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Characterization of Structurally Unusual Diiron N_xH_y Complexes

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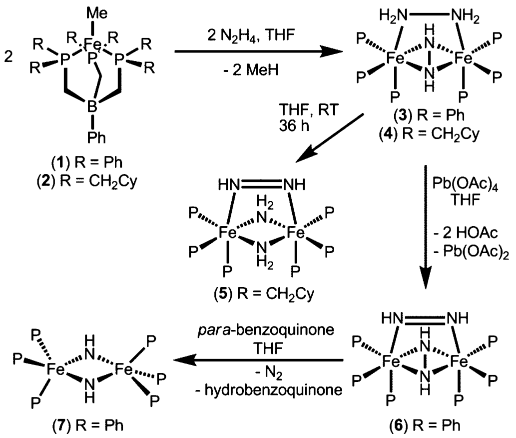
Mechanistic proposals concerning the pathway of N_2 reduction in biology at the MoFe-cofactor of nitrogenase continue to be advanced.[1] In addition to nitrogen, hydrazine[2] and diazene[1a] are nitrogenase substrates, and recent DFT calculations and spectroscopic studies suggest that whereas initial N_2 binding may occur at one iron center, diiron pathways may be involved at certain N_xH_y intermediate stages en route to ammonia formation.[1a,3] In this broad context, recent work has explored the synthesis and spectroscopic characterization of structurally unusual mono- and bimetallic iron complexes featuring nitrogenous ligand functionalities.[4,5] The demand for such model complexes continues in light of recent ENDOR and ESEEM spectroscopic data that has been obtained under turnover conditions at the cofactor.[1a,2,6] To date, there are few synthetic iron systems that feature parent hydrazine (N_2H_4),[7] hydrazido ($N_2H_2^{2-}$), diazene (N_2H_2),[8] amide (NH_2^-),[9] and imide (NH^{2-})[4d] ligands. Herein we describe the synthesis and characterization of a series of structurally distinct diiron complexes that feature each of these ligand types.

Entry into the N_xH_y chemistry of present interest is realized with the iron(II) alkyl precursors $[PhBP^R_3]FeMe$ {$[PhBP^R_3]$ = $PhB(CH_2PR_2)_3^-$; R = Ph, CH_2Cy}. These high-spin complexes are prepared either by addition of excess Me_2Mg to a benzene solution of $[PhBP^{Ph}_3]FeCl$ or by addition of MeLi to a thawing THF solution of $[PhBP^{CH_2Cy}_3]FeCl$. The room-temperature addition of 1 equiv of hydrazine to yellow THF solutions of either $[PhBP^{Ph}_3]FeMe$ (**1**) or $[PhBP^{CH_2Cy}_3]FeMe$ (**2**) results in the immediate release of methane and clean conversion to red and diamagnetic $\{[PhBP^{Ph}_3]Fe\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2H_4)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$ (**3**) or purple and diamagnetic $\{[PhBP^{CH_2Cy}_3]Fe\}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2H_4)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$ (**4**), respectively (Scheme 1). The solid-state structures of the diiron cores of **3** and **4** are nearly identical [see the Supporting Information (SI)]; that of **3** is shown in Figure 1. Its two iron centers are bridged by N_2H_4 and $N_2H_2^{2-}$ ligands. We assign the end-on bridging ligand as N_2H_4 and the side-bonded bridging ligand as $N_2H_2^{2-}$.[10] The N3−N4 bond distance of 1.429(3) Å in **3** is consistent with an N−N single bond, and hence, this ligand is best assigned as $N_2H_2^{2-}$ rather than HN═NH. The ^1H NMR spectrum (THF-d_8) of **3** reveals a solution structure similar to that observed in the solid state. A N_2H_4 resonance is noted at 2.54 ppm and a $N_2H_2^{2-}$ resonance at 2.59 ppm. Each of these peaks is split into an apparent doublet when **3** is prepared using $^{15}N_2H_4$ ($^1J_{NH}$ = 59.5 Hz for $N_2H_2^{2-}$; $^1J_{NH}$ = 72.0 Hz for N_2H_4). The broadness of the doublets precludes the resolution of higher-order N−H and H−H coupling.[11] The corresponding ^{15}N NMR spectrum shows a doublet at −10.0 ppm for $N_2H_2^{2-}$ and a triplet at 58.37 ppm for N_2H_4,[12] both of which collapse into singlets upon ^1H decoupling. Complex **4** displays similar ^{15}N NMR characteristics ($N_2H_2^{2-}$: 0.86 ppm, doublet, J = 45.2 Hz; N_2H_4: 50.86 ppm, triplet, J = 68.9 Hz).

