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Dinitrogen Chemistry from Trigonally Coordinated Iron and Cobalt Platforms

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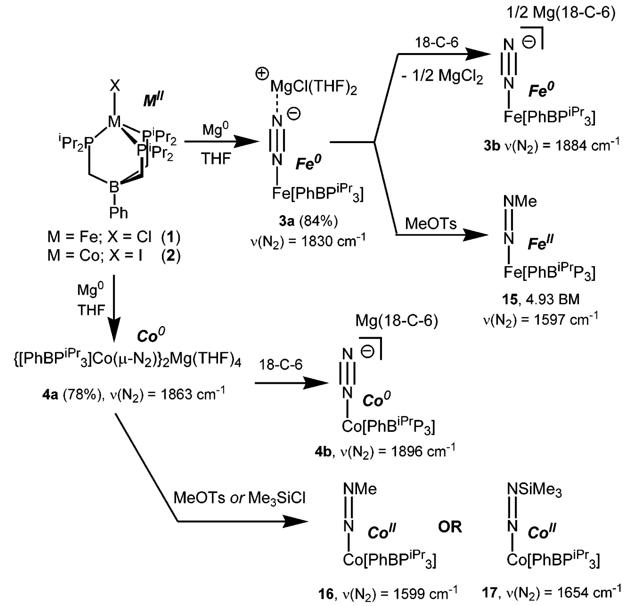
The Chatt-type nitrogen reduction scheme is well-established for certain molecular systems that feature molybdenum.[1] For example, Schrock has recently demonstrated that a single, amido-supported molybdenum center can support various N_2-derived intermediates (e.g., $M(N_2H)$, $M(N_2H_2)$, M(N), M(NH)), oxidation states, and redox couples to favorably mediate the complete reduction of nitrogen to ammonia in a catalytic fashion.[1c,d] One key feature of this and other competent N_2-reducing molybdenum systems is their ability to accommodate a π-acidic N_2 ligand, as well as π-basic functionalities derived from N_2 (e.g., N^{3-}, NH^{2-}), at a single site.[1,2] To date, very few first-row ion platforms allow N_2 to be taken up and derivatized in a similar fashion (e.g., $Fe(N_2) \rightarrow Fe(N_2H)$).[3,4] Iron is particularly noteworthy in this regard, given its possible if not likely role in biological (and industrial) nitrogen fixation.[5,6]

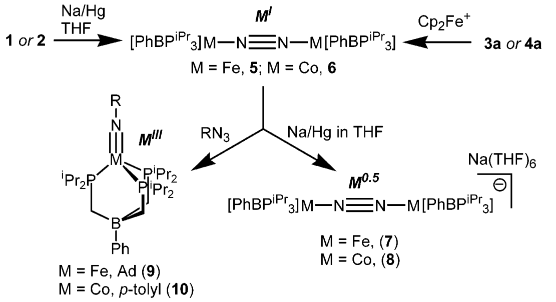
Recent work by our group has shown that trigonally coordinated iron and cobalt subunits of the form "$[PhBP_3]M$" ($[PhBP_3] = [PhB(CH_2PPh_2)_3]^-$) will support a strongly π-donating ligand at a fourth site along their pseudo-three-fold axis (e.g., $[PhBP_3]Fe{\equiv}NR$).[7] Simple electronic structure considerations suggest that these same $[PhBP_3]M$ subunits should also accommodate strongly π-acidic ligands at the fourth site,[7−9] a feature that might complement nitrogen reduction schemes at iron. Herein we demonstrate that second-generation "$[PhBP^{iPr}_3]Fe$" ($[PhBP^{iPr}_3] = [PhB(CH_2P^iPr_2)_3]^-$) and related cobalt systems coordinate, activate, and promote the methylation of nitrogen at the fourth binding site. Moreover, the N_2 ligand can be replaced by nitrene (NR) through an oxidative group-transfer reaction.[7,8a] The iron−N_2 species discussed are the first thoroughly characterized, 4-coordinate complexes of their type.[4]

