

**Chapter 3. Dinitrogen Chemistry from Trigonal­ly Coordinated Iron
and Cobalt Platforms**

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Abstract

This report establishes that trigonally coordinated “[PhBP^{*i*Pr}]₃M” platforms (M = Fe, Co) will support both π -acidic (N₂) and π -basic (NR) ligands at a fourth binding site. The N₂ complexes of iron that are described are the first thoroughly characterized examples to exhibit 4-coordinate geometry. Methylation of monomeric {Fe⁰(N₂)⁻} and {Co⁰(N₂)⁻} species successfully derivatizes the β -N atom of the coordinated N₂ ligand and affords the diazenido products {Fe^{II}(N₂Me)} and {Co^{II}(N₂Me)}, respectively. These are new transformations at iron and cobalt. 1-electron oxidation of the mononuclear M⁰(N₂)⁻ species produces dinuclear and synthetically versatile M^I(N₂)M^I complexes. These latter species provide clean access to the chemistry of the “[PhBP₃]M(I)” subunit. For example, addition of RN₃ to M^I(N₂)M^I results in oxidative nitrene transfer to generate [PhBP^{*i*Pr}]₃M \equiv NR with concomitant N₂ release.

3.1. Introduction

Chatt-type nitrogen reduction scenarios using coordination complexes are relatively well-established for a few metals.¹ For example, work with molybdenum systems^{1,2} has clearly demonstrated that a single metal center can accommodate various of the necessary N₂-derived intermediates (e.g., M(N₂H), M(N₂H₂), M(N), M(NH)), oxidation states, and redox couples to favorably mediate the complete reduction of nitrogen – perhaps even catalytically.^{1a,b} A key feature of these molybdenum systems is their ability to accommodate a π -acidic ligand such as N₂, as well as π -basic functionalities derived from N₂ (e.g., N³⁻).^{1a,1b,2b,2c} To date, very few first row ion platforms allow N₂ to be taken-up and derivatized in a similar fashion (e.g., Fe(N₂)→Fe(N₂R)).^{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 “[PhBP₃]M” ([PhBP₃] = [PhB(CH₂PPh₂)₃]⁻) accommodate a strongly π -donating ligand at a fourth site along their pseudo three-fold axis (e.g., [PhBP₃]Fe≡NR).⁷ Simple electronic structure considerations suggest that these same [PhBP₃]M subunits should also accommodate strongly π -acidic ligands at the fourth site,^{6a,7,8} a feature that might complement nitrogen reduction schemes at iron. Herein we demonstrate that second generation “[PhBP^{*i*Pr}₃]Fe” ([PhBP^{*i*Pr}₃] = [PhB(CH₂P^{*i*Pr})₃]⁻) and related cobalt systems coordinate, activate, and promote the methylation of nitrogen at the fourth binding site. Moreover, the N₂ ligand can be replaced by nitrene (NR) through an oxidative group transfer reaction.^{6,7b} The iron-N₂ species discussed are the first thoroughly characterized, 4-coordinate complexes of their type.⁸

3.2. Results and Discussion

Entry to this reaction manifold begins with the recently reported divalent precursors $[\text{PhBP}^{i\text{Pr}}_3]\text{MX}$ ($\text{M} = \text{Fe}$, $\text{X} = \text{Cl}$ (**2.2**), $\text{X} = \text{I}$ (**3.1**); $\text{M} = \text{Co}$, $\text{X} = \text{I}$ (**2.4**)).⁹ A THF solution of yellow **2.2**, yellow **3.1** or green **2.4** stirred under a blanket of nitrogen in the presence of Mg^0 produced the anionic, paramagnetic dinitrogen complexes $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Fe}(\text{N}_2)\}\{\text{MgCl}(\text{THF})_2\}$ (**3.2**, 84%), $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Fe}(\text{N}_2)\}_2\{\text{Mg}(\text{THF})_4\}$ (**3.3**, 65%), and $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Co}(\text{N}_2)\}_2\{\text{Mg}(\text{THF})_4\}$ (**3.4**, 78%) as red-brown and red crystals, respectively (Scheme 3.1). The IR spectra of **3.2**, **3.3**, and **3.4** show intense ν_{NN} bands at 1830, 1818 and 1863 cm^{-1} , respectively (see Table 3.1 for IR and bond length data). These bands shift to higher energy (1884 and 1896 cm^{-1}) upon addition of 18-crown-6 (18-C-6) to encapsulate the Mg^{2+} ion, generating $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Fe}(\text{N}_2)\}_2\{\text{Mg}(18\text{-C-6})\}$ (**3.5**), and $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Co}(\text{N}_2)\}_2\{\text{Mg}(18\text{-C-6})\}$ (**3.6**). An XRD study of single crystals of **3.3** and **3.4** both suffered from modest disorder, but confirmed a $\text{Mg}(\text{THF})_4^{2+}$ dication sandwiched by two anionic $\text{M}(\text{N}_2)^-$ units, in accord with related structure types (Figure 3.1).¹⁰ Both structures reveal a very short M-N bond at *ca.* 1.687 Å, indicative of significant π -bonding character between the metals and the dinitrogen ligand.

Gentle oxidation by ferrocenium (Cp_2Fe^+) in THF produced the neutral, dinuclear N_2 -bridged products $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Fe}\}_2(\mu\text{-N}_2)$ (**3.7**, 88%) and $\{[\text{PhBP}^{i\text{Pr}}_3]\text{Co}\}_2(\mu\text{-N}_2)$ (**3.8**, 92%) (Scheme 3.2). Both **3.7** and **3.8** were also obtained directly from halides **2.2** and **2.4** when Na/Hg amalgam was used as the reductant in place of Mg^0 . Furthermore, extended exposure of **3.7** and **3.8** to sodium amalgam produced the mixed valence ($\text{M}^0/\text{M}^{\text{I}}$) complexes $\{([\text{PhBP}^{i\text{Pr}}_3]\text{Fe})_2(\mu\text{-N}_2)\}[\text{Na}(\text{THF})_6]$ (**3.9**, 93%) and $\{([\text{PhBP}^{i\text{Pr}}_3]\text{Co})_2(\mu\text{-N}_2)\}[\text{Na}(\text{THF})_6]$ (**3.10**, 89%).

