

## Reduction of dinitrogen bound at an iron(0) centre

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It has been confirmed that the deprotonation–reprotonation of dinitrogeniron(II) complexes is a method of producing limited amounts of ammonia. However, the original postulate that such reactions involve an iron(0) dinitrogen complex as the key intermediate may be in error. The species originally identified as such is much more likely to have been a hydrido-complex impurity, and the ammonia-yielding intermediate remains uncharacterised.

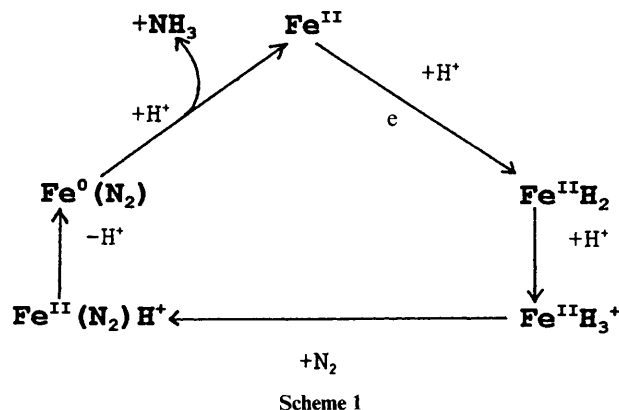
We recently described a system based on iron that was potentially cyclable and that gave ammonia in yields up to about 20% based upon the available reducing equivalents.<sup>1</sup> This system differs from nitrogen-reducing systems described before or since our original publication<sup>2</sup> in two important ways. First, the iron cycles through oxidation states which are conceivably attainable by a metalloenzyme, and secondly it uses protic rather than non-aqueous solvents.<sup>3</sup> The key to this cyclic system is successive deprotonation and reprotonation, which allows some of the bound dinitrogen to be protonated to ammonia but not to hydrazine. In addition, we showed that the deprotonation is equivalent to a reduction of the iron from oxidation state II to 0, and suggested that this kind of control by pH might be significant in nitrogenase function.<sup>1</sup>

There are now four similar systems<sup>1,4</sup> that can produce ammonia by successive deprotonation and reprotonation, and the basic mechanism for all four is set out in Scheme 1.<sup>1,3</sup> In every case the iron is supported by four ligating groups, generally tertiary phosphines, and these provide a stable ligand set that maintains the integrity of the complexes. In this paper we show that the overall yield of ammonia can be increased only marginally by varying acid and/or solvent, and also that although an iron(0) dinitrogen compound is indeed produced, it is unlikely that a simple complex is the key ammonia-producing intermediate.

## Results and Discussion

We commenced by attempting to optimise the yields of ammonia that we had reported earlier, by varying the temperature, solvent and acid. The methods used were essentially those already described,<sup>1</sup> the complex was  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$  (dmpe =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ), the temperature ambient (ca. 20 °C), the solvents were thf (tetrahydrofuran), toluene and methanol, and the base was  $\text{KOBu}^t$ . The data are presented in Table 1. It can be seen that the optimum yield was obtained with HCl in thf, but that it was only 14%.

Lowering the temperature to  $-40$  °C throughout the sequence of operations allowed us to raise the yield to 20% and this is the best that we have been able to achieve in any system. To avoid possible loss of dinitrogen when filtering, all such operations were performed under positive pressure. We also investigated two other iron dinitrogen complexes in the same fashion, namely  $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$  (depe =  $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$ )<sup>5</sup> and  $[\text{FeH}(\text{N}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$ .<sup>6</sup> In the first case  $[\text{FeCl}_2(\text{depe})_2]$  was isolated at the end of the



**Table 1** Yields (mmol) of ammonia produced after deprotonation–reprotonation at ambient temperature and base distillation from 1 mmol  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$  as a function of acid and solvent

Acid	Solvent		
	thf	Toluene	Methanol
HCl	0.088 (14)	0.021 (3.0)	0.063 (9.5)
$\text{H}_2\text{SO}_4$	0.065 (10)	0.019 (3.0)	0.051 (7.5)
$\text{HBF}_4 \cdot \text{Et}_2\text{O}$	0.060 (9.0)	0.019 (3.0)	0.060 (9.0)

