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A Five-Coordinate Phosphino/Acetate Iron(II) Scaffold That Binds N_2, N_2H_2, N_2H_4, and NH_3 in the Sixth Site

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S Supporting Information

ABSTRACT: A family of iron(II) complexes that coordinate dinitrogen, diazene, hydrazine, and ammonia are presented. This series of complexes is unusual in that the complexes within it feature a common auxiliary ligand set and differ only by virtue of the nitrogenous N_xH_y ligand that occupies the sixth binding site. The ability of an iron center to bind N_2, N_2H_2, N_2H_4, and NH_3 is important to establish in the context of evaluating catalytic N_2 reduction schemes that invoke these nitrogenous species. Such a scenario has been proposed as an iron-mediated, alternating reduction scheme within the cofactor of nitrogenase enzymes.

Owing to its biological and industrial relevance, establishing mechanisms for the reduction of N_2 to NH_3 is a longstanding goal of chemists.[1] Several mechanisms have been proposed for a metal-mediated reduction, with the distal (i.e., $M^nN{\equiv}N \rightarrow M^{n+3}{\equiv}N + NH_3 \rightarrow M^n + NH_3$) and alternating (i.e., $M^nN{\equiv}N \rightarrow M^nHN{=}NH \rightarrow M^nH_2NNH_2 \rightarrow M^n + 2\ NH_3$) mechanisms representing two limiting schemes.[1c,d,2] Schrock[3] and Nishibayashi[4] have respectively prepared mono- and dimolybdenum complexes that serve as catalysts for this transformation, the former of which is thought to proceed via a distal reduction scheme. To date, there are no examples of well-defined synthetic catalysts thought to proceed via the alternating reduction scheme, although it has been suggested that the biological reduction of N_2 to NH_3 at the FeMo cofactor of nitrogenase may proceed via such a mechanism.[5] Circumstantial support of such a hypothesis derives from the observation that both diazene and hydrazine are substrates for nitrogenase.[1d,5] Also, spectroscopic studies of the FeMo cofactor under turnover conditions appear to be consistent with an iron-bound NH_y species, which is also observed in the reduction of diazene and hydrazine.[5] Although the site of N_2 coordination and subsequent reduction remains a matter of uncertainty, recent studies have suggested that N_2 is reduced at one or more iron centers.[1d,6] Hence, there is much interest in preparing synthetic iron complexes that coordinate N_xH_y ligands[7] because they serve as structural and spectroscopic models to the postulated trapped intermediates.

Mono- and diiron complexes that coordinate N_2H_y ligands (y = 2, 3) remain relatively rare and exhibit both acid/base and redox reactivity.[7a−c,e,f] Despite this rich reactivity, there are no reported iron systems that can coordinate and/or interconvert a range of N_xH_y ligands that encompass the full range of sp, sp^2, and sp^3 hybridization at the nitrogen atoms, and the accompanying nitrogen-atom oxidation states 0, 1−, 2−, and 3−.[7g,h,8] Such systems are rare for any metal, with only two ruthenium[9] and one manganese[10] systems published in the literature. Herein we describe a series of iron complexes that coordinate N_2, N_2H_2, N_2H_4, and NH_3. These complexes feature identical auxiliary ligands, are all iron(II), and only differ in the extent that the nitrogenous ligand is reduced.

Access to the N_xH_y chemistry of present interest is realized using a five-coordinate iron(II) complex, $[PhBP^{CH2Cy}{}_3]Fe(OAc)$ (**1**; $[PhBP^{CH2Cy}{}_3] = PhB(CH_2P(CH_2Cy)_2)_3{}^-$). Complex **1** is quantitatively formed in the reaction between $[PhBP^{CH2Cy}{}_3]FeMe$ and 1 equiv of AcOH and is isolated as an analytically pure gray powder (Scheme 1). Five-coordinate **1** is paramagnetic with a room temperature solution magnetic moment of 4.5 μ_β.

Complex **1** serves as a scaffold for which L-type ligands can bind, generating low-spin six-coordinate mono- and diiron species. For example, cooling solutions of **1** under an N_2 atmosphere results in the coordination of 0.5 equiv of N_2 to generate the pink and diamagnetic μ-N_2 species $\{[PhBP^{CH2Cy}{}_3]Fe(OAc)\}_2(\mu\text{-}N_2)$ (**2**). Crystals of **2** suitable for diffraction can be grown from saturated Et_2O solutions of **2** stored at −35 °C in a glovebox, and its solid-state structure has been obtained (Figure 1a). The respective Fe−N and N−N distances of 1.874(3) and 1.120(5) Å indicate a small degree of N_2 activation.[11] Consistent with the small degree of N_2 activation, a ν(NN) stretch is observed at 2083 cm^{-1}, which shifts to 2010 cm^{-1} upon ^{15}N-isotopic labeling (calcd: 2012 cm^{-1}).

