there was no increase in the overall % N₂ converted.

Reaction of [Fe(N₂)(PP₃^{Cy})] **3 with TfOH.** Treatment of [Fe(N₂)(PP₃^{Cy})] **3** with TfOH in pentane afforded NH₄⁺ and N₂H₅⁺ in 14 and 4% yields respectively (Table 1). When the reaction was carried out with benzene as the solvent, NH₄⁺ and N₂H₅⁺ were obtained in 6 and 3% yields respectively.

As with the analogous complexes **1** and **2**, Cp*₂Co did not significantly increase the % N₂ converted for the reaction of complex **3** with TfOH.

For all three Fe complexes **1**, **2** and **3**, reaction with triflic acid afforded the protonated phosphine ligands at the end of the reaction, where the ligand was protonated either at the central or terminal positions or at both positions depending on the amount of acid present in the reaction mixture. For complex **1**, the main phosphorus-containing products were [HP(CH₂CH₂PPh₂)₃]⁺ and/or [HP(CH₂CH₂PPh₂H)₃]⁴⁺. For complex **2**, the main end product was P(CH₂CH₂P^{Pr}H)₃³⁺ where only the terminal phosphorus atoms are protonated. Complex **3** affords a mixture of both [P(CH₂CH₂PCy₂H)₃]³⁺ and/or [HP(CH₂CH₂PCy₂H)₃]⁴⁺. The formation of protonated phosphine ligand indicates that the structural integrity of the complexes is lost under the reaction conditions and presumably, Fe(II) is liberated into the reaction medium.

While we observed a significant solvent effect on the yield of the reduced products, we have not explored this in depth. The role of solvent may be important in the reduction process particularly in stabilizing the oxidized metal species following reaction of the metal dinitrogen complexes with acid. With the analogous Ru complexes [Ru(N₂)(PP₃^{Pr})] and [Ru(N₂)(PP₃^{Cy})], stable triflate and solvent complexes were isolated^[14] as the oxidized metal species after reduction of the nitrogen ligand.

Conclusions

A series of [Fe(N₂)(PP₃^R)] complexes [R = Ph, ⁱPr, Cy; PP₃^R = P(CH₂CH₂PR₂)₃] were synthesized and treatment of these complexes with triflic acid afforded ammonia in yields up to 23% with the highest yield from [Fe(N₂)(PP₃^{Ph})] **1** in pentane as the solvent. In all cases, hydrazine was also obtained as a product in yields up to 16% with the highest yield from [Fe(N₂)(PP₃^{Pr})] **2** in pentane as the solvent. This result confirms that Fe(0) can provide sufficient reducing power to effect the reduction of coordinated N₂. The bulky PP₃ ligands employed in this work were designed to partially encapsulate the metal center and to slow or inhibit the competing reaction of the metal center with acid.

While we examined a range of different acids, triflic acid provided the highest conversion of coordinated N₂ to reduced

products and this appears to reflect the fact that it is a strong acid with a weakly coordinating counterion. Other strong acids including [H(OEt₂)₂][B(C₆F₅)₄] also afforded ammonia and hydrazine but in lesser quantities and weaker acids afforded no (or negligible) amounts of hydrazine or ammonia. Stronger acids are probably required to protonate a weakly activated dinitrogen ligand and trigger the transfer of electrons from the metal to nitrogen.

While we have not studied it in detail, there is clearly a strong solvent dependence of the reaction. In other work with ruthenium complexes of dinitrogen,^[14] the spent (oxidized) form of the metal has been isolated as a complex with the solvent and we have postulated that there may be an important role for the solvent in stabilizing the oxidized state of the metal and hence providing an additional driving force for the reduction of dinitrogen.

The reactions we have described in this work are all batch reactions where the only source of electrons for the reduction of nitrogen is the low oxidation state of the starting metal complexes. Under the experimental conditions employed in this work, the addition of an external reductant (Cp*₂Co) was ineffective as a source of additional reducing power for the reduction and this probably reflects the fact that the strong reductant would have only a short lifetime in the strongly acidic reaction mixture.

Experimental Section

General experimental procedures are contained in the supplementary information as well as the procedure for quantifying ammonia and hydrazine using GC-MS. Tris[2-(diisopropylphosphino)ethyl]phosphine (PP₃^{Pr}), [FeCl(PP₃^{Pr})]⁺BPh₄⁻ and [Fe(N₂)(PP₃^{Pr})] **2** were prepared by literature methods or slight modifications thereof.^[10a] The complexes [FeCl(PP₃^{Ph})]⁺BPh₄⁻,^[24] [FeCl(PP₃^{Cy})]⁺BPh₄⁻^[25] and [Fe(N₂)(PP₃^{Cy})] **3**^[10c] were prepared using literature methods or slight modifications thereof.