The numbers in parentheses are % yields assuming that a maximum of two electrons is available to reduce each dinitrogen. The data are all corrected for blanks run on  $[\text{FeH}(\text{H}_2)(\text{dmpe})_2][\text{BPh}_4]$ , which were never greater than ca. 0.001 mmol. Higher yields were obtained at  $-40$  °C (see text).

reaction sequence in more than 80% yield, but the yield of ammonia was again at best 20%, operating at  $-20$  °C. We confirmed that simply adding HCl to  $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$  did not produce ammonia, consistent with an earlier kinetic study of Henderson.<sup>7</sup> In the second case we observed the characteristic purple colour of  $[\text{FeCl}\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+$ ,<sup>8</sup> and the yield of ammonia was again about 20% of the theoretical maximum.

What these data might imply for the mechanism of dinitrogen reduction by nitrogenase is not clear. They are not inconsistent with the Lowe–Thorneley kinetic model<sup>9</sup> that implies that five electrons must reach the dinitrogen-binding protein before any ammonia is observed. In our cases, and in the example of George *et al.*,<sup>4</sup> the results have been rationalised<sup>1</sup> on the basis that deprotonation of the  $\text{Fe}^{\text{II}}\text{H}(\text{N}_2)^+$  species produces an  $\text{Fe}^0(\text{N}_2)$  species such as  $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ . The formal two-electron reduction provides the reducing equivalents to convert

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the dinitrogen into ammonia upon reprotonation. We now review the evidence for the formation of iron(0) species in this fashion.

In our earlier papers<sup>1,2</sup> we presented evidence for the formation of  $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$  by deprotonation of  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2]^+$  with  $\text{KOBU}^1$ . This was (1) that the IR band assignable to  $\nu(\text{N}_2)$  at  $2093\text{ cm}^{-1}$  disappeared and was replaced by a band at  $1967\text{ cm}^{-1}$ , and (2) that the iron(0) dinitrogen complex exhibited a characteristic and plausible  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum in the form of an  $\text{A}_2\text{B}_2$  doublet, implying a trigonal-bipyramidal structure. This material was never isolated. The IR data were confirmed by nitrogen-15 labelling,<sup>1</sup> but it has been pointed out to us\* that the phosphorus spectrum we observed is very similar to that reported for *cis*- $[\text{FeH}_2(\text{dmpe})_2]$ <sup>10</sup> and that our NMR observation might well arise from this complex and not from the claimed dinitrogen complex.

This dihydride could have arisen from residual trihydride in the reaction mixture, since the reaction of the trihydride with dinitrogen is quite slow. Other results throw further doubt on the identification of  $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$  as the key intermediate in the protonation-deprotonation sequence. Komiya *et al.*<sup>5</sup> have described the preparation of  $[\text{Fe}(\text{N}_2)(\text{depe})_2]$  by reduction of  $[\text{FeCl}_2(\text{depe})_2]$  with sodium-naphthalene under  $\text{N}_2$ . This molecule is trigonal bipyramidal in the crystal, but its  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum ( $\delta -61.4$ ) is never more than a singlet within the accessible temperature range. Furthermore, it does not produce any ammonia or hydrazine when treated with acid.<sup>5</sup> We therefore reinvestigated our deprotonation reactions, paying particular attention to the purity of the reactants.

Upon deprotonating NMR-pure  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$  with  $\text{KOBU}^1$  we obtained a spectrum which contained a strong singlet at  $\delta -80.1$  with respect to  $\text{P}(\text{OMe})_3$  at ambient temperature, and this remained a singlet even at  $-50\text{ }^\circ\text{C}$ . The solution was stable under dinitrogen, but decomposed upon exposure to air. It lost dinitrogen (IR evidence) upon submitting to a vacuum and we could never isolate a clean solid. We also monitored the deprotonation of  $[\text{FeH}(\text{CO})(\text{dmpe})_2][\text{BPh}_4]^1$  with  $\text{KOBU}^1$  by IR spectroscopy, and observed the gradual disappearance of  $\nu(\text{CO})$  at  $1926\text{ cm}^{-1}$ , to be replaced by a new band at  $1830\text{ cm}^{-1}$ . The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of the deprotonated product was a singlet at  $\delta -77.5$ . This is consistent with the formation of  $[\text{Fe}(\text{CO})(\text{dmpe})_2]$ ,<sup>11</sup> which is apparently also formed when CO is bubbled through a solution containing  $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ . Continued reaction with CO generates a spectrum assigned previously to  $[\text{Fe}(\text{CO})_3(\text{dmpe})]$ .<sup>11</sup> The monocarbonyl was first reported by Tolman *et al.*<sup>11</sup> from the reaction of  $[\text{FeCl}_2(\text{dmpe})_2]$  and sodium-naphthalene under CO.