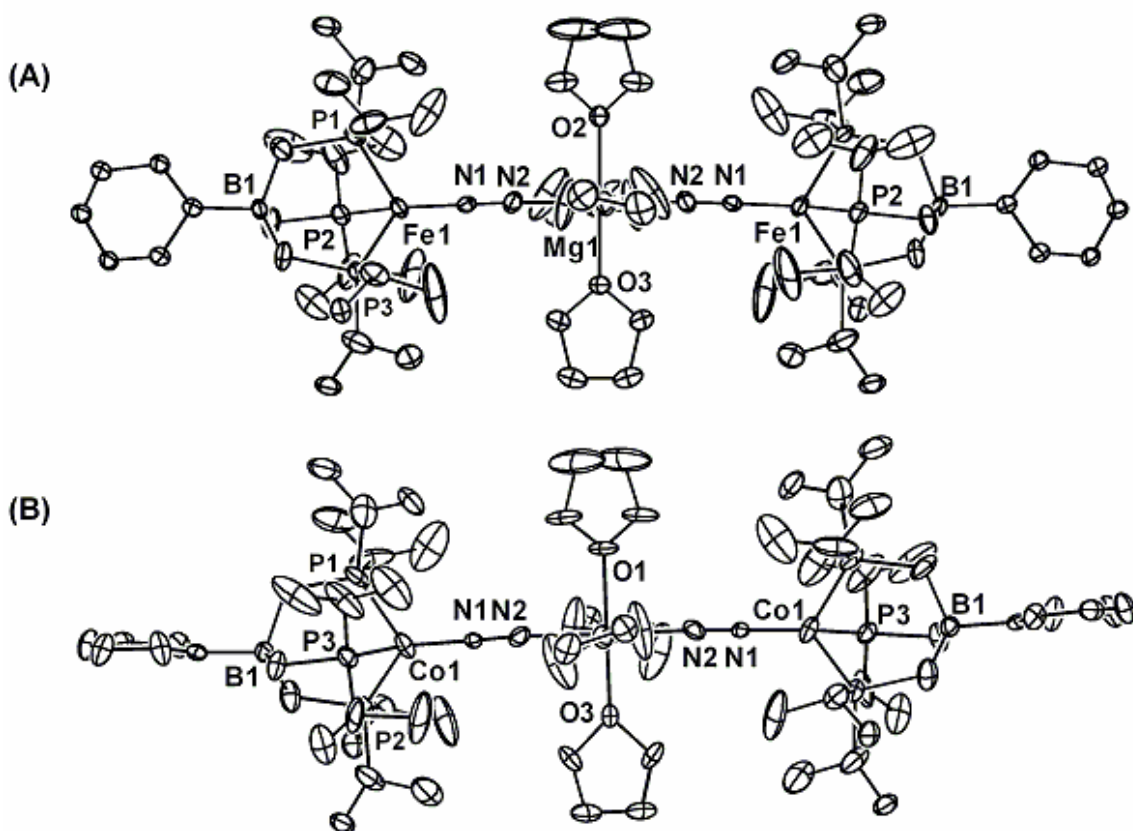
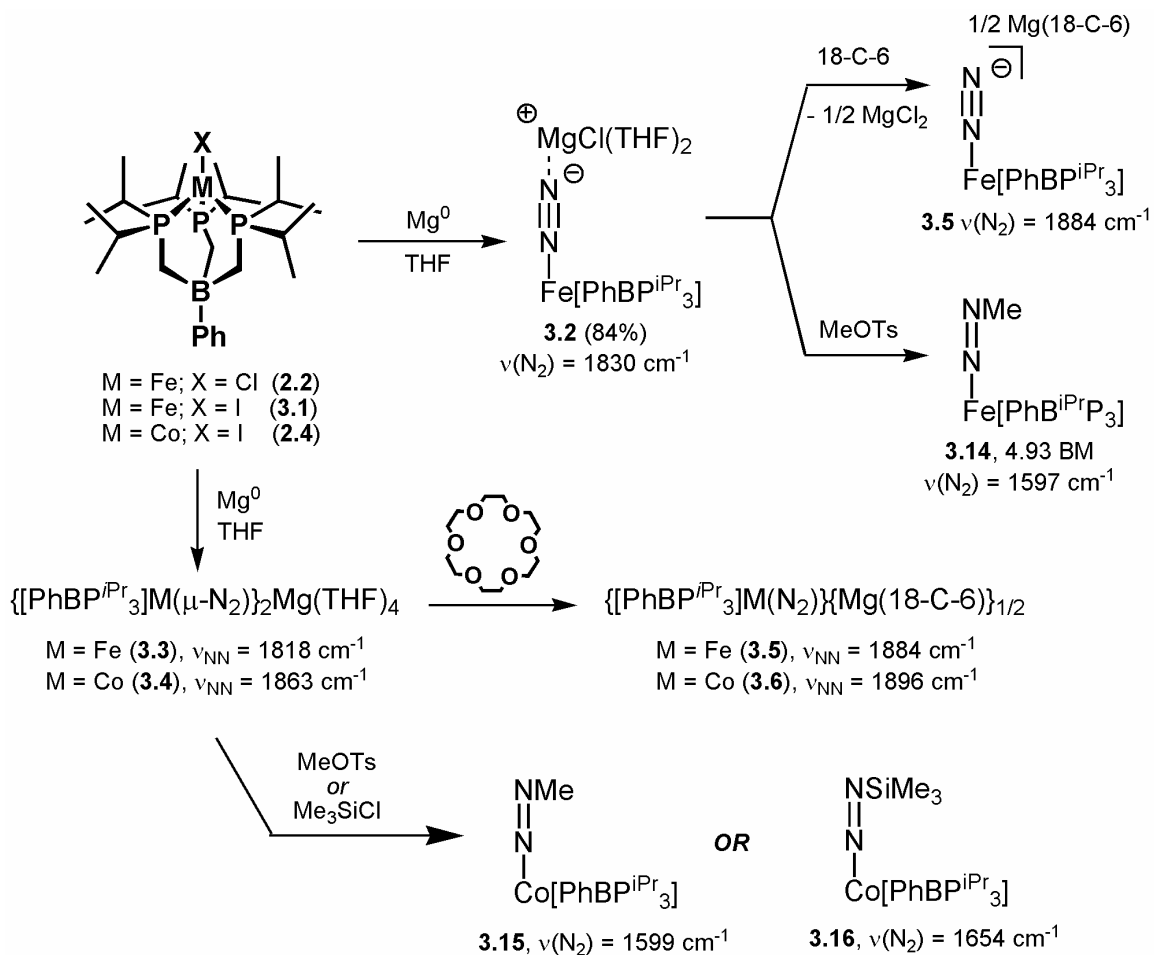


Figure 3.1. Displacement ellipsoid representation (25%) of (A) $\{([\text{PhBP}^{i\text{Pr}}_3]\text{Fe}(\mu\text{-N}_2))_2\}\{\text{Mg}(\text{THF})_4\}$ (**3.3**) and (B) $\{([\text{PhBP}^{i\text{Pr}}_3]\text{Co}(\mu\text{-N}_2))_2\}\{\text{Mg}(\text{THF})_4\}$ (**3.4**). Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (°), for **3.3**: Fe1-N1 1.686(8), N1-N2 1.158(9), N2-Mg1 2.128(9), Fe1-P1 2.293(3), Fe1-P2 2.311(3), Fe1-P3 2.286(3); Fe1-N1-N2 175.5(8), P1-Fe1-P2 96.72(11), P1-Fe1-P3 94.04(11), P2-Fe1-P3 95.54(13), N1-Fe1-P1 113.5(3), N1-Fe1-P2 137.0(2), N1-Fe1-P3 111.3(3), N1-N2-Mg1 162.5(8); for **3.4**: Co1-N1 1.687(3), N1-N2 1.155(3), N2-Mg1 2.103(4), Co1-P1 2.274(2), Co1-P2 2.211(2), Co1-P3 2.259(1); Co1-N1-N2 174.4(3), P1-Co1-P2 93.16(5), P1-Co1-P3 95.87(5), P2-Co1-P3 93.42(7), N1-Co1-P1 117.48(13), N1-Co1-P2 116.51(13), N1-Co1-P3 131.85(10), N1-N2-Mg1 168.1(4).

Scheme 3.1



X-ray diffraction data was obtained on single crystals of **3.9** and **3.10** and the molecular structure of **3.9** is shown in Figure 3.1. The structure of **3.10** is virtually identical (Figure 3.2).¹¹ A crystallographically imposed inversion center reflects one Fe (or Co) site into the other, implying that each half of the dinuclear complexes are isostructural and therefore, electronically delocalized at low temperature. A modest elongation of the N_2 ligand is observed in each case ($\text{N-N}'$ 1.171(4) for **3.9**, and 1.147(4) Å for **3.10**) and the local geometry of each metal center is best described as trigonal monopryramidal.