Preparation of [Fe(N₂)(PP₃^{Ph})] **1.** Potassium graphite (0.109 g, 0.809 mmol, 4.3 equiv) was added to a suspension of [FeCl(PP₃^{Ph})]⁺BPh₄⁻ (0.202 g, 0.187 mmol) in toluene (7 mL) under an atmosphere of nitrogen and the reaction mixture was stirred at room temperature for 4 d. The reaction mixture was filtered through diatomaceous earth to afford a dark orange-red solution. The solvent was removed under reduced pressure to give a red solid. Recrystallization from a mixture of benzene and hexane afforded [Fe(N₂)(PP₃^{Ph})] **1** as a red crystalline solid (71 mg, 94 μmol, 50% yield). Anal. Calcd for C₄₂H₄₂FeN₂P₄ (754.55): C, 66.86; H, 5.61; N, 3.71. Found: C, 67.11; H, 5.75; N, 3.23. ¹H NMR (THF-*d*₈, 400 MHz): δ 7.10 (m, 12H, *o*-H), 7.02 (m, 6H, *p*-H), 6.93 (m, 12H, *m*-H), 2.28 (m, 6H, CH₂), 1.86 (m, 6H, CH₂). ³¹P{¹H} NMR (THF-*d*₈, 162 MHz): δ 177.8 (q, ²J_{PP} = 41 Hz, 1P, P_C), 85.9 (d, 3P, P_T). IR: 3067w, 3040w, 2020s ν(N≡N), 1583m, 1570w, 1478s, 1431s, 1407m, 1330w, 1302w, 1272w, 1225w, 1185w, 1156w, 1082m, 1070m, 1055w, 1026m, 998w, 964w, 902w, 879m, 856m, 824m, 794s, 751m, 735s, 691s, 673s, 654w, 619w cm⁻¹. CCDC 1570094 contains the crystallographic data for this compound.

The ¹⁵N-labeled analogue [Fe(¹⁵N₂)(PP₃^{Ph})] was prepared by degassing a solution of [Fe(N₂)(PP₃^{Ph})] in THF-*d*₈ by three freeze-pump-thaw cycles, placing an atmosphere of ¹⁵N₂ gas in the headspace, then allowing the solution to stand for six days to allow exchange to occur (approximately

88% enrichment). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF- d_6 , 162 MHz): δ 177.8 (dq, $^2J_{\text{PP}} = 41$ Hz, $^2J_{\text{NP}} = 9$ Hz, 1P, PC), 85.9 (ddd, $^2J_{\text{PP}} = 41$ Hz, $^2J_{\text{NP}} = 5$ Hz, $^3J_{\text{NP}} = 2$ Hz, 3P, PT). $^{15}\text{N}\{^1\text{H}\}$ NMR (THF- d_6 , 41 MHz): δ -3.5 (m, 1N, N $_{\beta}$), -31.5 (m, 1N, N $_{\alpha}$).

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** with TfOH.

(i) In a typical reaction, TfOH (43 mg, 0.29 mmol) was added to the red suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ (23 mg, 30 μmol) in pentane (2 mL) under nitrogen. The reaction mixture was stirred at room temperature overnight during which time the solution decolorized and purple and white solids precipitated from the solution. The volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 using GC-MS. The main phosphorus-containing product at the end of the reaction was protonated PP_3^{Ph} $[\text{HP}(\text{CH}_2\text{CH}_2\text{PPh}_2\text{H})_3]^{4+}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- d_6 , 243 MHz): δ 55.6 (br, 1P, HP_C^+), 34.0 (br, 3P, HP_T).

(ii) In a typical reaction, TfOH (45 mg, 0.30 mmol) was added to the red suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ (22 mg, 29 μmol) in benzene (2 mL) under nitrogen. The purple suspension was stirred at room temperature overnight and the volatiles removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_4^+ and N_2H_5^+ . The main phosphorus-containing product at the end of the reaction was protonated PP_3^{Ph} $[\text{HP}(\text{CH}_2\text{CH}_2\text{PPh}_2\text{H})_3]^{4+}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- d_6 , 243 MHz): δ 55.5 (br, 1P, HP_C^+), 33.8 (br, 3P, HP_T , $(\text{HPP}_3^{\text{Ph}})^+$).