In solution, as in the solid state, **2** exists as a diiron species; the ^{15}N NMR spectrum of ^{15}N-**2** [(THF)-d_8, −75 °C] shows a single resonance at 328.6 ppm, which is split into a doublet by the *trans*-phosphine phosphorus atom ($^2J_{PN} \approx 15$ Hz). Despite formation of a diiron species, the coordinated N_2 ligand in **2** is labile, and warming solutions of **2** to room temperature regenerates **1**.

The treatment of **2** with 0.5 equiv of N_2H_4 at −78 °C generates the purple diiron species $\{[PhBP^{CH2Cy}{}_3]Fe(OAc)\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2H_4)$ (**3**; Scheme 1). The presence of a single ^{15}N NMR chemical shift for ^{15}N-**3** (δ = 103 ppm), coupled with a single NH_2 resonance in the ^1H NMR spectrum (δ = 2.51 ppm), indicates a bridging hydrazine ligand. As for **2**, the hydrazine ligand is labile; at −30 °C, resonances ascribed to both **1** and **3** are observed by ^1H NMR spectroscopy.

The hydrazine species **3** is not thermally stable and, at −10 °C, undergoes a disproportionation reaction to precipitate the dark-blue diazene species $\{[PhBP^{CH2Cy}{}_3]Fe(OAc)\}_2(\textit{trans}\text{-}\mu\text{-}\eta^1{:}\eta^1\text{-}N_2H_2)$ (**4**)

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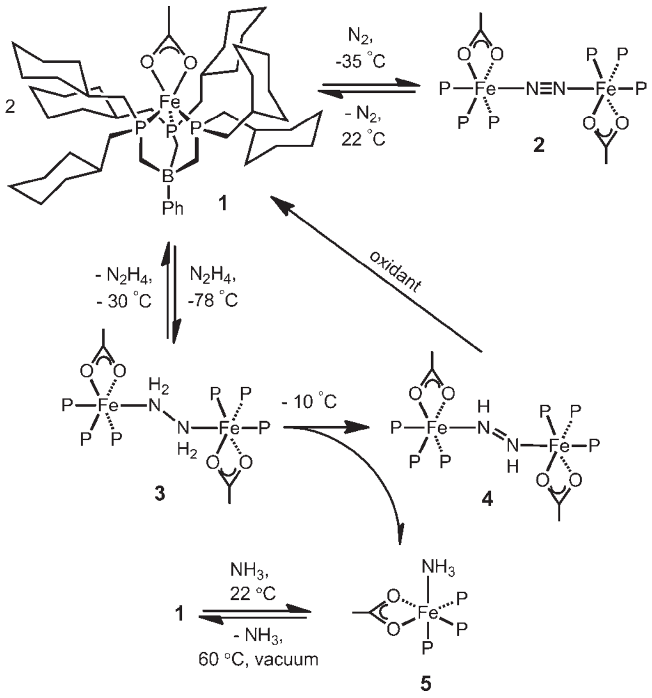
Scheme 1



