Base-Mediated Conversion of Hydrazine to Diazene and Dinitrogen at an Iron Center

Leslie D. Field,* Hsiu L. Li, and Alison M. Magill

School of Chemistry, University of New South Wales, New South Wales 2052, Australia

The treatment of the hydrazine complex *cis*-[Fe(N$_2$H$_4$)(dmpe)$_2$]$^{2+}$ with base afforded the diazene complex *cis*-[Fe(N$_2$H$_2$)(dmpe)$_2$]. This reaction is reversed by the treatment of the diazene complex with a mild acid, while treatment of the hydrazine complex with a mixture of KOBu^t and Bu^{t}Li afforded the dinitrogen complex [Fe(N$_2$)(dmpe)$_2$].

Biological or industrial conversion of dinitrogen to ammonia, as mediated by transition metals, must proceed through a series of intermediate stages.[1] The nature of the metal-bound intermediates provides vital information about the mechanism of the transformation. The formation of ammonia and hydrazine from iron dinitrogen complexes has been reported,[2,3] although few mechanistic studies have been undertaken.[4] Iron complexes of hydrazine and diazene are possible intermediates in the reduction of coordinated dinitrogen in such systems.

We recently reported the syntheses of a side-on-bound hydrazine complex, *cis*-[Fe(N$_2$H$_4$)(dmpe)$_2$]$^{2+}$ (**1**), as well as the first side-on-bound diazene complex, *cis*-[Fe(NH═NH)(dmpe)$_2$] [**2**; dmpe = 1,2-bis(dimethylphosphino)ethane].[5] The diazene complex was previously isolated by reduction of **1** (formed in situ by the treatment of *trans*-[FeCl$_2$(dmpe)$_2$] with hydrazine) with potassium graphite in

Scheme 1
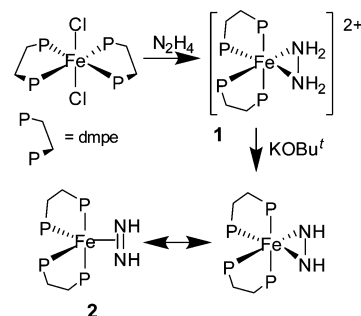
relatively poor yield (17%). We now report that this iron(0) diazene complex can also be synthesized in significantly improved yield (55%) by deprotonation of the dichloride salt of **1** with KOBu^t (Scheme 1). The purity of the product was also improved in that no *cis*-[FeH$_2$(dmpe)$_2$] was formed as a reaction byproduct using this route.

In an analogous reaction, the treatment of a solution of *trans*-[FeCl$_2$(dmpe)$_2$] and 1,2-diphenylhydrazine with KOBu^t afforded the iron(0) azobenzene complex *cis*-[Fe(PhN═NPh)(dmpe)$_2$] (**3**). No reaction was observed between the dichloride starting material with 1,2-diphenylhydrazine in the absence of KOBu^t, indicating that deprotonation of the disubstituted hydrazine is probably the first step in the reaction sequence.

Such a reaction gives rise to the question of whether **2** should be considered an iron(II) hydrazido(2−) complex or an iron(0) diazene π complex. A transition-metal complex bearing an alkene or an alkyne ligand may be considered as either (i) a metallacyclic complex where the metal has two anionic σ donors or (ii) a donor−acceptor π complex where bonding arises from electron donation from a filled *p* orbital of the ligand into a suitably directed vacant metal orbital and back-donation from an occupied metal *d* orbital into the antibonding π^* orbital of the ligand.[6,7] While these two models are often regarded as complementary, in reality, there is a continuum between the two extremes.[8] Theoretically,

(1) (a) Barney, B. M.; Lee, H. I.; Dos Santos, P. C.; Hoffmann, B. M.; Dean, D. R.; Seefeldt, L. C. *Dalton Trans.* **2006**, 2277–2284. (b) Kozak, C. M.; Mountford, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 1186–1189. (c) Schlogl, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 2004–2008. (d) Schrock, R. R. *Chem. Commun.* **2003**, 2389–2391. (e) Pool, J. A.; Bernskoetter, W. H.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 14326–14327. (f) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625. (g) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177–181.

