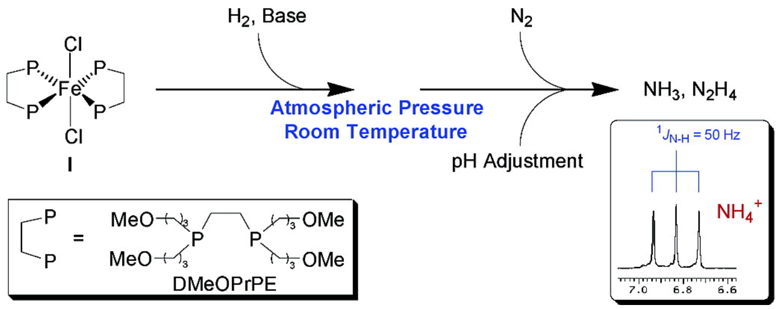
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Reduction of N to Ammonia and Hydrazine Utilizing H as the Reductant

John D. Gilbertson, Nathaniel K. Szymczak, and David R. Tyler

J. Am. Chem. Soc., **2005**, 127 (29), 10184-10185• DOI: 10.1021/ja053030g • Publication Date (Web): 02 July 2005



ACS Publications
High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Reduction of N_2 to Ammonia and Hydrazine Utilizing H_2 as the Reductant

John D. Gilbertson, Nathaniel K. Szymczak, and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

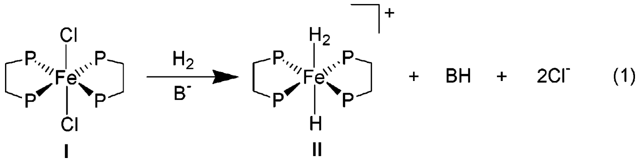
Received May 9, 2005; E-mail: dtyler@uoregon.edu

Homogeneous conversion of N_2 to NH_3 at room temperature and atmospheric pressure has been a coveted goal of chemists since Allen and Senoff[1] reported the first N_2 complex nearly 40 years ago. An enormous amount of fundamental chemistry has been discovered in pursuit of this goal. Among many impressive recent advances are Schrock's[2] report showing that N_2 can be reduced catalytically on a Mo^{III} center using separate external sources of H^+ and electrons and Peters's[3] report showing that Fe nitrides can be reduced with H^+ and external electrons to form NH_3. Fryzuk[4] has stressed the importance of bridging traditional Haber-type chemistry with organometallic chemistry by using H_2 as the source of both the H^+ and the electrons. Hidai[5] was partially able to accomplish this goal by reducing N_2 to NH_3 by reacting the acidic $Ru{-}H_2$ complex, *trans*-$[RuCl(H_2)(dppp)_2]X$ (where dppp = 1,2-bis(diphenylphosphino)propane and X = PF_6, BF_4, OTf, or BPh_4), derived from H_2, with *cis*-$W(PMe_2Ph)_4(N_2)_2$. However, the source of electrons was not H_2 but rather the sacrificial W^0 metal center. Chirik[6] has recently developed the only system to date, excluding Haber-Bosch, that produces NH_3 from N_2 and H_2. In this system, H_2 reacts homogeneously with the bimetallic Zr complex, $[(\eta^5\text{-}C_5Me_4H)_2Zr]_2(\mu^2, \eta^2, \eta^2\text{-}N_2)$.

A clue as to how H_2 might be used as the source of electrons in a room temperature and atmospheric pressure fixation scheme, complementary to the Chirik method, comes from the work of Leigh,[7−9] who devised the cycle shown in Scheme 1. Note that the $Fe(P_2)_2(H_2)H^+$ complex (P_2 = 1,2-bis(dimethylphosphino)ethane) is derived from a hydride source and H^+. In the subsequently formed N_2 complex, the hydride ligand can be reductively deprotonated, forming a five-coordinate Fe^0 complex. Addition of H^+ then yielded modest amounts of NH_3.