It would have been useful to have followed the sequence of deprotonation and reprotonation reactions using  $^{31}\text{P}$  or  $^{15}\text{N}$  NMR spectroscopy. The full experimental details for these reactions have been described in our previous paper,<sup>1</sup> in which we showed that subjection of the mixture after treatment with base to reduced pressure resulted in the complete loss of dinitrogen, though this was, in part, reversible. The practical difficulties associated with the system prevented us from studying the intermediates as closely as we would have wished.

We attempted to perform analogous studies with  $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$ . Upon addition of  $\text{KOBU}^1$  to a solution in thf the hydride band at  $1880\text{ cm}^{-1}$  disappeared though the dinitrogen band at  $2090\text{ cm}^{-1}$  did not move although it decreased in intensity, and a new band appeared at  $1812\text{ cm}^{-1}$ . Labelling with  $^{15}\text{N}$  showed that the last band was not due to  $\text{N}_2$ , and that unshifted  $\nu(\text{N}_2)$  was again detectable after deprotonation. The band at  $1812\text{ cm}^{-1}$  may be an aromatic

overtone arising from residual tetraphenylborate. No band obviously assignable to  $\nu(\text{N}_2)$  in  $[\text{Fe}(\text{N}_2)(\text{depe})_2]$  was observed.

The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of the deprotonated solution indicated a mixture of products, though there was a strong singlet at  $\delta -59.9$ , compared with  $\delta -61.4$  reported<sup>5</sup> for the Komiya compound,  $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ , so that it is possible that we had prepared the same compound, *inter alia*. Again, we could not isolate a pure solid, and parallel deprotonation, NMR and IR studies on  $[\text{FeH}(\text{N}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+$  also suggested that several products are formed along with the corresponding iron(0) dinitrogen complex.

## Conclusions

Our data confirm that an iron(0) complex, probably  $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ , is indeed formed by deprotonation in the dmpe system. The lowering of the band assigned to  $\nu(\text{N}_2)$  from  $2093$  in  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2]^+$  to  $1967\text{ cm}^{-1}$  is consistent with this. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum is now consistent with the data reported for the depe analogue reported by Komiya *et al.*<sup>5</sup> There are also considerable yields of ammonia, but it is not proven that the ammonia actually originates from this iron(0) dinitrogen complex. Its source nevertheless appears to be a labile dinitrogen complex, because the yield can be reduced by pumping on the reaction mixture. The carbonyl data also support the generation of an iron(0) complex.

The depe system did not provide direct evidence for the formation of the analogous depe iron(0) dinitrogen complex of Komiya *et al.*<sup>5</sup> which in any case does not produce ammonia upon treatment with acid. We would have expected a shift of  $\nu(\text{N}_2)$  from  $2090$  to  $1955\text{ cm}^{-1}$  upon deprotonation, but this was not observed. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR evidence is ambiguous, but since ammonia is nevertheless generated upon reacidification it would appear that another dinitrogen-containing species is also present. Henderson<sup>7</sup> showed that the reaction of  $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$  alone with HCl in thf does not produce ammonia, so that the deprotonation step is absolutely necessary.