(2) (a) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. *J. Am. Chem. Soc.* **2005**, *127*, 10184–10185. (b) George, T. A.; Rose, D. J.; Chang, Y. D.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1995**, *34*, 1295–1298. (c) Jezowska-Trzebiatowska, B.; Sobota, P. *J. Organomet. Chem.* **1972**, *46*, 339–343. (d) Borodko, Y. G.; Broitman, M. O.; Kachapina, L. M.; Shilov, A. E.; Ukhin, L. Y. *J. Chem. Soc., Chem. Commun.* **1971**, 1185–1186.

(3) Hall, D. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1996**, 3539–3541.

(4) Leigh, G. J. *J. Organomet. Chem.* **2004**, *689*, 3999–4005.

(5) Field, L. D.; Li, H. L.; Dalgarno, S. J.; Turner, P. *Chem. Commun.* **2008**, 1680–1682.

(6) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653–1662.

(7) Pidun, U.; Frenking, G. *Organometallics* **1995**, *14*, 5325–5336.

(8) Pidun, U.; Frenking, G. *J. Organomet. Chem.* **1996**, *525*, 269–278.
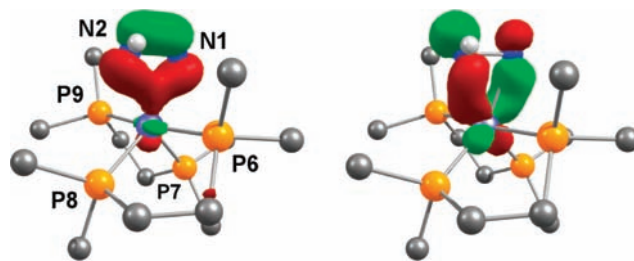
Table 1. CDA Results for **2**

basis set[a]	d	b	r	Δ
BS2	0.540	0.324	−0.415	−0.047
BS3	0.547	0.323	−0.417	−0.044

[a] BS2: 6-311G(2d,p) on iron and 6-31G(d) on other atoms. BS3: 6-311G(2d,p) and LANL2DZ ECP on iron and 6-31G(d) on other atoms; d = electron donation; b = back-donation; r = repulsive polarization; Δ = rest term.

the question of whether a metal−ligand bond should be classified as covalent or of the donor−acceptor type may be answered by charge decomposition analysis (CDA),[9] which has been used to determine the nature of bonding interactions in both transition-metal[6−8,10,11] and main-group[12] complexes. CDA considers the bonding in a complex in terms of the (fragment) molecular orbital interactions between two closed-shell fragments, in this case $Fe(dmpe)_2$ and $NH=NH$. CDA allows the relative amount of electron donation (d), back-donation (b), and the interaction between the occupied orbitals of both fragments leading to repulsive polarization (r) to be calculated. In addition, the rest term, Δ, resulting from the mixing of unoccupied orbitals on the two fragments is also determined. Δ is a highly sensitive indicator that may be used to determine the nature of the bonding interaction between two fragments: in donor−acceptor complexes, this term should be virtually zero.[6]

The bond lengths calculated with the B3LYP density functional and basis set BS1[13] are in good agreement with the experimental bond distances for **2**, and a comparison shows that the average difference for core bond lengths is 0.045 Å. The results of CDA calculations, using this optimized geometry with two different basis sets,[14] are given in Table 1.