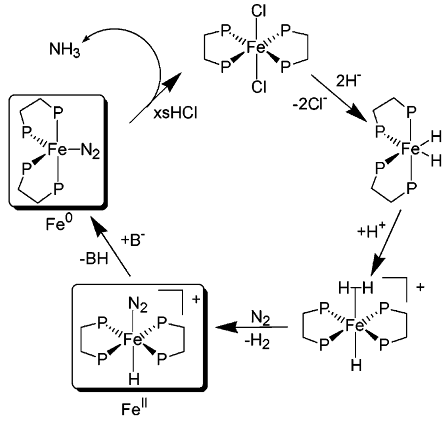
We reasoned that if it were possible to generate the $Fe(P_2)_2(H_2)H^+$ complex using H_2 (rather than a hydride source followed by an acid), then a Leigh-type cycle could be employed in a viable laboratory fixation reaction utilizing H_2 as the reductant. We report here the results of our study showing that this is indeed a workable approach.

We recently reported[10] that *trans*-$Fe(DMeOPrPE)_2Cl_2$ (DMeOPrPE = 1,2-bis(bis(methoxypropyl)phosphino)ethane) (**I**) reacted with H_2 to give *trans*-$[Fe(DMeOPrPE)_2H(H_2)]^+$ (**II**) and H^+ (eq 1).



(1)

Scheme 1. Leigh-type Cycle for the Reduction of N_2 to NH_3 on an Fe^{II} Center



This reaction occurs in H_2O, but is general for most common laboratory solvents.[11] The H_2 ligand can be quantitatively substituted by N_2, yielding a faint yellow solution of the *trans*-$[Fe(DMeOPrPE)_2H(N_2)]^+$ complex, **III**. Due to both the extreme solubility[11] of complexes containing the $Fe{-}(DMeOPrPE)_2$ moiety and the lability of the N_2 ligand (**III** decomposed when exposed to vacuum), the identity of **III** was determined spectroscopically. As shown in Figure 1, the ^1H NMR spectrum of the reaction mixture shows a quintet at δ −18.5 ($^2J_{PH}$ = 49 Hz), revealing the presence of the hydride ligand. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at δ 77.3 due to the *trans*-$Fe(P_2)_2$ unit. The resonance at δ 77.3 in the (proton coupled) ^{31}P spectrum was a doublet ($^2J_{PH}$ = 49 Hz), confirming the presence of the hydride. The terminally bound N_2 shows a characteristic sharp $\nu_{N\equiv N}$ at 2093 cm^{-1}. Inspection of the ^{15}N NMR spectrum of an $^{15}N_2$-enriched sample contained a resonance for each inequivalent nitrogen at δ −60.0 and −40.0.[12]

Following Leigh, the reductive deprotonation of **III** to produce an Fe^0 species was examined. Complex **III** was reacted with 2 equiv of KBu^tO in Et_2O/THF, yielding the orange Fe^0 species, $Fe(DMeOPrPE)_2(N_2)$ (**IV**; Scheme 2). As with complex **III**, the product was characterized spectroscopically in solution (**IV** decomposed when exposed to vacuum). As shown in Figure 2, the $^{31}P\{^1H\}$ NMR spectrum of a filtered reaction solution showed a singlet at δ 79.8.[14] The resonance at δ 79.8 in the (proton coupled) ^{31}P spectrum was also a singlet, confirming the removal of the hydride ligand. This result was further confirmed by inspection of the hydride region in the ^1H NMR spectrum, which showed that the quintet at δ −18.5, assigned to the hydride ligand in **III**, was gone.[16]

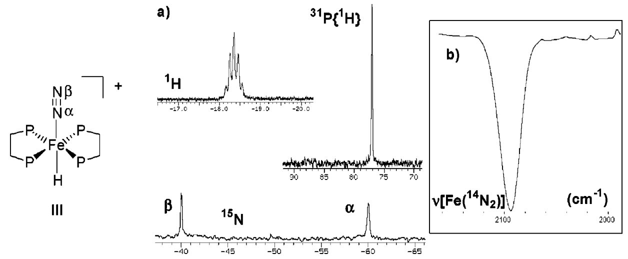
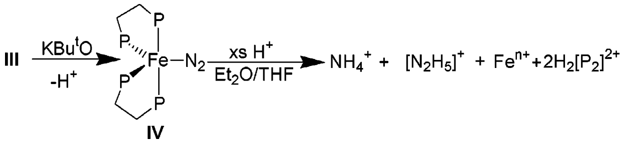


Figure 1. (a) ^{15}N NMR, $^{31}P\{^1H\}$ NMR (inset), ^1H NMR (inset), and (b) IR (toluene) for *trans*-$[Fe(DMeOPrPE)_2(N_2)H]^+$ (**III**).