Scheme 1



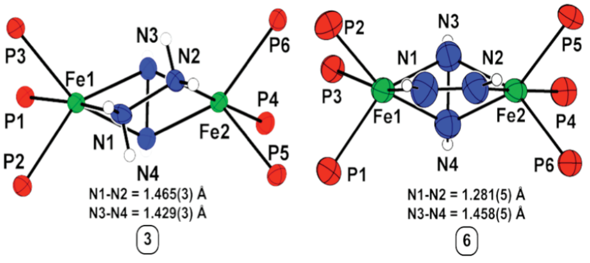


Figure 1. Solid-state molecular structures of the core atoms of **3** and **6**. See the SI for complete structures and details.

Whereas Sellmann previously reported a few examples of diiron $\mu\text{-}\eta^1\text{:}\eta^1$-HN═NH species,[8] the bimetallic iron cores of **3** and **4** are unique. Schrock has characterized a ditungsten $(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2H_4)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2H_2)$ complex whose core is closely related to those in **3** and **4**.[13]

Whereas solutions of **3** are stable for days at 60 °C, purple solutions of **4** are thermally unstable even at 22 °C ($t_{1/2}$ = 4 h) and decay quantitatively to the isolable green diamagnetic product $\{[PhBP^{CH_2Cy}_3]Fe\}(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2H_2)(\mu\text{-}NH_2)_2$ (**5**). Signature NMR data for **5** are as follows: Its ^1H NMR spectrum (THF-d_8) features three broad singlets at 16.21, −1.65, and −3.85 ppm, corresponding to bound HN═NH and diastereotopic NH_2^- protons, respectively. Each of these ^1H NMR resonances is split into a doublet upon ^{15}N labeling. Its ^{15}N NMR spectrum contains a doublet at 419.1 ppm ($^1J_{NH}$ = 65.1 Hz) that collapses to a singlet upon decoupling of the proton resonance at 16.21 ppm. The NH_2^- nitrogens are observed as a triplet at −58.1 ppm (J = 59.5 Hz).

The solid-state structure of **5** is shown in Figure 2. Both the Fe−N1 bond distance of 1.882(8) Å and the N1−N1′ bond distance of 1.283(15) Å are similar to those found in Sellmann's $Fe_2(\mu\text{-}\eta^1\text{:}\eta^1$-HN═NH) complex.[8] In addition, the Fe−N bond-distance contraction of 0.17 Å that occurs upon oxidation of hydrazine to diazene is also consistent with other structurally characterized diazene complexes[8,14] and is likely due to a combination of the smaller covalent radii of sp^2-hybridized nitrogen relative to sp^3-hybridized nitrogen and modest back-bonding. Notable in the structure of **5** is the presence of *cis*-diazene. Whereas monosub-

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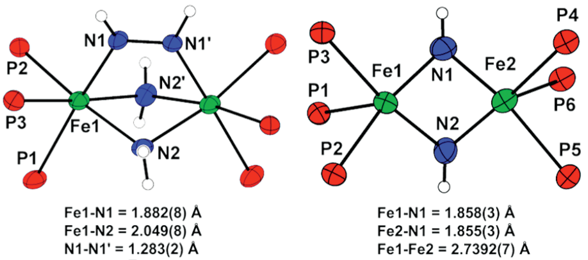
stituted diazenes (HN═NR) are known to bind transition metals in a cis conformation,[15] to our knowledge all known complexes of HN═NH show trans ligation. Hence, **5** appears to be structurally distinct in this context.[8]