Finally, the  $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  system exhibited an IR shift of about  $80$  rather than the expected  $130\text{ cm}^{-1}$  upon deprotonation, though this might well be due to a different geometry forced upon the system by the tetraphosphine, as well as the phenyl rather than the alkyl substituents. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum is not inconsistent with the presence of an iron(0) dinitrogen complex, which could also be the source of ammonia upon reprotonation. The data of George *et al.*<sup>4</sup> using a similar system with an analogous ligand,  $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ , are also consistent with the formation of an iron(0) complex,  $[\text{Fe}(\text{N}_2)\{\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]$ , but with the dinitrogen in an apical position in a trigonal-bipyramidal structure rather than in an equatorial position, shown unequivocally in the solid-state structure of  $[\text{Fe}(\text{N}_2)(\text{depe})_2]$ .<sup>5</sup> The George complex,<sup>4</sup> like our own, could not be obtained pure. It exhibited  $\nu(\text{N}_2)$  at  $1967\text{ cm}^{-1}$ , a shift of about  $120\text{ cm}^{-1}$  upon deprotonation, and the non-isolated complex yields hydrazine  $0.11$  mol per mol of presumed iron(0) complex and a trace of ammonia. These data are not inconsistent with ours.

The current situation is obviously unsatisfactory, because we are still unable to identify the key intermediates with any degree of certainty. However, we feel that there is probably another, reactive dinitrogen complex present here, as in the other systems, and a bridging dinitrogen complex with an IR-forbidden  $\nu(\text{N}_2)$  is a possibility. It may be that dinitrogen bridging to  $\text{K}^+$  or  $\text{Li}^+$ , as appropriate, is necessary to facilitate protonation to ammonia or hydrazine. We are currently searching for such complexes.

## Experimental

All operations were carried out under dry dinitrogen or argon, as appropriate, using standard Schlenk techniques. All solvents

\* We are very grateful to Professor Robin Perutz for the gentlemanly way he suggested to us that we might be in error.

were distilled under dinitrogen from appropriate drying agents. If dinitrogen needed to be excluded from the solvents this was achieved by degassing and saturating with argon before use. All IR spectra were obtained on a Perkin-Elmer 882 spectrometer, in Nujol mulls or in solution using balanced cells, NMR spectra on a JEOL GSX-270 machine, using deuteriated solvents [ $^1\text{H}$  referenced to  $\text{SiMe}_4$  and  $^{31}\text{P}$  to  $\text{P}(\text{OMe})_3$ ]. Microanalyses were carried out in the Nitrogen Fixation Laboratory or at Butterworths Microanalytical Laboratories. The diphosphines dmpe and depe were prepared according to published methods,<sup>12</sup>  $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  was obtained from Aldrich and used as received, and  $[\text{FeCl}_2(\text{dmpe})_2]$ ,<sup>13</sup>  $[\text{FeCl}_2(\text{depe})_2]$ ,<sup>13</sup>  $[\text{FeCl}\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$ ,<sup>6</sup>  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$ ,<sup>1,2</sup>  $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$ <sup>7</sup> and  $[\text{FeH}(\text{N}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$ <sup>8</sup> were prepared according to published methods.

### Deprotonation-reprotonation experiments

The complex  $[\text{FeH}(\text{N}_2)(\text{dmpe})_2][\text{BPh}_4]$  (0.75 g, 1.0 mmol) was dissolved in thf (30 cm<sup>3</sup>), affording an orange solution. An excess of  $\text{KOBU}^+$  (0.2 g) was added, and the solution became darker. After a few minutes of stirring a white precipitate was formed. The solution was stirred for 1.5 h, and the reaction was monitored by solution IR spectroscopy. The initial strong band assigned to  $\nu(\text{N}_2)$  at 2093 cm<sup>-1</sup> gradually disappeared and a broad band at 1967 cm<sup>-1</sup> gradually grew in intensity. The mixture was then filtered through Celite using a positive gas pressure to push it through the filter. This produced a clean orange filtrate which contains  $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ , as judged by the IR and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra ( $\delta - 80.1$ ).

Reprotonation experiments were undertaken in various ways, as detailed in Table 1. The acids used were anhydrous HCl, generated from  $\text{SiMe}_3\text{Cl}$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ . The following description is of a typical procedure.