10.1021/ja053030g CCC: $30.25

Scheme 2. Reductive Deprotonation of **III** to Form **IV**, Followed by Addition of Excess H^+ to **IV**



The IR spectrum of complex **IV** showed a band at 1966 cm^{-1}, assigned to $\nu_{N\equiv N}$.[17] This assignment was confirmed by isotopic substitution of the N_2 ligand. When $^{15}N_2$ was exchanged for the $^{14}N_2$ ligand in **IV**, the band at 1966 cm^{-1} decreased in intensity and a new band appeared at 1899 cm^{-1}, consistent with the predicted shift of 68 cm^{-1}.

The ^{15}N NMR spectrum of molecule **IV** showed a shift in the resonances at δ −60.0 and −40.0 to δ −47.5 and −43.5, respectively, both of which are doublets with $^1J_{NN} = 5$ Hz. The former resonance is assigned as N_α and the latter as N_β. These distinct resonances and the observation of a $\nu_{N\equiv N}$ band in the IR spectrum support the assignment of a terminally bound N_2 ligand in complex **IV**, that is, the complex is not a N_2-bridged dimer.

Completing the Leigh cycle, we observed that addition of an excess of triflic acid[18] to an Et_2O/THF solution of **IV** resulted in a color change from orange to colorless and the formation of a white precipitate. The ^1H NMR spectrum of the precipitate revealed the presence of NH_4^+ (15% per mole Fe in **III**).[19] $N_2H_5^+$ (minimum of 2% per mole Fe in **III**) was also detected,[20] as was $[H_2DMeOPrPE]^{2+}$ (by $^{31}P\{^1H\}$ NMR).

It is possible that the three electrons required for the reduction of N_2 to NH_3 come from the Fe in a Chatt-type scheme.[22] However, it is more likely that only two electrons come from each Fe^0 center.[23] This type of mechanism could involve the formation of an $Fe(N_2)Fe$ dimer[24] that is susceptible to stepwise addition of H^+ followed by subsequent one-electron reductions yielding hydrazine[30] (hence two electrons from each Fe center). Disproportionation of the hydrazine could then account for the formation of ammonia. However, it is not clear how addition of H^+ to the system would cause dimer formation, and without the characterization of the intermediate species, any proposed mechanism is purely speculative. Current studies are underway to optimize the reactions and characterize the reduction intermediates.

This work shows that it is possible to utilize H_2 as the reductant in the room temperature and atmospheric pressure laboratory fixation of N_2 to yield mixtures of NH_3 and N_2H_4. The hydride ligand in **III** is a direct result of the heterolysis of H_2 (eq 1), thus making H_2 the source of electrons for the Fe^{II} to Fe^0 reduction. These two electrons are presumably used in the subsequent reduction of N_2. When eq 1 is substituted into the Leigh cycle, all of the transformations occur by adjustment of the pH. It is intriguing to suggest, therefore, that it should be possible to carry out an N_2 reduction scheme in H_2O via simple pH adjustment. The fact that the $Fe(DMeOPrPE)_2$ scaffold is soluble in H_2O (**III** can be generated in H_2O)[11] lends credence to the possibility of such a scheme. Investigations are underway to optimize the reaction conditions and to study the fixation cycle in H_2O using the H^+ produced in eq 1 as the source of H^+ in Scheme 2.

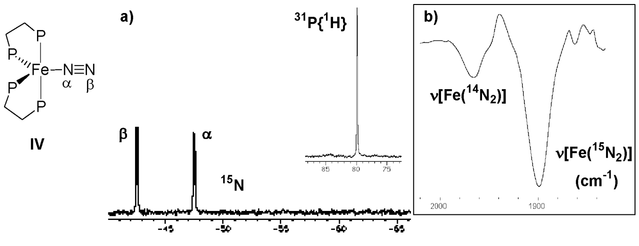


Figure 2. (a) ^{15}N NMR, $^{31}P\{^1H\}$ NMR (inset), and (b) IR (toluene) for mixture of $^{14}N_2$ and $^{15}N_2$ $Fe(DMeOPrPE)_2(N_2)$ (**IV**).

