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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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^n-N≡N → M^{n+3}≡N + NH_3 → M^n + NH_3) and alternating (i.e., M^n-N≡N → M^n-HN=NH → M^n-H_2N-NH_2 → M^n + 2 NH_3) mechanisms representing two limiting schemes.[1c,d,2] Schrock[3] and Nishibayashi[4] have respectively prepared mono- and di-molybdenum 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, though 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] Though 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] as they serve as structural and spectroscopic models to the postulated trapped intermediates.

Mono- and di-iron complexes that coordinate N_2H_y ligands (y = 2,3) remain relatively rare, and exhibit both acid/base and redox reactivity.[7a–c,7e,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 N-atom oxidations 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 5-coordinate iron(II) complex, [PhBP$^{CH2Cy}_3$]Fe(OAc) (**1**) ([PhBP$^{CH2Cy}_3$] = PhB(CH$_2$P(CH$_2$Cy)$_2$)$_3^-$). Complex **1** is quantitatively formed in the reaction between [PhBP$^{CH2Cy}_3$]FeMe and one equiv of AcOH, and is isolated as an analytically pure grey 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 6-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 **2**, {[PhBP$^{CH2Cy}_3$]Fe(OAc)}$_2$(μ-N_2). Crystals of **2** suitable for diffraction can be grown from saturated Et$_2$O solutions of **2** stored at −35 °C in the glove-box, 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} that shifts to 2010 cm^{-1} upon ^{15}N-isotopic labeling (calc'd: 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 phosphorous 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**.

Treatment of **2** with 0.5 equiv N_2H_4 at −78 °C generates the purple diiron species {[PhBP$^{CH2Cy}_3$]Fe(OAc)}$_2$(μ-η^1:η^1-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 ^{1}H 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 ^{1}H 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)}$_2$(*trans*-μ-η^1:η^1-N_2H_2) (**4**) 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 ^{1}H{^{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 caption for fitting 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 SI). 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 dataset is compromised by a total molecule disorder, in which

18 % of the molecules are translocated along the b-axis of the P2(1)/c unit cell. Though 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 6-coordinate diiron(II) bridging diazene complexes.[7a,7e]Further, the N-N distance of 1.31(1) Å is in good agreement with that predicted from the $^3J_{HH}$ coupling constant.

Comparison of the structures for μ-N$_2$ **2** and μ-N$_2$H$_2$ **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 (that are *cis* to the N$_2$H$_y$ ligand) are nearly equivalent. Only the Fe-P distance to the phosphine that is *trans* to the N$_2$H$_y$ 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**, the ammonia in the latter species presumably generated from the dis-proportionation of free diazene. In contrast, the *cis* diazene in the related complex, {[PhBP^{CH2Cy}$_3$]Fe}$_2$(μ-η^1:η^1-N$_2$H$_2$)(μ-NH$_2$)$_2$ is stable in solution for days at 60 °C.[7e] As 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$_2$H$_4$ **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). Though **5** is stable in solution at room temperature, heating solutions of **5** under vacuum results in NH$_3$ loss and 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:

$$N_2H_4 \xrightarrow[-\ 2\ NH_3]{+\ N_2H_4} N_2H_2 \xrightarrow[-\ 2\ NH_3]{+\ N_2H_4} N_2$$
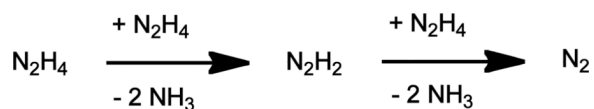
To determine whether μ-N$_2$H$_2$ **4** further reacts with hydrazine to generate N$_2$ and NH$_3$, 0.95 equiv of ^{15}N$_2$H$_4$ was added to a THF solution of **4**, and both the reaction volatiles and residual solids were analyzed by NMR spectroscopy. ^{1}H NMR analysis of the volatiles established the formation of ^{15}NH$_3$ (ca. 50 % yield) and no ^{14}NH$_3$. ^{1}H and ^{31}P NMR spectroscopy of the residual solids indicates 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$_2$H$_4$, which itself is reduced to NH$_3$.

