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Synthesis and Characterization of an Iron(II) η^2-Hydrazine Complex

Justin L. Crossland, Lev N. Zakharov, and David R. Tyler*

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

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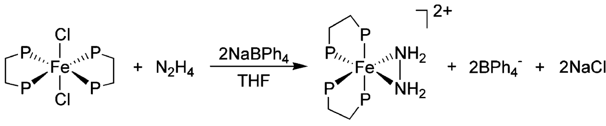
The iron phosphine complex *cis*-[Fe(DMeOPrPE)$_2$(η^2-N$_2$H$_4$)][BPh$_4$]$_2$ {DMeOPrPE = 1,2-bis[bis(methoxypropyl)phosphino]ethane} was synthesized and structurally characterized. The structure exhibits the first η^2 coordination of hydrazine to iron, which may be relevant to intermediates trapped during nitrogenase turnover. The reaction of **I** with acid results in the formation of ammonia via a disproportionation reaction.

The mechanism of the biological reduction of N$_2$ to ammonia mediated by nitrogenase enzymes remains unknown in spite of significant efforts aimed at elucidating potential intermediates.[1−5] The active site of nitrogenase can contain iron, molybdenum, or vanadium; howevern iron is the only metal common to all nitrogenase enzymes, suggesting that iron is the site of N$_2$ binding and reduction.[6] Recent biochemical studies have suggested that the site of N$_2$ binding is the belt iron atoms in the FeMo cofactor and that N$_2$ reduction likely occurs at this site.[7−9]

Hydrazine has also been shown to be a substrate of nitrogenase[10,11] and has been trapped as an intermediate during enzyme turnover.[12,13] Several hydrazine complexes containing various transition metals have previously been synthesized,[14] yet there are relatively few examples containing iron (and the coordination mode to iron is always end-on).[15−23] Herein we describe the synthesis of an iron(II) hydrazine complex that shows unusual η^2-hydrazine coordination, as well as the initial studies on the reactivity of this complex. This work follows from a previous paper in which we described the protonation of Fe^0(N$_2$)(DMeOPrPE)$_2$ {DMeOPrPE = 1,2-bis[bis(methoxypropyl)phosphino]ethane}, resulting in the reduction of N$_2$ to ammonia and hydrazine.[24] Examination of potential intermediates can help us identify the mechanism of N$_2$ reduction using iron phosphine complexes[24−26] and may also provide insights into the mechanism of nitrogenase.

The synthesis of *cis*-[Fe(DMeOPrPE)$_2$(η^2-N$_2$H$_4$)][BPh$_4$]$_2$ (**I**) proceeded smoothly from the reaction of *trans*-FeCl$_2$(DMeOPrPE)$_2$ with 1 equiv of hydrazine in the presence of a chloride abstractor (eq 1). The complex was isolated by removal of the solvent in vacuo and trituration of the resulting oil with diethyl ether to yield **I** as an orange powder.



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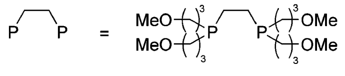

DMeOPrPE

As shown in Figure 1, the room temperature ^{31}P{^{1}H} NMR spectrum of **I** exhibits two triplets at 75.9 and 62.5 ppm, with $^2J_{\mathrm{P-P}}$ = 36 Hz. These data are indicative of a cis arrangement of the bidentate phosphine ligands. The ^{1}H

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* To whom correspondence should be addressed. E-mail: dtyler@uoregon.edu.

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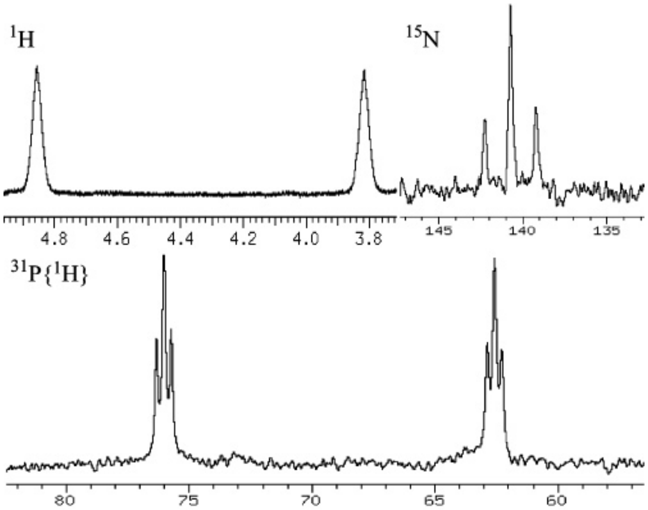

Figure 1. NMR spectra of **I**: ^1H (top left); ^{15}N (top right); $^{31}P\{^1H\}$ (bottom).