The addition of 2.2 equiv of $Pb(OAc)_4$ to red **3** leads to oxidation of the bound N_2H_4[16] to afford green and diamagnetic $\{[PhBP^{Ph}{}_3]Fe\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2H_2)(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2H_2)$ (**6**) as the major product along with release of acetic acid. The solid-state structure of **6** is shown in Figure 1. Most striking is the presence of both an $\eta^1{:}\eta^1$-bridging *cis*-HN═NH ligand and a $\mu\text{-}\eta^2{:}\eta^2$ $HN{-}NH^{2-}$ ligand. To our knowledge, **6** is the only transition-metal complex featuring the N_2H_2 ligand in each of its limiting states of oxidation. The N1−N2 bond distance of 1.281(5) Å for the ligand assigned as HN═NH is similar to that found for the bridging HN═NH ligand of **5**. The N3−N4 bond distance of 1.458(5) Å for the ligand assigned as $N_2H_2{}^{2-}$ is slightly elongated compared with that of the $N_2H_2{}^{2-}$ ligand of **3**. The average $Fe{-}N_{diazene}$ bond distance of 1.89 Å is appreciably shorter than the average $Fe{-}N_{hydrazido^{2-}}$ bond distance of 1.99 Å.

As was observed for **3** and **4**, the structure of **6** is preserved in solution. In the ^1H NMR spectrum (C_6D_6) of **6**, broad singlets at 13.20 and 4.16 ppm are assigned to the HN═NH and $N_2H_2{}^{2-}$ protons, respectively; both of these peaks are split into apparent broad doublets when samples of **6** are prepared using ^{15}N-enriched **6**. The ^{15}N NMR spectrum of **6** contains a doublet at 58.0 ppm ($^1J_{NH} = 58.1$ Hz) for the $N_2H_2{}^{2-}$ nitrogens and a doublet of doublets at 407.5 ppm ($^1J_{NH} = 69.2$ Hz, $J \approx 20$ Hz) corresponding to the HN═NH ligand.

Complex **6** can further be oxidized with *p*-benzoquinone to cleanly generate a new diamagnetic species, $\{[PhBP^{Ph}{}_3]Fe\}_2(\mu\text{-}NH)_2$ (**7**), along with *p*-hydrobenzoquinone as a byproduct. In order to ascertain the fate of the bound diazene, the reaction was analyzed with a Toepler pump apparatus, and the evolution of 1 equiv of N_2 was confirmed. This complex can alternatively be prepared by addition of 5 equiv of *p*-benzoquinone to **3**. The ^{31}P NMR spectrum of **7** displays a single resonance at 32.5 ppm at 22 °C. The ^1H NMR spectrum shows a single set of $[PhBP^{Ph}{}_3]$ resonances, with an additional singlet at 25.3 ppm that integrates to one proton per $[PhBP^{Ph}{}_3]$; when **7** is prepared using isotopically enriched **3**, the singlet at 25.04 ppm is split into a doublet ($^1J_{NH} = 64.0$ Hz). The ^{15}N NMR spectrum displays a doublet at 563.5 ppm. On the basis of these NMR data as well as IR data (see the SI), the solution structure of **7** is assigned as diferric $\{[PhBP^{Ph}{}_3]Fe\}_2(\mu\text{-}NH)_2$. The spectroscopic data for the bridging NH ligand in **7** is similar to that previously reported for $\{([PhBP^{Ph}{}_3]Fe)_2(\mu\text{-}NH)(\mu\text{-}H)\}\{Na\}$.[4d]



5

7

Figure 2. Solid-state molecular structures of the core atoms of **5** and **7**. See the SI for complete structures and details.

Crystals of **7** can be grown from a THF/cyclopentane solution, and its solid-state structure is shown in Figure 2. The bridging imides are disordered over three positions (see the SI) and modeled satisfactorily with a population ratio of 0.93:0.75:0.32. The average Fe−N distance of 1.84 Å is ~0.17 Å longer than that found in $\{[PhBP^{Ph}{}_3]Fe_2(\mu\text{-}NH)(\mu\text{-}H)\}\{Na\}$.[4d] The average Fe−P distance of 2.33 Å is ~0.075 Å longer than those found in **3** and **6**, consistent with its assignment as an antiferromagnetically coupled diiron(III) complex.

In conclusion, we have characterized a series of structurally fascinating diiron N_xH_y species that contain hydrazine, hydrazido, and *cis*-diazene bridges. Thermal and oxidative transformations also lead to unusual examples of diiron species featuring μ-NH_2 and μ-NH ligands. In certain instances, low-temperature experiments revealed the presence of intermediate species. Ongoing work concerns detailed vibrational characterization of the species described herein, in addition to mechanistic studies.

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Supporting Information Available: Detailed experimental procedures and characterization data for **1**−**7** and crystallographic details for **3**−**7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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