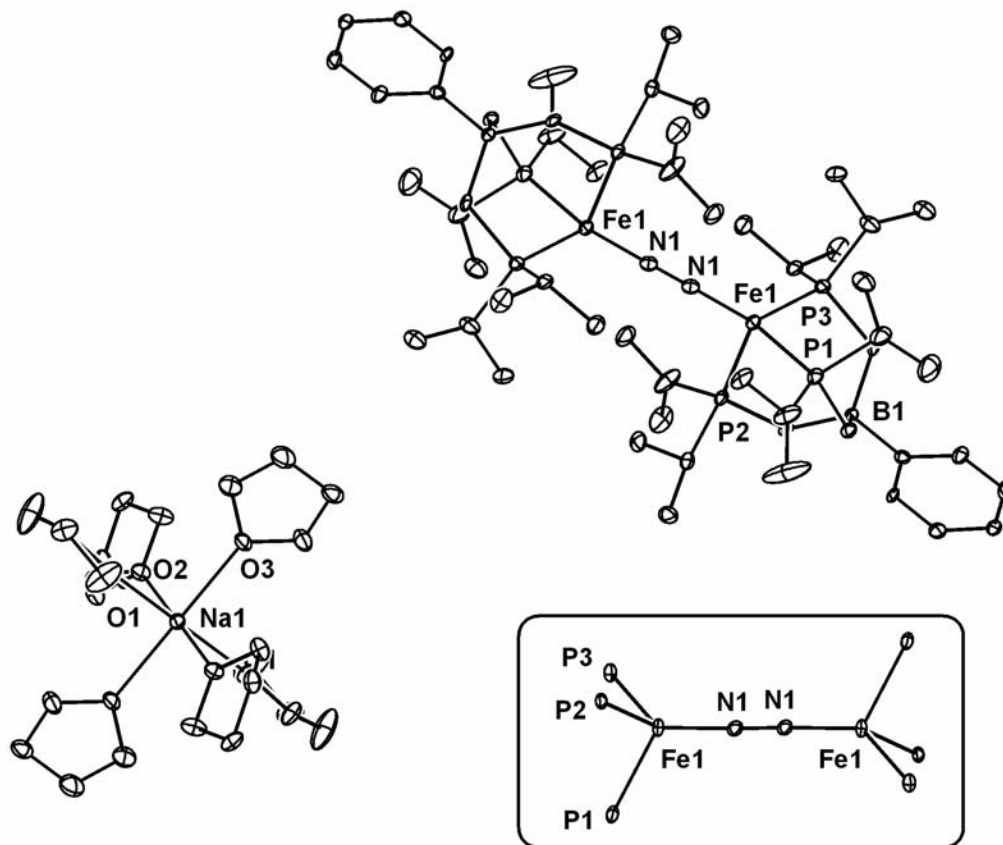


Figure 3.2. Displacement ellipsoid representation of $\{([\text{PhBP}^{i\text{Pr}}_3]\text{Fe})_2(\mu\text{-N}_2)\}\{\text{Na}(\text{THF})_6\}\cdot\text{THF}$ (**3.9**) with anion core highlighted in inset. Hydrogen atoms and non-coordinating solvent molecules have been removed for clarity. Selected bond distances (Å) and angles (°), for **3.9**: 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).

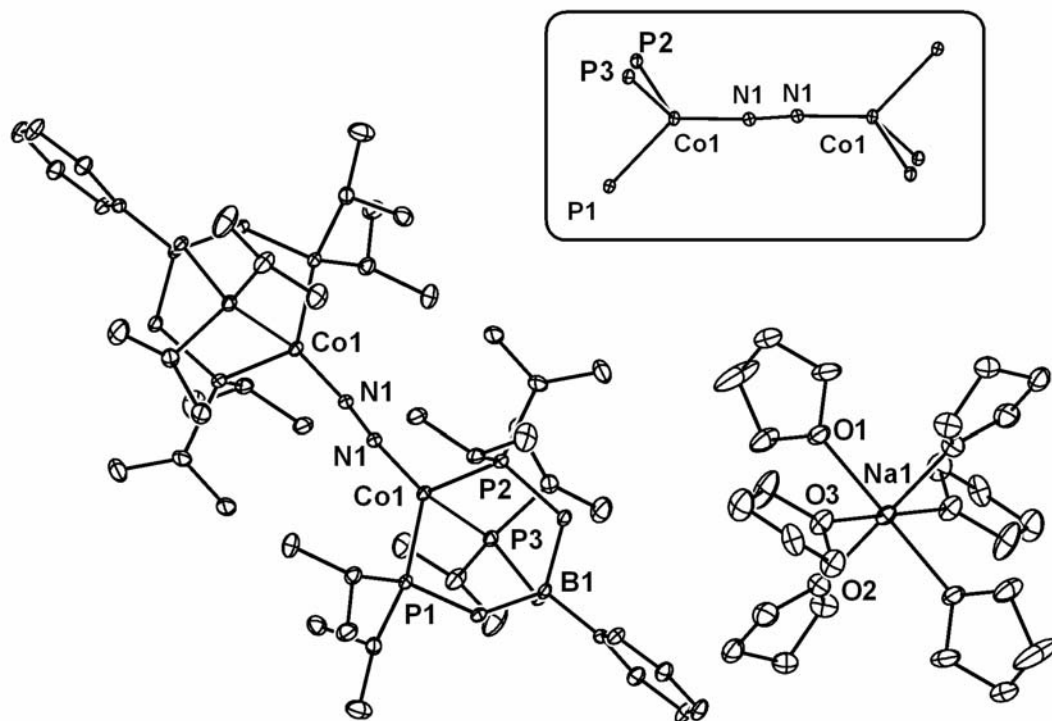
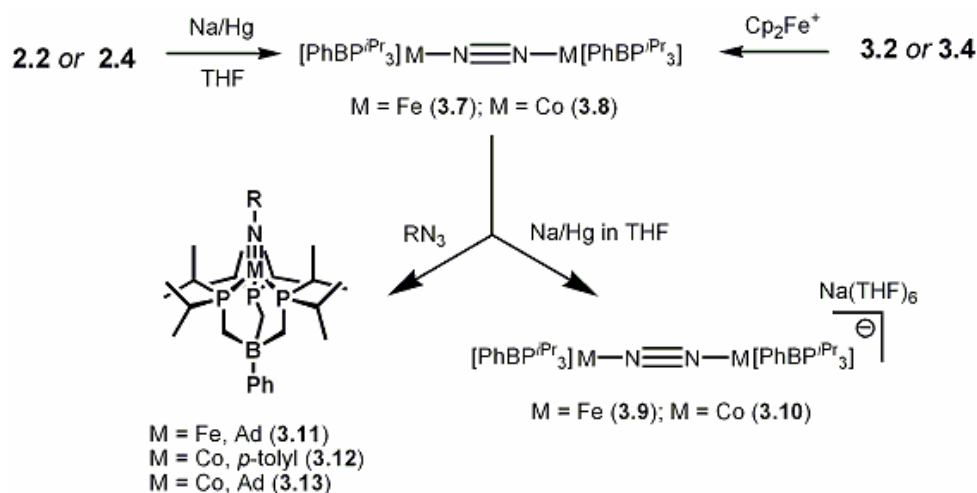


Figure 3.3. Displacement ellipsoid representation of $\{([\text{PhBP}^{i\text{Pr}}_3]\text{Co})_2(\mu\text{-N}_2)\}\{\text{Na}(\text{THF})_6\}\cdot\text{THF}$ (**3.10**) with anion core highlighted in inset. Hydrogen atoms and non-coordinating solvent molecules have been removed for clarity. Selected bond distances (Å) and angles ($^\circ$), for **3.10**: Co-N 1.805(2), N-N' 1.147(4), Co-P1 2.232(1), Co-P2 2.230(1), Co-P3 2.249(1); N'-N-Co 174.6(3), P1-Co-P2 95.10(3), P1-Co-P3 93.58(3), P2-Co-P3 93.53(3), N-Co-P1 133.30(8), N-Co-P2 122.95(8), N-Co-P3 108.39(8).