Though **1** can serve as a hydrazine disproportionation catalyst (in the presence of 10 equiv of N$_2$H$_4$, a 16 % yield of NH$_3$ is obtained), the reaction is hampered by ligand degradation; in addition to **1** and **5**, (CH$_2$Cy)$_2$PMe and other, unidentifiable products are present in the resulting ^{1}H 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. Though 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 H-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, $[Na][C_{10}H_8]$) and acids (i.e. HOAc, HOTf, $[lutH][BPh_4]$), 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, treatment of **4** with oxidants (e.g. *p*-benzoquinone, $Pb(OAc)_4$) results in formation of **1**, which may proceed through μ-N_2 **2**. These results are perhaps not unexpected when one considers the respective gas-phase BDE of NN-H$^\bullet$ (*ca.* 0 kcal/mol) and HNN-H$^\bullet$ (60.8 kcal/mol).[16] As the N_2 is weakly activated in **2**, addition of a net H-atom to **2** would likely generate a high energy and $Fe_2(\mu$-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.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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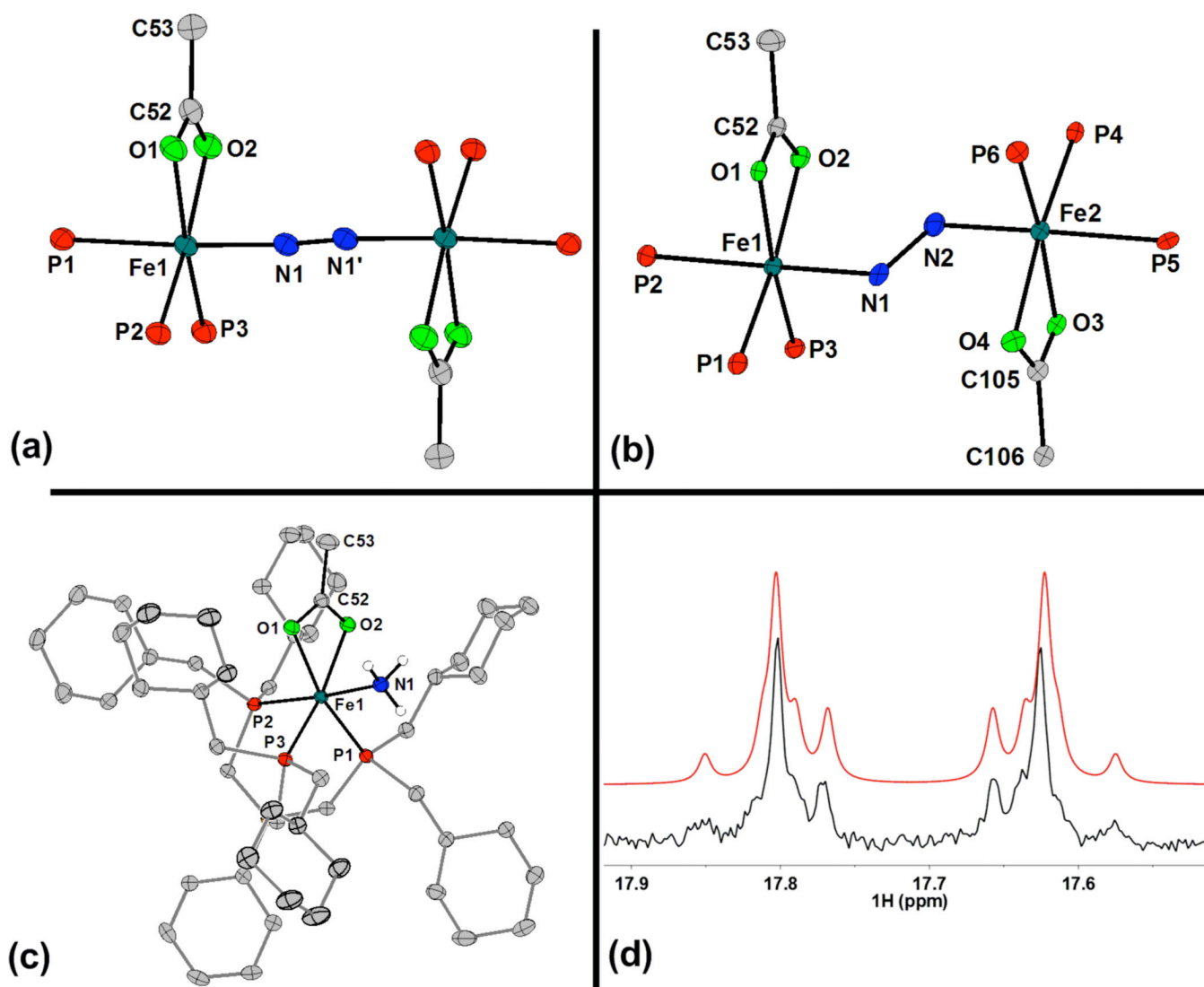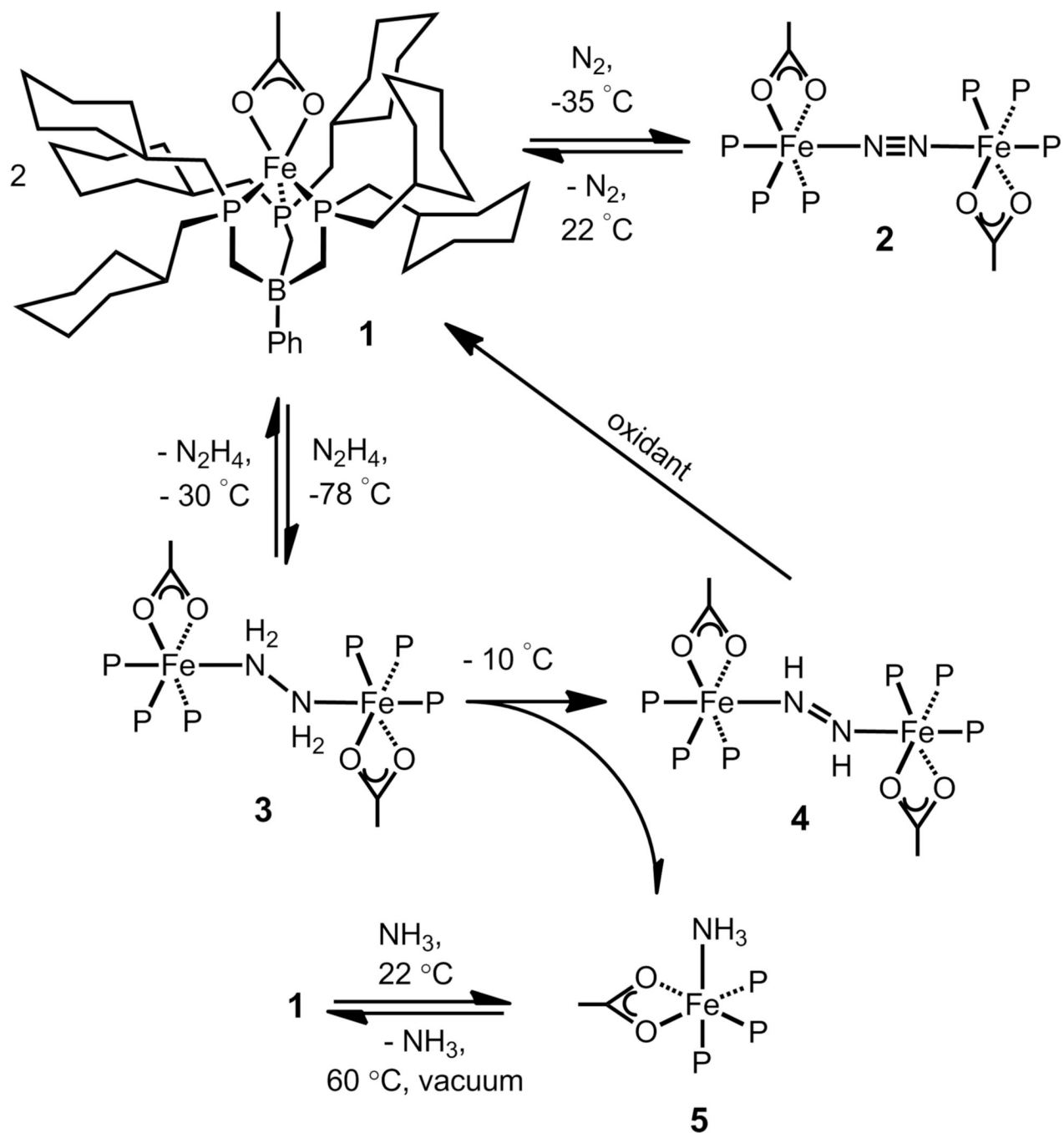16. Warren JJ, Tronic TA, Mayer JM. Chem. Rev. 2010; 110:6961. [PubMed: 20925411]

Figure 1.
Displacement ellipsoid (50%) representation of (a) the core atoms of μ-N$_2$ **2**, (b) the core atoms of μ-N$_2$H$_2$ **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 (°) 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 (°) 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 ^{1}H{^{31}P} NMR spectrum (C$_6$D$_6$, 25 °C) of ^{15}N-**4** indicating the AA'XX' splitting pattern (experimental, black; fit, red). The data was fit with MestReNova using the following parameters: δ = 17.72, $^1J_{NH}$ = −71.0 Hz, $^2J_{NH}$ = −1.1 Hz, $^3J_{HH}$ = 21.0 Hz, $^1J_{NN}$ = 12.0 Hz, linewidth = 3.5 Hz.

Scheme 1.