The donation to back-donation ratio (d/b), ca. 1.7, shows that there is significant back-donation from the metal center to the unoccupied orbitals on the ligand. The orbitals involved in donation and back-donation are shown in Figure 1. The rest term Δ is virtually zero,[15] which clearly shows that

(9) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352–9362.
(10) (a) Dapprich, S.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 354–357. (b) Boehme, C.; Frenking, G. *Organometallics* **1998**, *17*, 5801–5809. (c) Szilagyi, R. K.; Frenking, G. *Organometallics* **1997**, *16*, 4807–4815. (d) Dapprich, S.; Frenking, G. *Organometallics* **1996**, *15*, 4547–4551. (e) Vyboishchikov, S. F.; Frenking, G. *Theor. Chem. Acc.* **1999**, *102*, 300–308.
(11) Decker, S. A.; Klobukowski, M. *J. Am. Chem. Soc.* **1998**, *120*, 9342–9355.
(12) Frenking, G.; Dapprich, S.; Kohler, K. F.; Koch, W.; Collins, J. R. *Mol. Phys.* **1996**, *89*, 1245–1263.
(13) Geometry optimization was undertaken using the B3LYP density functional and BS1: 6-311+G(2d,p) basis set and LANL2DZ ECP on iron, together with the 6-31G(d) basis set on all other atoms using *Gaussian03*. CDA was performed with the *CDA2.1* program developed by S. Dapprich and G. Frenking (available from ftp.chemie.uni-marburg.de) using the B3LYP/BS2 (6-311G(2d,p) basis set on iron, together with the 6-31G(d) basis set on all other atoms) or the B3LYP/BS3 (6-311G(2d,p) basis set and LANL2DZ ECP on iron, together with the 6-31G(d) basis set on all other atoms). AIM calculations were performed with *AIMAll* (version 08.05.04), Todd A. Keith, 2008 (available from aim.tkgristmill.com).
(14) The inclusion of an all-electron basis set did not have any deleterious effects on the CDA undertaken here, with the results being virtually identical regardless of the basis set used.
(15) For donor−acceptor complexes, the absolute value of Δ is generally <0.05. For example, see: Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717–774. Vyboishchikov, S. F.; Frenking, G. *Chem.−Eur. J.* **1998**, *8*, 1428–1438, and ref 8.

Figure 1. Donation (left) and back-donation (right) orbitals for **2**. Hydrogen atoms on phosphine ligands have been omitted for clarity.

Table 2. AIM Results for **2**

	$\rho(r_c)^a$	$\nabla^2\rho(r)^a$
Fe−N1	0.095	0.350
Fe−N2	0.094	0.349
N1−N2	0.377	−0.573
N1−Fe−N2	0.473	
Fe−P6	0.077	0.219
Fe−P7	0.089	0.204
Fe−P8	0.089	0.210
Fe−P9	0.083	0.227

[a] $\rho(r_c)$ = electron density; $\nabla^2\rho(r)$ = Laplacian of electron density.

complex **2** is a donor−acceptor π complex between diazene and iron(0) rather than a hydrazido fragment binding to an iron(II) metal center.

Further evidence that **2** should be considered as a donor−acceptor complex is provided by Bader's Atoms In Molecules (AIM) theory.[16] AIM theory calculates the electron density, $\rho(r)$, and the Laplacian of the electron density, $\nabla^2\rho(r)$, which yields information regarding the nature of the bonding.[11,16,17] The results of the AIM analysis are shown in Table 2. For all of the Fe−N and Fe−P bonds, the values of the Laplacian are typical of systems with closed-shell, donor−acceptor interactions.[11,18]
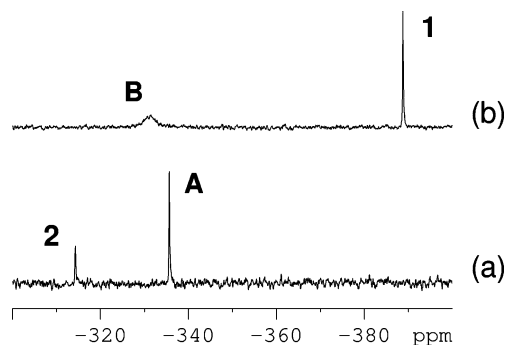
Quite remarkably, the deprotonation of the hydrazine complex **1** to form the diazene complex **2** is reversible, and the reaction of **2** with the weak acid 2,6-lutidinium triflate reforms the hydrazine complex **1**. This was proven by labeling the hydrazine complex with ^{15}N and monitoring the reaction mixture with NMR spectroscopy. Upon treatment of the poorly soluble orange dichloride salt of hydrazine complex **1** with KOBu^t in tetrahydrofuran-d_8 (THF-d_8), a yellow solution formed and a ^{15}N NMR signal at −314.4 ppm for diazene complex **2** was observed (Figure 2a). Residual uncoordinated hydrazine (**A**) at −335.8 ppm was also present. After the addition of 2,6-lutidinium triflate, a color change to orange and two broad doublets at 5.06 and 4.21 ppm ($^1J_{H-N}$ = 79 Hz) for the protons on the hydrazine ligand of **1** were observed in the ^1H NMR spectrum as well as a ^{15}N signal at −388.8 ppm (Figure 2b), indicating that the initial deprotonation was indeed reversible. A broad signal for hydrazinium ($NH_3NH_3^{2+}$, **B**) at −331.5 ppm from