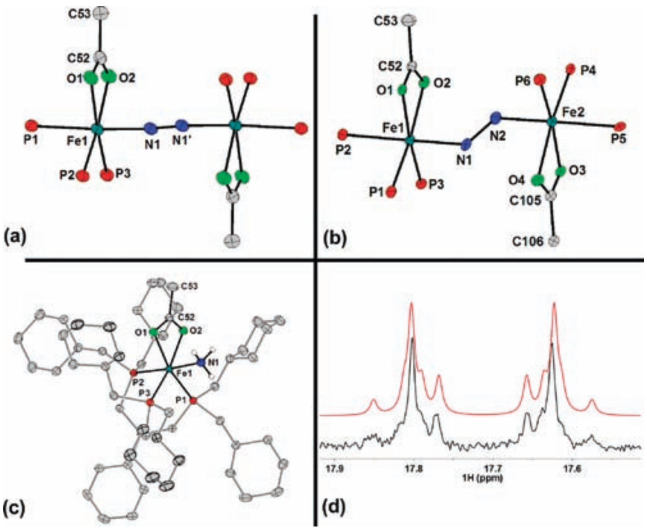


Figure 1. Displacement ellipsoid (50%) representation of (a) the core atoms of μ-N_2 **2**, (b) the core atoms of μ-N_2H_2 **4** (major component only), and (c) **5**. Protons that were not located in the difference map have been removed for clarity. Select bond distances (Å) and angles (deg) for **2**: Fe1−P1 2.285(1), Fe1−P2 2.2319(9), Fe1−P3 2.2361(9), Fe1−O1 2.076(2), Fe1−O2 2.083(2), Fe1−N1 1.874(3), N1−N1′ 1.120(5); Fe1−N1−N1′ 174.9(3). Select bond distances (Å) and angles (deg) for **4**: Fe1−P1 2.219(3), Fe1−P2 2.311(4), Fe1−P3 2.240(4), Fe1−O1 2.082(8), Fe1−O2 2.110(7), Fe1−N1 1.902(8), Fe2−N2 1.898(8), N1−N2 1.31(1); Fe1−N1−N2 128.1(7), Fe2−N2−N1 129.0(7). (d) Diazene resonance in the $^1H\{^{31}P\}$ NMR spectrum (C_6D_6, 25 °C) of ^{15}N-**4** indicating the AA′XX′ splitting pattern (experimental, black; fit, red). The data were simulated with MestReNova using the following parameters: δ = 17.72 ppm, $^1J_{NH}$ = −71.0 Hz, $^2J_{NH}$ = −1.1 Hz, $^3J_{HH}$ = 21.0 Hz, $^1J_{NN}$ = 12.0 Hz, and line width = 3.5 Hz.

from solution, leaving the ammonia complex $[PhBP^{CH2Cy}{}_3]$-$Fe(OAc)(NH_3)$ (**5**; Scheme 1) in the supernatant.

The presence of a bridging trans diazene ligand in **4** is readily discerned by NMR spectroscopy. A resonance centered at 434 ppm is observed in the ^{15}N NMR spectrum of ^{15}N-**4**, indicative of a moderately activated diazene ligand.[7e,f,12] In the corresponding $^1H\{^{31}P\}$ NMR spectrum, an AA′XX′ multiplet centered at 17.72 ppm is observed, consistent with the presence of a bridging diazene ligand (Figure 1d; see the caption for simulation parameters). The relatively large $^3J_{HH}$ of 21.0 Hz suggests a trans ligation, and the magnitude of the $^3J_{HH}$ coupling in π-conjugated systems can further be used to infer bond distances;[13] a linear relationship exists between $^3J_{HH}$ and the N−N bond distance for trans-ligated diazene complexes (see the Supporting Information). The observed $^3J_{HH}$ of 21.0 Hz suggests an N−N bond distance of ca. 1.31 Å in **4**, between that expected for an N−N single and a double bond.

The solid-state structure of **4** was obtained, and the core atoms of the structure are shown in Figure 1b. The quality of the data set is compromised of a total molecule disorder, in which 18% of the molecules are translocated along the *b* axis of the *P*2(1)/*c* unit cell. Although the diazene protons could not be located in the difference map, the structure confirms the trans diazene ligation. The average Fe−N−N angle of 128.5° is consistent with sp^2-hybridized nitrogen atoms, and the metrical parameters about the Fe−NH−NH−Fe core are similar (within error) to those of other six-coordinate diiron(II) bridging diazene complexes.[7a,e] Further, the N−N distance of 1.31(1) Å is in good agreement with that predicted from the $^3J_{HH}$ coupling constant.

A comparison of the structures for μ-N_2 **2** and μ-N_2H_2 **4** indicates little reorganization of the auxiliary ligands of the iron centers and a net $2e^-/2H^+$ difference in the nitrogenous ligand. In both structures, the acetate ligands reside on opposite faces of the dinuclear framework, and the Fe−O and Fe−P distances (which are cis to the N_2H_y ligand) are nearly equivalent. Only the Fe−P distance to the phosphine that is trans to the N_2H_y ligand significantly changes, with a ca. 0.02 Å elongation upon going from **2** to **4**, consistent with a stronger trans influence exerted by diazene than dinitrogen.

Worth noting is that the trans diazene in **4** is prone to dissociation. Heating a toluene solution of **4** to 60 °C for 2 h results in complete transformation to acetate **1** and ammonia complex **5**, with the ammonia in the latter species presumably generated from disproportionation of free diazene. In contrast, the cis diazene in the related complex $\{[PhBP^{CH2Cy}{}_3]Fe\}_2(\mu$-$\eta^1{:}\eta^1$-$N_2H_2)(\mu$-$NH_2)_2$ is stable in solution for days at 60 °C.[7e] Because the cis isomer of free diazene is less stable than the trans isomer,[14] the robustness observed in the latter species is likely due to the presence of additional bridging ligands that strengthen the fidelity of the bimetallic unit.