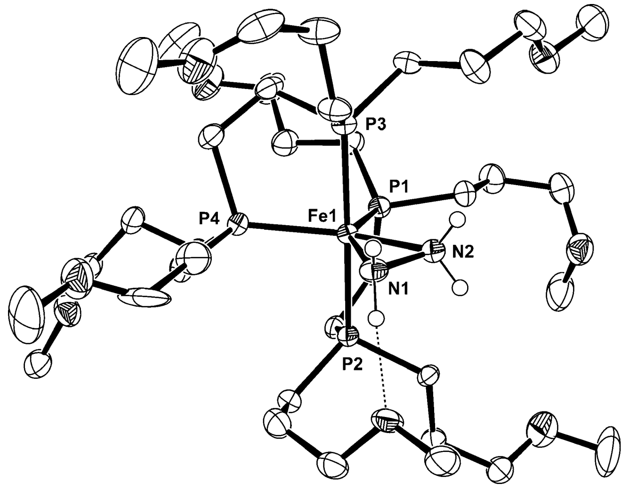

Figure 2. Molecular structure of **I**. The tetraphenylborate anions and hydrogen atoms of the phosphine ligands have been omitted for clarity. The intramolecular hydrogen bond is shown by the dashed line (1.955 Å). Selected bond distances (Å) and angles (deg): N1−N2 1.442(3), Fe−N1 1.993(2), Fe−N2 2.006(2), Fe−P1 2.2315(8), Fe−P2 2.2716(8), Fe−P3 2.2769(8), Fe−P4 2.2324(8), N1−N2−Fe 68.37(14), N2−N1−Fe 69.36(14), N1−Fe−N2 42.28(10), N1−Fe−P4 109.49(8), N2−Fe−P1 105.23(7).

NMR spectrum reveals the presence of two broad singlets at 4.8 and 3.8 ppm, which are assigned to the hydrazine protons (Figure 1). There are two proton resonances due to the idealized C_2 symmetry of the molecule imparted by the bidentate phosphine ligands.

To confirm the η^2-coordination geometry of the hydrazine, the ^{15}N isotopologue of **I** was synthesized. The ^{15}N NMR spectrum showed a single triplet resonance at 140.5 ppm ($^1J_{N-H}$ = 77 Hz); turning on the ^1H decoupler caused the resonance to become a singlet, confirming equivalent nitrogen atoms, each bound to two protons (Figure 1).[27] IR spectroscopy showed the presence of N−H stretches at 3313, 3227, 3117, and 2932 cm^{-1} (see the Supporting Information).

To investigate the solid-state structure, red-orange crystals of **I** were grown by layering a THF solution with hexane and analyzed by X-ray diffraction. The molecular structure of **I** (Figure 2) shows the η^2-coordination geometry of hydrazine to the iron center.[30] The geometry about the iron center is pseudooctahedral, with the hydrazine occupying two equatorial sites. The N−N bond distance of 1.442 Å agrees with previous η^2-hydrazine complexes and is consistent with an N−N single bond.[34] The structure also shows one methoxypropyl arm of the ligand acting as a hydrogen-bond acceptor to a hydrazine hydrogen atom.

The coordination geometry of the coordinated hydrazine has significance for the mechanism of nitrogenase. Previously described iron hydrazine complexes have all shown monodentate or bridging coordination modes; to our knowledge, **I** is the first example of η^2-hydrazine coordination to iron. As previously mentioned, a hydrazine intermediate was recently trapped during nitrogenase turnover. ^{15}N NMR ENDOR spectroscopy of this intermediate revealed the presence of a single type of ^{15}N nucleus, which is consistent with a symmetric coordination mode of the hydrazine.[12,13] This symmetric coordination mode could either be a bridging species (μ) or a mononuclear bidentate species (η^2).

While there are examples of hydrazine bridging two iron centers,[18,22,23] until now there has been no evidence for η^2-hydrazine coordination to iron. Complex **I** suggests that the trapped hydrazine intermediate in nitrogenase could have an η^2-coordination mode. Therefore, both binuclear and mononuclear mechanisms of nitrogen fixation should be considered when formulating the mechanism of N_2 reduction in nitrogenase enzymes.

Initial reactivity studies were undertaken to examine the competence of **I** in producing hydrazine and/or ammonia (eq 2). The addition of excess 1 M triflic acid to a Et_2O/THF solution of **I** resulted in the formation of 21% NH_4^+ and 64% $N_2H_5^+$ (per 1 mol of Fe).[35,38]

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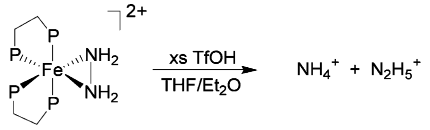

I

(2)

Because no electron equivalents are present, the formation of ammonia must be the result of disproportionation of hydrazine (eq 3).[39] Disproportionation of hydrazine in the presence of transition metals has been previously observed.[40−42]

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (3)$$

Because the addition of acid to complex **I** results in the formation of ammonia, the η^2-hydrazine complex could potentially be an intermediate during the protonation reaction of iron(0) phosphine dinitrogen complexes.[24−26] This species could result from the addition of four protons to a (μ-N_2)-(Fe^0P_4)$_2$ dimer, followed by loss of an $Fe^{II}P_4$ fragment. The observed yields of ammonia could then be the result of disproportionation of **I**.[24] Complex **I** could also result from the addition of $2e^-$ and $2H^+$ to an iron(II) diazene species. Current studies are underway to test these hypotheses.

In summary, we have described the synthesis and molecular structure of an iron(II) hydrazine complex that shows a rare η^2-coordination geometry. Upon the addition of acid to this complex, ammonia was detected, suggesting disproportionation of the coordinated hydrazine. Biochemical studies have shown that the mechanism of nitrogenase likely goes through a symmetrically bound hydrazine intermediate during N_2 reduction. Previously, the only known examples of symmetric iron hydrazine species contained bridging hydrazine. The η^2 coordination of hydrazine to iron(II) has now been shown to be possible and must be considered a potential structure for the trapped hydrazine intermediate in nitrogenase.

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Supporting Information Available: Experimental details, spectroscopic data, and X-ray crystallographic information including the CIF file of **I**. This material is available free of charge via the Internet at http://pubs.acs.org

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