An authentic sample of $[\text{HP}(\text{CH}_2\text{CH}_2\text{PPh}_2\text{H})_3]^{4+}$ was prepared for spectroscopic comparison by reaction of $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ with TfOH (see Supplementary Material).

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1 with TfOH and CoCp^*_2 .** In a typical reaction, TfOH (53 mg, 0.35 mmol) in pentane (0.5 mL) was added to a suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ (30 mg, 40 μmol) and CoCp^*_2 (79 mg, 0.24 mmol) in pentane (2 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 days and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** with HCl.

A solution of HCl (2 M in diethyl ether, 0.11 mL, 0.23 mmol) was syringed into a red suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ (22 mg, 29 μmol) in benzene (2 mL) under nitrogen. The color of the reaction mixture went through a series of changes from red to yellow then to pale pink after stirring at room temperature overnight. The volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** with $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$.

(i) In a typical reaction, $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.237 g, 0.286 mmol) was added to a suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** (27 mg, 36 μmol) in benzene (2 mL) under nitrogen. The reaction mixture was stirred at room temperature for 3 days in which time the color changed from red to purple. The volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

(ii) $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.210 g, 0.254 mmol) was added to a suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** (24 mg, 32 μmol) in diethyl ether (2 mL) under nitrogen. The reaction mixture was stirred at room temperature for

3 days in which time the color changed from red to purple. The volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

(iii) In a typical reaction, $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.193 g, 0.233 mmol) was added to a suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** (22 mg, 29 μmol) in pentane (3 mL) under nitrogen. The reaction mixture was stirred at room temperature overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** with $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)_4]$.

(i) In a typical reaction, $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)_4]$ (0.281 g, 0.278 mmol) and $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** (26 mg, 34 μmol) in benzene (5 mL) were stirred at room temperature under nitrogen overnight. The volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

(ii) $[\text{H}(\text{OEt}_2)_2][\text{B}(\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2)_4]$ (0.250 g, 0.247 mmol) was added to a suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Ph}})]$ **1** (23 mg, 30 μmol) in diethyl ether (5 mL) under nitrogen and the reaction mixture stirred at room temperature overnight. The volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Pr}})]$ **2** with TfOH.

(i) In a typical reaction, TfOH (47 mg, 0.31 mmol) was added to a solution of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Pr}})]$ **2** (19 mg, 35 μmol) in pentane (2 mL) under nitrogen. The orange solution turned colorless and a purple brown solid precipitate formed. After stirring at room temperature for 1.5 h, the volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_4^+ and N_2H_5^+ . The main phosphorus-containing product at the end of the reaction was protonated PP_3^{Pr} $[\text{P}(\text{CH}_2\text{CH}_2\text{P}^{\text{Pr}}_2\text{H})_3]^{3+}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- d_6 , 122 MHz): δ 38.0 (d, $^3J_{\text{PP}} = 34$ Hz, 3P, HP_T^+), -9.1 (br s, 1P, PC).

(ii) In a typical reaction, TfOH (45 mg, 0.30 mmol) was added to a solution of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Pr}})]$ **2** (24 mg, 37 μmol , contained 14% $[\text{FeH}_2(\text{PP}_3^{\text{Pr}})]$) in benzene (2 mL) under nitrogen. The orange solution turned colorless and a whitish precipitate formed. The reaction mixture was stirred at room temperature overnight and the volatiles removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_4^+ and N_2H_5^+ . The main phosphorus-containing product at the end of the reaction was protonated PP_3^{Pr} $[\text{P}(\text{CH}_2\text{CH}_2\text{P}^{\text{Pr}}_2\text{H})_3]^{3+}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- d_6 , 162 MHz): δ 37.0 (d, $^3J_{\text{PP}} = 36$ Hz, 3P, HP_T^+), -9.9 (q, 1P, PC).

An authentic sample of $[\text{P}(\text{CH}_2\text{CH}_2\text{P}^{\text{Pr}}_2\text{H})_3]^{3+}$ was prepared for spectroscopic comparison by reaction of $[\text{P}(\text{CH}_2\text{CH}_2\text{P}^{\text{Pr}}_2\text{H})_3]^{3+}$ with TfOH (see Supplementary Material).