Scheme 3.2



Complexes **3.7** and **3.8** provided clean access to the “[PhB^{iPr}P₃]M(I)” fragment, as exemplified in their ability to undergo rapid oxidation upon addition of either tolyl- or adamantylazide to afford trivalent imide products. For example, burgundy [PhB^{iPr}P₃]Fe≡NAd (**3.11**; 69%), red [PhB^{iPr}P₃]Co≡N-*p*-tolyl (**3.12**, 93%), and red [PhB^{iPr}P₃]Co≡NAd (**3.13**, 96%) were isolated and thoroughly characterized (Scheme 3.2), and the solid-state structures of each were determined.¹¹ The crystal structure of complex **3.11** (Figure 3.3(A)) 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.^{6b} The crystal structures of the Co complexes **3.12** and **3.13** (Figure 3.3 B and C) reveal similar features. The Co-N bond for **3.12** and **3.13** is consistently short (1.667(1) Å and 1.642(1) Å, respectively), while maintaining a nearly linear Co-N-C bond vector (173° and 176°, respectively). Most striking on comparing the structures for complexes **3.11** - **3.13** is the contraction of the M-P bond lengths on going from the *S* = ½ Fe(III) imide **3.11** (P_{av} = 2.273 Å) to the singlet Co(III) imides, **3.12** (P_{av} = 2.200 Å)

and **3.13** ($P_{av} = 2.200 \text{ \AA}$). The Fe-P bonds are likely expanded due to the unpaired electron on Fe.

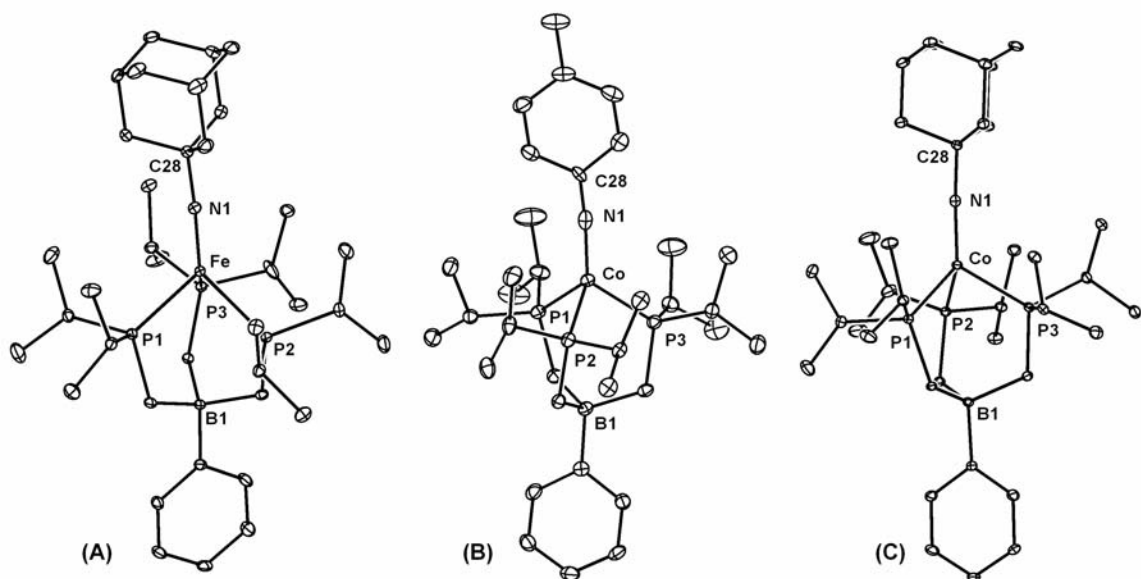


Figure 3.4. Displacement ellipsoid representation of (A) $[\text{PhBP}^{i\text{Pr}}_3]\text{Fe}\equiv\text{NAd}$ (**3.11**), (B) $[\text{PhBP}^{i\text{Pr}}_3]\text{Co}\equiv\text{NAd}$ (**3.12**), and (C) $[\text{PhBP}^{i\text{Pr}}_3]\text{Co}\equiv\text{NAd}$ (**3.13**). Hydrogen atoms have been removed for clarity. Selected bond distances (\AA) and angles ($^\circ$), for **3.11**: Fe-N1 1.638(2), Fe-P1 2.260(1), Fe-P2 2.297(1), Fe-P3 2.263(1); C28-N1-Fe 176.0(2), P1-Fe-P2 91.05(2), P1-Fe-P3 91.56(3), P2-Fe-P3 92.39(3), N1-Fe-P1 121.62(7), N1-Fe-P2 130.03(7), N1-Fe-P3 120.27(7); for **3.12**: Co-N1 1.667(1), Co-P1 2.200(1), Co-P2 2.190(1), Co-P3 2.213(1); C28-N-Co 173.16(15), P1-Co-P2 92.91(2), P1-Co-P3 92.09(2), P2-Co-P3 92.77(2), N1-Co-P1 123.72(6), N1-Co-P2 118.77(6), N-Co-P3 127.57(6); for **3.13**: Co-N1 1.642(1), Co-P1 2.208(1), Co-P2 2.205(1), Co-P3 2.193(1); C28-N-Co 176.14(18), P1-Co-P2 91.57(3), P1-Co-P3 92.60(3), P2-Co-P3 91.70(3), N1-Co-P1 121.25(7), N1-Co-P2 123.00(7), N-Co-P3 127.24(7).

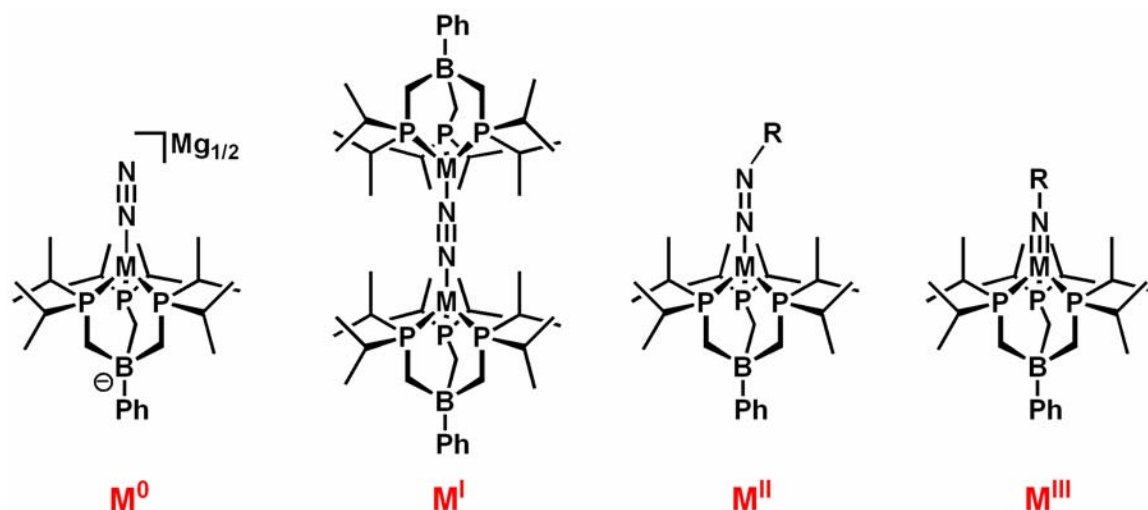
The anionic N₂-adducts **3.3** and **3.4** were well poised for further elaboration at the coordinated N₂ functionality. This is significant because the direct conversion of coordinated N₂ to a coordinated diazenido (N₂R⁻) and/or hydrazido (N₂R₂²⁻) species by simple addition of an electrophile (e.g., R⁺) on a first row transition metal has, to our knowledge, not been established.^{5,8} We were thus gratified to find that the simple addition of methyltosylate (MeOTs) to a THF solution of **3.3** effected a modest color change from brown to gold, along with a concomitant shift in its ν_{NN} vibration to 1597 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^{*i*Pr}₃]Fe-N=NMe (**3.14**, 56%), consistent with its magnetic susceptibility ($S = 2$, 4.93 μ_{B} , Evans). A similar protocol converted **3.4** to the amber colored complex [PhBP^{*i*Pr}₃]Co-N=NMe (**3.15**, 68%), which exhibited a very similar ν_{NN} stretch (1599 cm⁻¹) and a solution moment consistent with low spin cobalt(II) (1.92 μ_{B}). Complex **3.4** reacted cleanly with trimethylsilylchloride to generate [PhBP^{*i*Pr}₃]Co-N=NSiMe₃ (**3.16**, 79%; $\nu_{\text{NN}} = 1654$ 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 iodide **2.4** in the presence of Me₃SiCl and Na/Hg amalgam under nitrogen.