(16) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1994.
(17) Frenking, G.; Sola, M.; Vyboishchikov, S. F. *J. Organomet. Chem.* **2005**, *690*, 6178–6204.
(18) By way of comparison, the Laplacian of the electron density in the iron−alkyne bond of the donor−acceptor complex $Fe(CO)_4(C_2H_2)$ was shown to be 0.358. In contrast, the Laplacian of the electron density for the C−C bond (at −1.008) was found to be consistent with that of shared, covalent interactions.[11]

Figure 2. $^{15}N\{^1H\}$ NMR spectra (THF-d_8, 298 K, 41 MHz, referenced to nitromethane) of **1** (a) after the addition of KOBu^t and (b) after the addition of 2,6-lutidinium triflate (**A** = NH_2NH_2; **B** = $NH_3NH_3^{2+}$).

protonation of residual hydrazine was also detected in the reprotonation step. To the best of our knowledge, the reversible interconversion of an iron(II) hydrazine to an iron(0) diazene is unprecedented in the literature.

After several weeks, ^{15}N NMR signals at -364.4 ppm for ammonium (NH_4^+)[19] and at -417.6 ppm for an ammine complex cis-$[FeCl(NH_3)(dmpe)_2]^+$ (**4**) were detected in the reaction mixture. The identity of **4** was confirmed by the preparation of an authentic sample by the treatment of trans-$[FeCl_2(dmpe)_2]$ with a saturated solution of ammonia in THF.[20] The reaction of hydrazine complex **1** with 2,6-lutidinium triflate to form NH_4^+ and ammine complex **4** has been verified independently.

The treatment of ^{15}N-labeled hydrazine complex **1** with a mixture of KOBu^t and Bu^{t}Li (Schlosser base)[21] in hexane afforded the end-on-bound dinitrogen complex $[Fe(N_2)(dmpe)_2]$ (**5**),[3,22,23] as shown by IR and ^{15}N NMR

Scheme 2
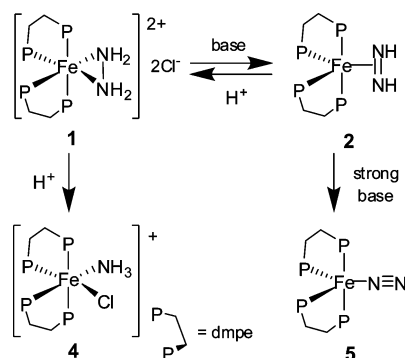
spectroscopy (Scheme 2). An absorbance at 1928 cm^{-1} for $\nu(^{15}N_2)$ matched exactly with that of an authentic sample of $[Fe(^{15}N_2)(dmpe)_2]$ prepared by the reduction of trans-$[FeCl_2(dmpe)_2]$ with KC_8 in hexane under nitrogen followed by placement of the solution under an atmosphere of $^{15}N_2$. In the ^{15}N NMR spectrum, two resonances at -47.7 and -48.7 ppm were observed, which agree with those for the authentic sample. The reaction probably proceeds via successive deprotonation of the coordinated hydrazine to form a coordinated diazene and then elimination of H_2 to form the dinitrogen species.[25]

We have demonstrated the chemistry of iron diazene and hydrazine complexes, which now link iron dinitrogen, diazene, hydrazine, and ammine complexes in a chain of chemical interconversions. These results may lend further insight into the mechanism of nitrogen reduction at early-transition-metal centers.