Entry to this reaction manifold begins with the recently reported precursors $[PhBP^{iPr}_3]MX$ (M = Fe, X = Cl (**1**); M = Co, X = I (**2**)).[9] A THF solution of yellow **1** or green **2**, stirred under a blanket of nitrogen in the presence of Mg^0, produced the anionic, paramagnetic dinitrogen complexes $\{[PhBP^{iPr}_3]Fe(N_2)\}\{MgCl(THF)_2\}$ (**3a**, 84%) and $\{[PhBP^{iPr}_3]Co(N_2)\}_2\{Mg(THF)_4\}$ (**4a**, 78%) as red-brown and red crystals, respectively (Scheme 1). An XRD study of single crystals of **4a** suffered from modest disorder but confirmed a $Mg(THF)_4{}^{2+}$ dication sandwiched by two anionic $Co(N_2)^-$ units, in accord with related structure types.[10,11] The IR spectra of **3a** and **4a** show intense ν_{NN} bands that shift to higher energy upon addition of 18-crown-6 (18-C-6) to encapsulate the Mg^{2+} ion ($\nu_{NN(^{15}NN)}$ in cm^{-1} for **3a**, 1830(1769); **3b**, 1884(1822); **4a**, 1863(1802); **4b**, 1896(1842)). Gentle oxidation by ferrocenium (Cp_2Fe^+) in THF produced the neutral, dinuclear N_2-bridged products $\{[PhBP^{iPr}_3]Fe\}_2(\mu\text{-}N_2)$ (**5**, 88%) and $\{[PhBP^{iPr}_3]Co\}_2(\mu\text{-}N_2)$ (**6**, 92%) (Scheme 2). Both **5** and **6** were also obtained directly from halides **1** and **2** when Na/Hg amalgam was used as the reductant in place of Mg^0. Furthermore, extended exposure of **5** and **6** to sodium amalgam produced the mixed-valence (M^0/M^I) complexes $[(\{PhBP^{iPr}_3]Fe)_2(\mu\text{-}N_2)][Na(THF)_6]$ (**7**, 93%) and $[([PhBP^{iPr}_3]Co)_2(\mu\text{-}N_2)][Na(THF)_6]$ (**8**, 89%). XRD data were obtained on single crystals of **7** and **8**, and the molecular structure of **7** is shown in Figure 1. The structure of **8** is isomorphous and isostructural.[11] A crystallographically imposed inversion center reflects one-half of each dinuclear anion into the other, suggesting that these species are likely delocalized at low temperature. A modest elongation of the N_2 ligand is observed in each case (N−N′ 1.171(4) for **7**, and 1.147(4) Å for **8**), and the local geometry of each metal center is perhaps best described as trigonal monopyramidal, with N_2 lying in an equatorial position.

Scheme 1



Scheme 2



Complexes **5** and **6** provided clean access to the "$[PhB^{iPr}P_3]M^I$" fragment, as exemplified by their ability to undergo rapid oxidation upon addition of either tolyl or adamantyl azide to afford trivalent imide products. For example, burgundy $[PhBP^{iPR}_3]Fe{\equiv}NAd$ (**9**, 69%) and red $[PhBP^{iPr}_3]Co{\equiv}N$-*p*-tolyl (**10**, 93%) were isolated and thoroughly characterized (Scheme 2), and the solid-state structure of each was determined.[11] The crystal structure of complex **9** (Figure 2) features a very short Fe−N bond (1.638(2) Å) and an almost linear Fe−N−C bond vector (176°), consistent with the triple-bond formulation we have proposed previously.[7]

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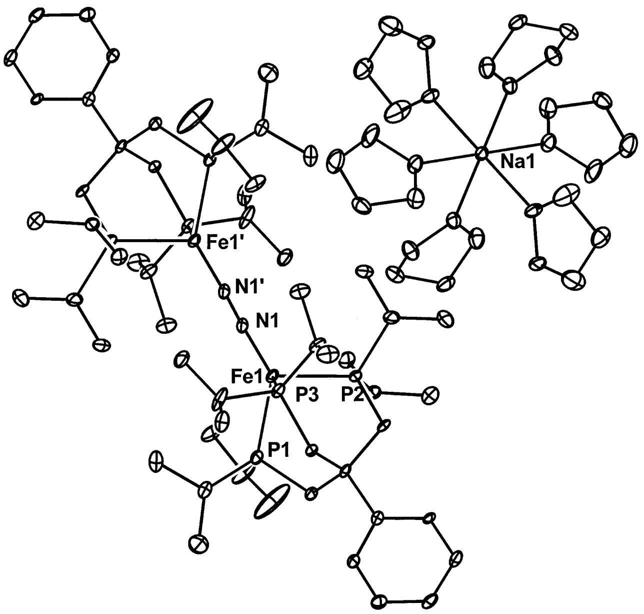

Figure 1. Displacement ellipsoid representation of {([PhBP$^{iPr}_3$]Fe)$_2$(μ-N$_2$)}{Na(THF)$_6$} (**7**). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (deg), for **7**: Fe−N 1.813(2), N−N′ 1.171(4), Fe−P1 2.292(1), Fe−P2 2.278(1), Fe−P3 2.290(1); N′−N−Fe 178.0(3), P1−Fe−P2 96.93(4), P1−Fe−P3 97.96(4), P2−Fe−P3 97.22(4), N−Fe−P1 118.88(9), N−Fe−P2 109.66(9), N−Fe−P3 129.83(9).