Table 3.1. Structural and Infrared data for complexes presented in Chapter 3.

Complex	#	d_{M-N}	d_{N-N}	$\nu_{NN} (\nu_{15N15N})$ (cm^{-1})
$\{\text{PhBP}^{i\text{Pr}}_3\text{Fe}(\text{N}_2)\} \{\text{MgCl}(\text{THF})_2\}$	3.2	--	--	1830 (1769)
$\{\text{PhBP}^{i\text{Pr}}_3\text{Fe}(\text{N}_2)\}_2 \{\text{Mg}(\text{THF})_4\}$	3.3	1.686(8)	1.158(9)	1818
$\{\text{PhBP}^{i\text{Pr}}_3\text{Co}(\text{N}_2)\}_2 \{\text{Mg}(\text{THF})_4\}$	3.4	1.687(3)	1.155(3)	1863 (1802)
$\{\text{PhBP}^{i\text{Pr}}_3\text{Fe}(\text{N}_2)\}_2 \{\text{Mg}(18\text{-C-6})\}$	3.5	--	--	1884 (1822)
$\{\text{PhBP}^{i\text{Pr}}_3\text{Co}(\text{N}_2)\}_2 \{\text{Mg}(18\text{-C-6})\}$	3.6	--	--	1896 (1842)
$\{\text{PhBP}^{i\text{Pr}}_3\text{Fe}\}_2(\mu\text{-N}_2)^a$	3.7	1.811(5), 1.818(5)	1.138(6)	--
$[(\text{PhBP}^{i\text{Pr}}_3\text{Fe})_2(\mu\text{-N}_2)][\text{Na}(\text{THF})_6]$	3.9	1.813(2)	1.171(4)	--
$[(\text{PhBP}^{i\text{Pr}}_3\text{Co})_2(\mu\text{-N}_2)][\text{Na}(\text{THF})_6]$	3.10	1.805(2)	1.147(4)	--
$[\text{PhBP}^{i\text{Pr}}_3\text{Fe}\equiv\text{NAd}]$	3.11	1.638(2)	--	--
$[\text{PhBP}^{i\text{Pr}}_3\text{Co}\equiv\text{N-}p\text{-tolyl}]$	3.12	1.667(1)	--	--
$[\text{PhBP}^{i\text{Pr}}_3\text{Co}\equiv\text{NAd}]$	3.13	1.642(1)	--	--
$[\text{PhBP}^{i\text{Pr}}_3\text{Fe-N=NMe}]$	3.14	--	--	1597 (1538)
$[\text{PhBP}^{i\text{Pr}}_3\text{Co-N=NMe}]$	3.15	--	--	1599 (1542)
$[\text{PhBP}^{i\text{Pr}}_3\text{Co-N=NSiMe}_3]$	3.16	--	--	1654 (1596)

^a Structure presented in Chapter 4.

Scheme 3.3



3.3 Conclusions.

These data allow us to summarize several salient features of the chemistry described herein: The $[\text{PhBP}^{i\text{Pr}}_3]$ ligand can isolate a single iron (or cobalt) center in a pseudo-tetrahedral environment in which a single binding site is compatible with coordination of N_2 , diazenido (N_2Me), and imide (NR) — an electronically diverse series of N-donor ligands. Moreover, N_2 uptake/coordination by 4-coordinate iron (and cobalt) has been established for the formal oxidation states $\text{Fe}(0)$, $\text{Fe}(+0.5)$, and $\text{Fe}(+1)$. Methylation of $\text{Fe}^0(\text{N}_2)^-$ to produce $\text{Fe}^{\text{II}}(\text{N}_2\text{Me})$ constitutes a 2-electron redox process at iron — the first of its type — also true of the cobalt system. Moreover, the availability of a separate 2-electron redox process, that of oxidative nitrene transfer ($\text{FeL}^{\text{I}} \rightarrow \text{Fe}^{\text{III}}\equiv\text{NR}$) — emphasizes that the “[$\text{PhBP}^{i\text{Pr}}_3$] Fe ” platform can support four formal oxidation states (Fe^0 , Fe^{I} , Fe^{II} , Fe^{III} see Scheme 3.3), in addition to two discrete 2-electron redox couples ($\text{Fe}^{0/\text{II}}$ and $\text{Fe}^{\text{I}/\text{III}}$). These features collectively motivate our further development of the present systems as *functionally* relevant models for nitrogen fixation.^{3,4,12}

3.4 Experimental Section

3.4.1 General Considerations. All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N₂ gas followed by passage through an activated alumina column. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. Deuterated solvents were degassed and stored over activated 3-Å molecular sieves prior to use. THF-*d*₈ was dried by passage over activated alumina and stored over activated sieves prior to use. [PhBP^{*i*Pr}₃][Tl] (**2.1**), [PhBP^{*i*Pr}₃]FeCl (**2.2**), and [PhBP^{*i*Pr}₃]CoI (**2.4**) were prepared as previously reported.⁹ [Fc][BPh₄]¹¹ and *p*-tolylazide¹² were prepared according to literature procedures. Adamantylazide (Aldrich), chlorotrimethylsilane (Strem), and methyl tosylate (Aldrich) were used as received without further purification. ¹⁵N-Labeled N₂ gas was purchased from Cambridge Isotope Laboratory. All reagents were purchased from commercial vendors and used without further purification unless explicitly stated. Elemental analyses were carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on Varian Mercury 300 MHz, Joel 400 MHz, and Inova 500 MHz spectrometers, unless otherwise noted. ¹H NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts are reported relative to an external standard of 85% H₃PO₄. IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software. UV-vis measurements were taken on a Hewlett Packard 8452A diode array spectrometer using a quartz crystal cell with a

Teflon cap. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

3.4.2. X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

3.4.3. Syntheses of Compounds.

[PhBPⁱPr₃]FeI (3.1). A solution of [PhBPⁱPr₃]Ti (**2.1**) (200 mg, 0.292 mmol) in THF (5 mL) was added to a stirring suspension of FeI₂ (90.3 mg, 0.292 mmol) in THF (5 mL) at room temperature. After stirring for 6 h, the resulting yellow solution was filtered through a Celite pad and then evaporated to dryness in vacuo. The yellow-brown solids were dissolved in benzene (15 mL) and filtered again through a Celite pad and evaporated to dryness. The yellow solids were washed repeatedly with petroleum ether (3 x 10 mL) and dried in vacuo. Crystallization from a petroleum ether/diethyl ether mixture afforded an analytically pure, crystalline product (176 mg, 91%). ¹H NMR (C₆D₆, 300 MHz): δ 30 (s), 14.98 (s), 14.63 (s), 12.3 (bs), -0.4 (bs), -19.2 (bs). Evans Method (C₆D₆): 5.33 μ_B. Anal. Calcd for C₂₇H₅₃BIFeP₃: C, 48.60; H, 8.01. Found: C, 48.39; H, 8.10.