Acknowledgment. This work was supported by the NSF IGERT. Dr. M. Strain is acknowledged for NMR insights.

Supporting Information Available: Text describing experimental details, synthesis of the CO analogues of **III** and **IV**, and selected NMR and IR data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Allen, A. D.; Senoff, C. V. *J. Chem. Soc., Chem. Commun.* **1965**, 621.
(2) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.
(3) Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2004**, *126*, 6254.
(4) Fryzuk, M. D.; Love, J. B.; Rettig, S. J.; Young, V. G. *Science* **1997**, *275*, 1445.
(5) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540.
(6) Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.
(7) Leigh, G. J.; Jimenez-Tenorio, M. *J. Am. Chem. Soc.* **1991**, *113*, 5862.
(8) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. *J. Chem. Soc., Dalton Trans.* **1993**, 3041.
(9) Hall, D. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1996**, 3539.
(10) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *Inorg. Chem.* **2004**, *43*, 3341.
(11) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. Manuscript in preparation.
(12) The ^{15}N NMR spectrum is consistent with the previously reported DMPE and DEPE analogues.[13] In the case of DMPE, unresolvable $^1J_{N-N}$ was also reported.
(13) Field, L. D.; Hazari, N.; Lin Li, H.; Luck, I. *J. Magn. Reson. Chem.* **2003**, *41*, 709.
(14) The resonance remained a singlet even on lowering the temperature to 193 K. The structures of product **IV** with the analogous DMPE[9] and DEPE[15] ligands are also accepted to be trigonal bipyramidal.
(15) Hirano, M.; Akita, M.; Kubo, H.; Fukuoka, A.; Komiya, S. *J. Chem. Soc., Dalton Trans.* **1997**, 3453.
(16) To further characterize species **III** and **IV**, the CO analogues were generated. See Supporting Information for details.
(17) Note that the $\Delta\nu$ from 2093 to 1966 cm^{-1} in going from **III** to **IV** is indicative of increased π-back-bonding in **IV** relative to **III**, as expected in going from Fe^{II} to Fe^0. Similar shifts in the stretching frequency have been observed for the DMPE[9] and DEPE[15] analogues.
(18) When the reactions were carried out with an excess of a mineral acid, such as HCl, only decomposition products were observed.
(19) The NH_4^+ was quantified by integration of the NH_4^+ resonance with respect to an internal reference of ferrocene.[2,3]
(20) $N_2H_5^+$ was determined colorimetrically.[21] The formation of a presumed hydrazine−triflic acid adduct prevented quantification via ^1H NMR. The ^1H NMR spectrum, however, suggests that much more than 2% hydrazine is being formed in the reaction. See Supporting Information.
(21) Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006.
(22) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
(23) The fate of the Fe depends on the concentration of the H^+ used in Scheme 2. When smaller amounts of acid are used, significant amounts of Fe^{II} as **II** and **III** are detected.[11] Note that a similar protonation of **III** resulted in no detectable ammonium or hydrazinium. See Supporting Information for details.
(24) It has been established that $M(N_2)M$-type complexes are susceptible to protonation at the bridging dinitrogen.[25−29]
(25) Manriquez, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 6229.
(26) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.
(27) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 8185.
(28) Leigh, G. J.; Prieto-Alcon, R.; Sanders, J. R. *J. Chem. Soc., Chem. Commun.* **1991**, 921.
(29) Dilworth, J. R.; Henderson, R. A.; Hills, A.; Hughes, D. L.; Macdonald, C.; Stephens, A. N.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1990**, 1077.
(30) This type of mechanism has been proposed,[31] where an Fe^0 species was shown to produce significant amounts of hydrazine upon addition of H^+.
(31) George, T. A.; Rose, D. J.; Chang, Y.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1995**, *34*, 1295.

JA053030G