The disproportionation reaction of μ-N_2H_4 **3** also generates the ammonia species **5**, whose solid-state structure is shown in Figure 1c. This species can alternatively be prepared by the addition of excess NH_3 to a THF solution of **1** (Scheme 1). Although **5** is stable in solution at room temperature, heating solutions of **5** under vacuum results in NH_3 loss and the formation of **1**.

Hydrazine disproportionation reactions to generate diazene and ammonia have been observed at diruthenium[9b,15] and diiron[7d,e] centers and can be regarded as the first step in the disproportionation of hydrazine to dinitrogen and ammonia:

$$N_2H_4 \xrightarrow[-2NH_3]{+N_2H_4} N_2H_2 \xrightarrow[-2\ NH_3]{+N_2H_4} N_2$$

To determine whether μ-N_2H_2 **4** further reacts with hydrazine to generate N_2 and NH_3, 0.95 equiv of $^{15}N_2H_4$ was added to a THF solution of **4**, and both the reaction volatiles and residual solids were analyzed by NMR spectroscopy. ^1H NMR analysis of the volatiles established the formation of $^{15}NH_3$ (ca. 50% yield) and no $^{14}NH_3$. ^1H and ^{31}P NMR spectroscopy of the residual solids indicated that acetate **1** and ammonia **5** were the major iron-containing products, with ^{14}N **4** present as a minor species. These results are consistent with a disproportionation mechanism in which the bound diazene is oxidized to N_2 by free N_2H_4, which itself is reduced to NH_3.

Although **1** can serve as a hydrazine disproportionation catalyst (in the presence of 10 equiv of N_2H_4, a 16% yield of NH_3 is obtained), the reaction is hampered by ligand degradation; in addition to **1** and **5**, $(CH_2Cy)_2PMe$ and other, unidentifiable products are present in the resulting ^1H and ^{31}P NMR spectra.

The ability to isolate iron complexes that only differ in the extent of reduction of the nitrogenous ligand suggests the possibility that these complexes may be interconverted via redox reactions. Although the cyclic voltammogram of μ-N_2 **2** (obtained at −35 °C) shows a quasi-reversible reduction at ca. −2.2 V, the chemical reduction of **2** with $[Na][C_{10}H_8]$ results in a mixture of unidentifiable products. Attempts to chemically reduce μ-N_2 **2** to μ-N_2H_4 **4** at −78 °C with well-defined hydrogen-atom-transfer agents (i.e., catechol, hydroquinone, Bu_3SnH, cyclohexadiene, and PhSH) or with combinations of reductants (i.e., $Cp^*{}_2Fe$, $Cp^*{}_2Co$, Cp_2Co, and $[Na][C_{10}H_8]$) and acids (i.e., HOAc, HOTf, and $[lutH][BPh_4]$) did not yield the desired transformation, and in most instances, **1** was the only identifiable iron-containing species present (ligand degradation also occurred). In contrast, the treatment of **4** with oxidants (e.g., *p*-benzoquinone and $Pb(OAc)_4$) results in the formation of **1**, which may proceed through μ-N_2 **2**. These results are perhaps not unexpected when one considers the respective gas-phase bond dissociation energies of NN-$H^\bullet$ (ca. 0 kcal/mol) and HNN-$H^\bullet$ (60.8 kcal/mol).[16] Because N_2 is weakly activated in **2**, the addition of a net hydrogen atom to **2** would likely generate a high energy $Fe_2(\mu\text{-}NNH^\bullet)$ intermediate that would decay back to **2**. To circumvent such an intermediate, the direct reduction of **2** to **4** may call for a concerted $2e^-/2H^+$ transfer.

In summary, a series of mono- and diiron(II) complexes that coordinate nitrogen, diazene, hydrazine, and ammonia in an available sixth coordination site have been prepared and characterized. These complexes are structurally related to one another by the ancillary ligands and differ only by the coordinated N_xH_y ligand and, hence, present an attractive synthetic system for studying aspects of an alternating N_2 reduction scheme. The finding that μ-N_2H_4 **3** and μ-N_2H_2 **4** react with free hydrazine, reducing the latter to NH_3 as the former is oxidized, suggests that a similar reactivity pattern merits consideration in the reduction of diazene by nitrogenase.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystallographic details for **2**, **4**, and **5** in CIF format, detailed experimental procedures, and characterization data for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) In ref 7g, the authors report an $Fe(\eta^2\text{-}N_2H_2)$ diazene species. However, the structural and NMR parameters of this species (ref 7c) are very similar to those of an $Fe_2(\mu\text{-}\eta^2\text{-}N_2H_2{}^{2-})$ hydrazido(2−) species that we have reported (ref 7e), suggesting that this complex may be better described as a hydrazido(2−) rather than a diazene species.

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