{[PhBPⁱPr₃]Fe(N₂)}{MgCl(THF)₂} (3.2): A solution of [PhBPⁱPr₃]FeCl (**2.2**) (100 mg, 0.175 mmol) in THF (2 mL) was added to a stirring suspension of Mg⁰ powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature. After stirring for 12 h, the resulting orange-amber solution was filtered, then evaporated to dryness in vacuo. The brown solids were dissolved in THF (2 mL) and the solution was filtered once again. Vapor

diffusion of petroleum ether into the THF filtrate resulted in the precipitation of brown solids. This brown solid was dried under vacuum to afford analytically pure product (113 mg, 84%). ^1H NMR (THF- d_8 , 300 MHz): δ 26.8, 18.07 (bs), 13.5, 12.4, 3.53 (THF), 1.73 (THF), -6.35 (bs). UV-vis (THF) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 373 (3200), 909 (620). Evans Method (THF- d_8): 2.92 μB . IR: (THF/KBr) $\nu_{\text{NN}} = 1830 \text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{35}\text{H}_{69}\text{BClFeMgN}_2\text{O}_2\text{P}_3$: C, 54.65; H, 9.04; N, 3.64. Found: C, 54.60; H, 9.19, N, 3.33.

{{[PhBP^{*i*Pr}]₃Fe(¹⁵N₂)}}{MgCl(THF)₂} (3.2-¹⁵N₂) A solution of **2.2** (220 mg, 0.38 mmol) in THF (10 mL) was added to a suspension of Mg powder (100 mg, 4.1 mmol) in THF (20 mL) under a counter-flow of Argon gas into a 200 mL sealable Schlenk bomb reactor in the dry box. The headspace of the bomb was then evacuated under vacuum. The solution was degassed via 3 freeze-pump-thaw cycles and then exposed to one atmosphere of labeled ¹⁵N₂ gas (ca. 8.3 mmol). The reaction was stirred for 24 h at room temperature by which time the solution turned a dark red brown. The reaction workup followed the same protocol as that described for **3.2** (233 mg, 79%). Spectroscopic features in the ^1H NMR were identical for those reported for **3.2**. IR: (THF/KBr) $\nu_{\text{NN}} = 1769 \text{ cm}^{-1}$.

{{[PhBP^{*i*Pr}]₃Fe(N₂)}}₂{Mg(THF)₄} (3.3): A solution of [PhBP^{*i*Pr}]₃FeI (**3.1**) (65 mg, 0.15 mmol) in THF (2 mL) was added to a stirring suspension of Mg⁰ powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature. After stirring for 12 h, the resulting red solution was filtered through a Celite pad. Vapor diffusion of petroleum ether into the THF filtrate resulted in the precipitation of large red crystals. Suitable crystals were selected for an X-ray diffraction study. The red crystals were isolated by decanting the remaining solution and drying under vacuum to afford analytically pure product (101 mg,

68%). ^1H NMR (THF- d_8 , 300 MHz): δ 14.0, 11.6, 10.8, 4.8, 3.58 (THF), 1.73 (THF), 0.9, -6.2 (bs). Evans Method (THF- d_8): 5.11 μB . IR: (THF/KBr) $\nu_{\text{NN}} = 1818\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{70}\text{H}_{138}\text{B}_2\text{Fe}_2\text{MgN}_4\text{O}_4\text{P}_6$: C, 58.25; H, 9.64, N, 3.88. Found: C, 57.99; H, 9.58; N 3.90.

{[PhBP^{*i*Pr}]₃Co(N₂)₂]₂[Mg(THF)₄] (3.4): A solution of [PhBP^{*i*Pr}]₃CoI (**2.4**) (100 mg, 0.15 mmol) in THF (2 mL) was added to a stirring suspension of Mg⁰ powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature. After stirring for 12 h, the resulting red solution was filtered and then evaporated to dryness in vacuo. The red solids were dissolved in THF (2 mL) and the solution was filtered once again. Vapor diffusion of petroleum ether into the THF filtrate resulted in the precipitation of large red crystals. Suitable crystals were selected for an X-ray diffraction study. The red crystals were isolated by decanting the remaining solution and drying under vacuum to afford analytically pure product (169 mg, 78%). ^1H NMR (THF- d_8 , 300 MHz): δ 18.5 (bs), 13.6, 12.1, 11.8, 6.3, 3.58 (THF), 1.73 (THF), 0.9, -19.5 (bs). UV-vis (THF) λ_{max} , nm (ϵ , $\text{M}^{-1}\text{ cm}^{-1}$): 985 (580). Evans Method (THF- d_8): 2.01 μB . IR: (THF/KBr) $\nu_{\text{NN}} = 1863\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{70}\text{H}_{138}\text{B}_2\text{Co}_2\text{MgN}_4\text{O}_4\text{P}_6$: C, 58.00; H, 9.60, N, 3.87. Found: C, 57.41; H, 9.75; N 3.50.

{[PhBP^{*i*Pr}]₃Co(¹⁵N₂)₂]₂[Mg(THF)₄] (3.4-¹⁵N₂): A solution of **2.4** (200 mg, 0.30 mmol) in THF (10 mL) was added to a suspension of Mg powder (100 mg, 4.1 mmol) in THF (20 mL) under a counter-flow of Argon gas into a 100 mL sealable Schlenk bomb reactor in the dry box. The headspace of the bomb was then evacuated under vacuum. The solution was degassed via 3 freeze-pump-thaw cycles and then exposed to one atmosphere of labeled ¹⁵N₂ gas (ca. 4.1 mmol). The reaction was stirred for 24 h at room

temperature by which time the solution turned a dark red color. The reaction workup followed the same protocol as that described for **3.4** (181 mg, 87%). The product was analyzed and proved identical to **3.4** according to its ^1H NMR. IR: (THF/KBr) $\nu_{\text{NN}} = 1802\text{ cm}^{-1}$.

{{PhBP^{iPr}₃Fe(N₂)₂Mg(18-C-6) (3.5)}: A solution of **2.2** (45 mg, 0.078 mmol) in THF (2 mL) was added to a stirring suspension of Mg^0 powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature. After stirring for 16 h, the resulting orange-amber solution was filtered to remove excess Mg^0 and insoluble residue. A solution of 18-crown-6 (24 mg, 0.091 mmol) in THF (1 mL) was added to the orange-amber filtrate and the solution was stirred for 2 h at room temperature. This solution was then filtered to remove a white precipitate. The volatiles were evaporated in vacuo to yield a brown solid that was then washed with petroleum ether (2 x 3 mL). The brown solid was dried under vacuum to afford analytically pure product (92 mg, 82.5%). ^1H NMR (THF-*d*₈, 300 MHz): δ 13.8, 11.8, 10.6, 4.8, 3.92, 0.9, -6.5 (bs). IR: (THF/KBr) $\nu_{\text{NN}} = 1884\text{ cm}^{-1}$. Anal. Calcd for $\text{C}_{66}\text{H}_{130}\text{B}_2\text{Fe}_2\text{MgN}_4\text{O}_6\text{P}_6$: C, 55.86; H, 9.23; N, 3.95. Found: C, 55.69; H, 9.32; N, 3.99.