Supporting Information Available: Experimental conditions, spectroscopic data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801856Q

(19) The ^{15}N NMR chemical shift for ammonium was verified by a comparison with an authentic sample of ammonium triflate prepared in situ in THF.

(20) trans-$[FeCl_2(dmpe)_2]$ (100 mg, 0.234 mmol) was dissolved in an ammonia-saturated solution of THF (3 mL) under nitrogen and the solution left to stand in a sealed flask for 9 days. The purple precipitate formed was collected by filtration, dissolved in methanol, and added to a solution of NaBPh$_4$ (99 mg, 0.29 mmol) in methanol. The flaky dark-pink crystalline solid was collected by filtration, washed with methanol, and dried in vacuo (0.126 g, 71%). Elem anal. Calcd for $C_{36}H_{55}BClFeNP_4 \cdot CH_4O$ (759.84): C, 58.5; H, 7.8; N, 1.8. Found: C, 58.5; H, 7.9; N, 1.9%. $^1H\{^{31}P\}$ NMR (THF-d_8, 400 MHz): δ 7.28 (m, 8H, o-Ph), 6.87 (m, 8H, m-Ph), 6.73 (m, 4H, p-Ph), 3.27 (s, 3H, CH_3OH), 3.05 (br, 1H, CH_3OH), 2.12−1.63 (m, 6H, CH_2, overlap with THF-d_8 residual), 1.55 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.47−1.36 (m, 5H, CH_2 and NH_3), 1.44 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 1.07 (s, 6H, 2 × CH_3), 0.87 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (THF-d_8, 162 MHz): δ 73.0 (ddd, $^2J_{P_A-P_B}$ = 32.8 Hz, $^2J_{P_A-P_C}$ = 41.4 Hz, $^2J_{P_A-P_D}$ = 41.2 Hz, 1P, P_A), 63.7 (ddd, $^2J_{P_B-P_C}$ = 50.3 Hz, $^2J_{P_B-P_D}$ = 146.0 Hz, 1P, P_B), 60.9 (ddd, $^2J_{P_C-P_D}$ = 31.4 Hz, 1P, P_C), 56.0 (ddd, 1P, P_D). $^{15}N\{^1H\}$ NMR (THF-d_8, 41 MHz, from HN-HSQC): δ −417.1 (correlation with ^1H δ 1.41, NH_3). IR: 3537m, 3340m, 3321m, 3261w, 3232w, 3189w, 3055m, 3040m, 1620w, 1578m, 1558w, 1422s, 1302m, 1281m, 1266w, 1240s, 1186w, 1176w, 1131w, 1075w, 1033w, 1020s, 931s, 892s, 842s, 801w, 750s, 733s, 707s, 651m, 611s cm^{-1}.

(21) Schlosser, M.; Strunk, S. Tetrahedron Lett. **1984**, 25, 741−744.

(22) Leigh, G. J.; Jimenez-Tenorio, M. J. Am. Chem. Soc. **1991**, 113, 5862−5863.

(23) The dinitrogen complex **5** is the major product in the reaction and is formed in a yield of approximately 30% from **1** (by NMR spectroscopy). Complex **5** is unstable and decomposes under reduced pressure,[3,22,24] and it was not possible to determine an isolated yield.

(24) Hills, A.; Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Rowley, A. T. J. Chem. Soc., Dalton Trans. **1993**, 3041.

(25) The possibility that the reaction proceeds by loss of diazene followed by disproportionation to yield hydrazine and free dinitrogen, which can be trapped by iron(0), can be discounted. The reaction is done using ^{15}N-labeled $[Fe(N_2H_4)(dmpe)_2]^{2+}$ **1** under a ^{14}N atmosphere, and there is little incorporation of ^{14}N into the product $Fe(N_2)(dmpe)_2$ **5** by IR spectroscopy.