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Pr}})]$ **2 with TfOH and CoCp^*_2 .** In a typical reaction, TfOH (61 mg, 0.41 mmol) in pentane (0.5 mL) was added to a solution of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Pr}})]$ **2** (32 mg, 50 μmol , contained 14% $[\text{FeH}_2(\text{PP}_3^{\text{Pr}})]$) and CoCp^*_2 (0.10 g, 0.30 mmol) in pentane (2 mL) under nitrogen. The dark brown solution turned into a brown suspension. The reaction was stirred at room temperature overnight and the volatiles removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 .

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **3** with TfOH.

(i) In a typical reaction, TfOH (25 mg, 0.17 mmol) in pentane (0.5 mL) was added to a solution of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **3** (16 mg, 18 μmol , contained 8% $[\text{FeH}_2(\text{PP}_3^{\text{Cy}})]$ **4** in pentane (2 mL) under nitrogen. The orange suspension was stirred at room temperature overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 . The main phosphorus-containing products at the end of the reaction were $[\text{P}(\text{CH}_2\text{CH}_2\text{PCy}_2\text{H})_3]^{3+}$ and $[\text{HP}(\text{CH}_2\text{CH}_2\text{PCy}_2\text{H})_3]^{4+}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- d_6 , 162 MHz): δ 52.3 (br, HPc^+), 27.9 (br, HP^+), -9.15 (br, Pc).

(ii) In a typical reaction, TfOH (38 mg, 0.25 mmol) was added to a solution of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **3** (46 mg, 58 μmol , contained 8% $[\text{FeH}_2(\text{PP}_3^{\text{Cy}})]$ **4** in a mixture of benzene (0.4 mL) and benzene- d_6 (0.1 mL) under nitrogen. The orange solution turned very pale yellow and a pale yellow precipitate formed. The reaction mixture was left to stand at room temperature for 3 days and the volatiles then removed under reduced pressure. The residue was dissolved in DMSO- d_6 or DMSO and analyzed for NH_3 and N_2H_4 . The main phosphorus-containing product at the end of the reaction was $[\text{P}(\text{CH}_2\text{CH}_2\text{PCy}_2\text{H})_3]^{3+}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (DMSO- d_6 , 162 MHz): δ 29.0 (d, $^3J_{\text{FP}} = 35$ Hz, 3P, HP^+), -10.0 (q, 1P, Pc).

An authentic sample of $[\text{P}(\text{CH}_2\text{CH}_2\text{PCy}_2\text{H})_3]^{3+}$ was prepared for spectroscopic comparison by reaction of $[\text{P}(\text{CH}_2\text{CH}_2\text{P}^{\text{Pr}}\text{H})_3]^{3+}$ with TfOH (see supplementary material).

Reaction of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **3 with TfOH and Cp^*_2Co .** TfOH (91 mg, 0.61 mmol) was added to a suspension of $[\text{Fe}(\text{N}_2)(\text{PP}_3^{\text{Cy}})]$ **3** (25 mg, 29 μmol , contained 7% $[\text{FeH}_2(\text{PP}_3^{\text{Cy}})]$ **4** and Cp^*_2Co (63 mg, 0.19 mmol) in pentane (4 mL) under nitrogen. The brown suspension was stirred at room temperature overnight and the volatiles were removed under reduced pressure. The residue was dissolved in DMSO and analyzed for NH_3 and for N_2H_4 .

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Conflict of interest

The authors declare no conflicts of interest.

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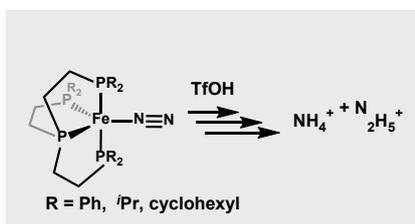
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FULL PAPER

In the presence of strong acids, coordinated N_2 in $[Fe(N_2)(PP_3R)]$ ($PP_3R = P(CH_2CH_2PR_2)_3$; $R = Ph, iPr, Cy$) is reduced to a mixture of ammonia and hydrazine. The bulky PP_3 ligands were designed to partially encapsulate the metal center and to slow or inhibit the competing reaction of the metal center with acid.

**Nitrogen reduction to ammonia**

Leslie D. Field,* Hsiu L. Li, Scott J. Dalgarno and Ruaraidh D. McIntosh

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Ammonia and Hydrazine from coordinated Dinitrogen by Complexes of Iron(0)