{{PhBP^{iPr}₃Fe(¹⁵N₂)₂Mg(18-C-6) (3.5-¹⁵N₂)}: A solution of **3.2-¹⁵N₂** (20 mg, 0.026 mmol) in THF (2 mL) was added to a solution of 18-crown-6 (13.7 mg, 0.05 mmol) in THF (1 mL) under a blanket of Argon gas in a 25 mL Schlenk round-bottom flask at room temperature. The reaction was stirred for 30 min at room temperature. The reaction workup followed the same protocol as that described for **3.5**. Spectroscopic features in the ^1H NMR were identical for those reported for **3.5**. IR: (THF/KBr) $\nu_{\text{NN}} = 1822\text{ cm}^{-1}$.

{{PhBP^{iPr}₃Co(N₂)₂Mg(18-C-6) (3.6): A solution of **2.4** (52 mg, 0.078 mmol) in THF (2 mL) was added to a stirring suspension of Mg⁰ powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature. After stirring for 10 h, the resulting red-orange solution was filtered. A solution of 18-crown-6 (21 mg, 0.078 mmol) in THF (1 mL) was added to the red-orange filtrate. The resulting solution was stirred for 45 minutes, during which time the color changed to an intense red-orange. The volatiles were removed in vacuo to afford a red-orange solid that was then washed with petroleum ether (2 x 3 mL). The resulting residue was dried under vacuum to afford analytically pure material (101 mg, 91%). ¹H NMR (THF-*d*₈, 300 MHz): δ 18.4 (bs), 13.5, 12.1, 11.8, 5.9, 3.82, 1.2, -19.5 (bs). IR: (THF/KBr) ν_{NN} = 1896 cm⁻¹. Anal. Calcd for C₆₆H₁₃₀B₂Co₂MgN₄O₆P₆: C, 55.61; H, 9.19; N, 3.93. Found: C, 55.60; H, 9.42; N, 3.88.

{{PhBP^{iPr}₃Co(¹⁵N₂)₂Mg(18-C-6) (3.6-¹⁵N₂): A solution of **3.4-¹⁵N₂** (20 mg, 0.014 mmol) in THF (2 mL) was added to a solution of 18-crown-6 (7.3 mg, 0.03 mmol) in THF (1 mL) under a blanket of Argon gas in a 25 mL Schlenk round-bottom flask at room temperature. The reaction was stirred for 30 min at room temperature. The reaction workup followed the same protocol as that described for **3.6**. The product was analyzed and proved identical to **3.6** according to its ¹H NMR. IR: (THF/KBr) ν_{NN} = 1842 cm⁻¹.

{{PhBP^{iPr}₃Fe₂(μ-N₂) (3.7): A 0.5 weight % Na/Hg amalgam (2.8 mg, 0.132 mmol of sodium dissolved in 560 mg of mercury) was stirred in THF (5 mL) for several minutes. A solution of **2.2** (75 mg, 0.131 mmol) in THF (1 mL) was added to the vigorously stirring amalgam at room temperature under nitrogen. After stirring for 4 h, the resulting brown solution was filtered (filter paper/pipet) to remove insoluble residues.

The volatiles were then removed in vacuo. The resulting brown solids were dissolved in THF (3 mL), to which petroleum ether was then added (2 mL). Storing this solution at -33 °C for 20 h resulted in the precipitation of an amorphous brown solid. These solids were isolated by decanting the remaining solution, and then washed with petroleum ether (2 x 3 mL). The isolated solids were dried under a blanket of nitrogen (in the glove box) to afford analytically pure material (127 mg, 88%). Note: the isolated solids are highly unstable to benzene, which caused decomposition of this material to as yet unidentified products. ^1H NMR (THF- d_8 , 300 MHz): δ 26.83 (s), 18.13 (bs), 13.50, 12.36, 7.30, 0.85, -5.02, -6.30 (bs). UV-vis (THF) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 372 (6700), 905 (1200). Evans Method (THF- d_8): 4.12 μ_{B} (calculated per Fe center). Anal. Calcd for $\text{C}_{54}\text{H}_{106}\text{B}_2\text{Fe}_2\text{N}_2\text{P}_6$: C, 58.82; H, 9.69; N, 2.54. Found: C, 58.88; H, 9.88; N, 2.38.

Synthesis of 3.7 by oxidation of 3.2: A solution of **3.2** (25 mg, 0.039 mmol) in THF (3 mL) was added in two portions to a stirring slurry of $[\text{Cp}_2\text{Fe}][\text{BPh}_4]$ (19.7 mg, 0.039 mmol) in THF (3 mL) at room temperature. The color of the solution progressed from the red-amber of **3.2** to a darker brown color over the period of 6 h. This color change was accompanied by the disappearance of the ν_{NN} band (1830 cm^{-1}) of **3.2**. After this time, the precipitate was filtered to afford a brown filtrate. Upon isolation by removal of solvent in vacuo, the product was analyzed and proved identical to **3.7** according to its ^1H NMR, UV-Vis spectrum, and independent combustion analysis. Several diamagnetic products (less than 10% by ^1H NMR) also formed during this reaction; thus, the reduction of **2.2** by sodium-amalgam provides a cleaner synthesis of **3.7**.

{{PhBP^{iPr}₃Co}₂(μ -N₂) (3.8): A 0.5 weight % Na/Hg amalgam (2.0 mg, 0.087 mmol of sodium dissolved in 420 mg of mercury) was stirred in THF (5 mL). A solution of **2.4** (60 mg, 0.090 mmol) in THF (1 mL) was added to the amalgam at room temperature. After stirring for 6 h, the resulting pale rose solution was filtered to remove insoluble residues. Petroleum ether (2 mL) was added drop-wise to the THF solution. The solution was then stored at -33 °C for 10 h which resulted in the deposition of large, pale purple crystals. The crystals were isolated by decanting the remaining solution and allowing the crystals to dry under a blanket of nitrogen (in the glove box), affording analytically pure material (92 mg, 92%). Note: the isolated crystals proved unstable to benzene, which caused decomposition to as yet unidentified products. ¹H NMR (THF-*d*₈, 300 MHz): δ 17.34 (bs), 6.63, 6.36, 0.91 (bs). UV-vis (THF) λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 745 (170), 948 (270). Evans Method (THF-*d*₈): 3.01 μ_B (calculated per Co center). Anal. Calcd for C₅₄H₁₀₆B₂Co₂N₂P₆: C, 58.50; H, 9.64; N, 2.53. Found: C, 57.88; H, 9.72; N, 2.45.

Synthesis of 3.8 by oxidation of 3.4: A solution of **3.4** (30 mg, 0.021 mmol) in THF (3 mL) was added in two portions to a stirring slurry of [Fc][BPh₄] (10.5 mg, 0.021 mmol) in THF (3 mL) at room temperature. The color of the solution progressed from the cherry-red of **3.4** to a turbid, colorless solution over the period of 1 h. The color change was accompanied by the disappearance of the ν_{NN} (1863 cm⁻¹) of **3.4** by IR. After this time, the precipitate was filtered to provide a pale rose filtrate. The product of the oxidation was identical to **3.8** as ascertained by ¹H NMR and UV-vis spectroscopies, and an independent combustion analysis.