A solution containing  $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$  in thf prepared as above was cooled to the required temperature and treated with an excess of HCl. This resulted in a pink solution, which turned green slowly on stirring due to the formation of  $[\text{FeCl}_2(\text{dmpe})_2]$ . After stirring for 3 h the solvent was removed *in vacuo*. The residue was base-distilled from 10% aqueous KOH and the volatiles collected in 0.5 mol dm<sup>-3</sup>  $\text{H}_2\text{SO}_4$  (15 cm<sup>3</sup>). The ammonia was determined by the indophenol test.<sup>14</sup>

The reactions with  $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$  were carried out as described for the dmpe complex, but deprotonation resulted in a yellow rather than an orange solution and a white precipitate. Infrared monitoring showed that the band at 2090 cm<sup>-1</sup> did not disappear completely, and a new band formed at 1812 cm<sup>-1</sup>. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum revealed signals at  $\delta - 59.9$  (s) (intense),  $-92.9$  (d) (weak), and  $-160.1$  (m) (about as intense as the first resonance) in  $[\text{H}_8]\text{thf}$ . The reprotonation followed the pattern described for the dmpe analogue. Yields of ammonia were best using anhydrous HCl in thf, and were about 15% at ambient temperature and 20% at  $-40^\circ\text{C}$ .

The deprotonation of  $[\text{FeH}(\text{N}_2)\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}][\text{BPh}_4]$  was carried out similarly, yielding a yellow solution, in which a new IR band at 2020 cm<sup>-1</sup> replaced that at 2100 cm<sup>-1</sup>. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum showed resonances at  $\delta - 72.1$  (s),  $-83.0$  (s) and  $-154.1$  (s) in  $[\text{H}_8]\text{thf}$ . Reprotonation generated the characteristic purple colour of  $[\text{FeCl}\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}]^+$ , as well as producing ammonia.

The best yield at ambient temperature was also about 15%, using anhydrous HCl and thf. In this case we did not attempt to optimise the yield.

### Deprotonation of $[\text{FeH}(\text{CO})(\text{dmpe})_2][\text{BPh}_4]$

To a yellow solution of  $[\text{FeH}(\text{CO})(\text{dmpe})_2][\text{BPh}_4]$  (0.70 g, 1.0 mmol) in thf (30 cm<sup>3</sup>) was added an excess of  $\text{KOBU}^+$  (0.20 g). The solution darkened, and was stirred for 1.5 h before filtering through Celite. The reaction was monitored by IR spectroscopy, and the initial  $\nu(\text{CO})$  band at 1926 cm<sup>-1</sup> was replaced by a band characteristic of  $[\text{Fe}(\text{CO})(\text{dmpe})_2]$  at 1830 cm<sup>-1</sup>.<sup>11</sup> The product solution showed a singlet resonance at  $\delta - 77.5$  in  $[\text{H}_8]\text{thf}$ .

### Synthesis of $[\text{FeH}(\text{N}_2)(\text{depe})_2][\text{BPh}_4]$

Unenriched dinitrogen complex (0.75 g, 0.95 mmol) prepared in the usual way was dissolved in thf (50 cm<sup>3</sup>) in a flask (100 cm<sup>3</sup>) equipped with a stirrer bar and greaseless tap. The solution was frozen in liquid nitrogen and the flask evacuated on a high-vacuum line. [ $^{15}\text{N}_2$ ]Dinitrogen was pumped into the flask using a Toepler pump. The frozen mixture was allowed to thaw and the contents of the closed flask were then stirred for 2 h on a water-bath at 40 °C. The gas over the solution was then recovered by refreezing the mixture and using the Toepler pump. After thawing the mixture again the solution was filtered through Celite under argon. Concentration and addition of EtOH afforded a deep yellow solid, which was filtered off, washed with EtOH and Et<sub>2</sub>O, and dried *in vacuo*. Yield 0.64 g, 85%. IR:  $\nu(^{15}\text{N}_2)$  2042 cm<sup>-1</sup>.

Treatment of a thf solution of this complex with  $\text{KOBU}^+$  did not affect the band at 2042 cm<sup>-1</sup>, but the band observed in the nitrogen-14 experiment at 1812 cm<sup>-1</sup> was also generated from the  $^{15}\text{N}$ -labelled compound.

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