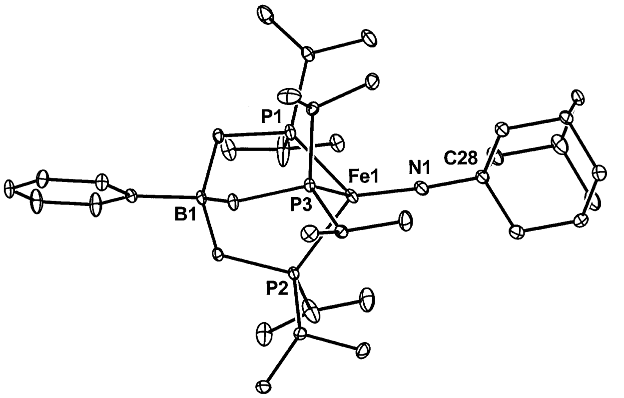

Figure 2. Displacement ellipsoid representation of [PhBP$^{iPr}_3$]Fe≡NAd (**9**). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (deg), for **9**: Fe−N 1.638(2), Fe−P1 2.260(1), Fe−P2 2.297(1), Fe−P3 2.263(1); C28−N−Fe 176.0(2), P1−Fe−P2 91.05(2), P1−Fe−P3 91.56(3), P2−Fe−P3 92.39(3), N−Fe−P1 121.62(7), N−Fe−P2 130.03(7), N−Fe−P3 120.27(7).

Structural data for related **10** have been placed in the Supporting Information.

The anionic N$_2$ adducts **3** and **4** appear well-poised for further elaboration at the coordinated N$_2$ functionality. This is significant because the direct conversion of coordinated N$_2$ to a coordinated diazenido (N$_2$R$^-$) and/or hydrazido (N$_2$R$_2$$^{2-}$) species by simple addition of an electrophile (e.g., R$^+$) has, to our knowledge, not been established for a first-row transition metal ion.[3,4] We were thus gratified to find that the simple addition of methyl tosylate (MeOTs) to a THF solution of **3** effected a modest color change from brown to gold, along with a concomitant shift in its $\nu_{NN(^{15}NN)}$ vibration to 1597(1538) cm^{-1}, characteristic of a coordinated, monodentate diazenido functionality.[1] A neutral, benzene-soluble product was isolated from the reaction mixture that analyzed as the diazenido complex [PhBP$^{iPr}_3$]Fe−N=NMe (**11,** 56%), consistent with its magnetic susceptibility ($S = 2$, 4.93 μ_B, Evans). A similar protocol converted **4a** to the amber-colored complex [PhB^{iPr}P$_3$]Co−N=NMe (**12**, 68%), which exhibited a very similar $\nu_{NN(^{15}NN)}$ stretch 1599(1542) cm^{-1} and a solution moment indicative of low-spin cobalt(II) (1.92 μ_B). Complex **4a** also reacted cleanly with trimethylsilyl chloride to generate [PhBP$^{iPr}_3$]Co−N=NSiMe$_3$ (**13**, 79%; $\nu_{NN(^{15}NN)} = 1654(1596)$ cm^{-1}; 2.08 μ_B). The latter product could be obtained in good yield by a more direct procedure that involved stirring a solution of chloride **2** in the presence of Me$_3$SiCl and Na/Hg amalgam under nitrogen.

These data allow us to summarize several salient features of the chemistry described herein: The [PhBP$^{iPr}_3$] ligand has been used to isolate a single iron center in a pseudo-tetrahedral environment in which a single binding site is compatible with coordination of N$_2$, diazenido (N$_2$Me), and imide (NR). Moreover, N$_2$ uptake/coordination by 4-coordinate iron has been established for the formal oxidation states M(0), M(+0.5), and M(+1). Methylation of Fe^0(N$_2$)$^-$ to produce Fe^{II}(N$_2$Me) constitutes a two-electron redox process at iron. The additional observation of a separate two-electron redox process, that of oxidative nitrene transfer (FeL^I → Fe^{III}≡NR), establishes that the "[PhBP$^{iPr}_3$]Fe" platform will support four formal oxidation states (Fe^0, Fe^I, Fe^{II}, Fe^{III}), in addition to two discrete two-electron redox couples (Fe$^{0/II}$ and Fe$^{I/III}$). An analogous set of observations has been made with the related cobalt system. These features collectively motivate further development of the present first-row systems into possible models for functional nitrogen fixation.

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Supporting Information Available: Complete experimental procedures and characterization data, and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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