[{[PhBP^{iPr}]₃Fe}₂(μ-N₂)]Na(THF)₆ (3.9): A 0.5 weight % Na/Hg amalgam (15 mg, 0.65 mmol of sodium dissolved in 3 g of mercury) was stirred in THF (5 mL) for several minutes. A solution of **2.2** (75 mg, 0.131 mmol) in THF (1 mL) was added to the vigorously stirring amalgam at room temperature. After stirring for 13 h, the resulting red-brown solution was filtered (filter paper/pipet) to remove insoluble residues. The THF solution was then slowly layered with petroleum ether (2.5 mL) so as to just begin precipitation of the salts. The slightly turbid mixture was then re-dissolved by shaking and allowed to stand for 48 h at room temperature. Dark brown crystals deposited during this time that were isolated by decanting the remaining solution. A suitable crystal was selected for an X-ray diffraction study. The crystals were dried in vacuo to afford analytically pure material (189 mg, 93%). ¹H NMR (THF-*d*₈, 300 MHz): δ 25.8, 16.10 (bs), 13.22, 12.10, 9.47 (bs), 3.64 (THF), 1.85 (THF), -6.84 (bs). UV-vis (THF) λ_{max}, nm (ε, M⁻¹ cm⁻¹): 374 (2800), 905 (570). Anal. Calcd for C₇₈H₁₅₄B₂Fe₂N₂NaO₆P₆: C, 60.12; H, 9.96; N, 1.80. Found: C, 59.61; H, 10.22; N 1.82.

[{[PhBP^{iPr}]₃Co}₂(μ-N₂)]Na(THF)₆ (3.10): A 0.5 weight % Na/Hg amalgam (9 mg, 0.39 mmol of sodium dissolved in 1.8 g of mercury) was stirred in THF (5 mL) for several minutes. A solution of **2.4** (50 mg, 0.075 mmol) in THF (1 mL) was then added to the vigorously stirring amalgam at room temperature. After stirring for 12.5 h, the resulting red-brown solution was filtered to remove insoluble material. The THF solution was then layered with petroleum ether (2.5 mL), which slowly caused some solids to precipitate. The turbid mixture was then re-dissolved by thorough shaking and allowed to stand for 24 h at room temperature. Dark red-brown crystals deposited during this time that were then isolated by decanting the supernatant. A suitable crystal was selected

for an X-ray diffraction study. The crystals were dried *in vacuo* to afford analytically pure material (104 mg, 89%). ^1H NMR (THF- d_8 , 300 MHz): δ 24.23, 18.48 (bs), 16.85 (bs), 12.12, 11.56, 3.58 (THF), 1.73 (THF), 0.14, -1.97 (bs), -3.62, -4.53, -19.45 (bs). UV-vis (C_6H_6) λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 566 (210), 969 (450). Anal. Calcd for $\text{C}_{78}\text{H}_{154}\text{B}_2\text{Co}_2\text{N}_2\text{NaO}_6\text{P}_6$: C, 59.89; H, 9.92; N, 1.79. Found: C, 59.57; H, 9.64; N, 1.84.

[PhBP^{*i*Pr}]₃Fe \equiv NAd (3.11): Complex **3.7** was generated *in situ* by the following procedure: A 0.5 weight % Na/Hg amalgam (3.6 mg, 0.157 mmol of sodium dissolved in 720 mg of mercury) was stirred in THF (5 mL). A solution of **2.2** (60 mg, 0.105 mmol) in THF (1 mL) was added to the amalgam at room temperature. After stirring for 8 h, the resulting red-brown solution was filtered to remove insoluble material, providing a solution of **3.7**. A solution of adamantylazide (20.2 mg, 0.105 mmol) in THF (0.5 mL) was then added to this red-brown solution. The resulting solution was stirred at room temperature for 28 h, during which time the solution color turned to a deep red. The solution was filtered, layered with petroleum ether (2 mL), and stored at -33 °C for 36 h. Opaque red crystals deposited during this time were isolated by decanting the remaining liquor. A suitable crystal was selected for an X-ray diffraction study. The crystals were dried *in vacuo* to afford analytically pure material (49.6 mg, 69%). ^1H NMR (C_6D_6 , 300 MHz): δ 56.4, 38.4, 20.2, 13.1, 12.2, 9.45, 9.15, 5.65 (dd), 2.76, -0.78, -5.93, -7.13, -31.4. Evans Method (C_6D_6): 1.94 BM. Anal. Calcd for $\text{C}_{37}\text{H}_{68}\text{BFeNP}_3$: C, 64.73; H, 9.98; N, 2.04. Found: C, 65.13; H, 10.08; N, 1.98.

[PhBP^{*i*Pr}]₃Co \equiv N-*p*-tol (3.12): Complex **3.8** was generated *in situ* by the following procedure: A 0.5 weight % Na/Hg amalgam (1.4 mg, 0.06 mmol of sodium dissolved in 276 mg of mercury) was stirred in THF (3 mL). A solution of **2.4** (40 mg,

0.060 mmol) in THF (1 mL) was added to the amalgam at room temperature. After stirring for 6 h, the resulting pale-rose solution was filtered (filter-paper/pipet) to remove insoluble material. A solution of *p*-tolylazide (8 mg, 0.06 mmol) in THF (0.5 mL) was then added to the pale-rose colored solution, which caused a dramatic color change to a deep red. The solution was stirred for 1 h and the volatiles were then removed in vacuo. The resulting red solid was washed with petroleum ether (3 x 5 mL). Crystals of **3.12** were grown by extracting the red solid into benzene and slowly allowing petroleum ether to diffuse into this solution. The red crystals that formed were isolated by decanting off the remaining solution and drying in vacuo (36 mg, 93%). Suitable crystals were selected for an X-ray diffraction study. ^1H NMR (C_6D_6 , 300 MHz): δ 7.90 (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 7.5$ Hz, 2H), 7.54 (t, $J = 6.9$ Hz, 2H), 7.31 (t, $J = 7.8$ Hz, 1H), 6.63 (d, $J = 7.5$ Hz, 2H), 2.00 (bs, 6H), 1.58 (s, 3H), 1.43 (dd, $J = 5.4, 12.6$ Hz, 18H), 1.21 (bs, 18H), 0.50 (bs, 6H). ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): δ 85 (bs). Anal. Calcd for $\text{C}_{34}\text{H}_{60}\text{BCoNP}_3$: C, 63.26; H, 9.37; N, 2.17. Found: C, 63.18; H, 9.36; N, 2.08.

[PhBP^{*i*Pr}]₃Co \equiv NAd (3.13): Complex **3.8** was generated *in situ* by the following procedure: A 0.5 weight % Na/Hg amalgam (1.4 mg, 0.06 mmol of sodium dissolved in 276 mg of mercury) was stirred in THF (3 mL). A solution of **2.4** (40 mg, 0.060 mmol) in THF (1 mL) was added to the amalgam at room temperature. After stirring for 6 h, the resulting pale-rose solution was filtered (filter-paper/pipet) to remove insoluble material. A solution of adamantylazide (16 mg, 0.09 mmol) in THF (0.5 mL) was then added to the pale-rose colored solution, which caused a dramatic color change to a deep red. The solution was stirred for 1 h and the volatiles were then removed in vacuo. The resulting red solid was washed with petroleum ether (3 x 5 mL). Crystals of **3.13** were grown by

extracting the red solid into benzene and slowly allowing petroleum ether to diffuse into this solution. The red crystals that formed were isolated by decanting off the remaining solution and drying in vacuo (36 mg, 88 %). Suitable crystals were selected for an X-ray diffraction study. ^1H NMR (C_6D_6 , 300 MHz): δ 7.52 (t, $J = 6.9$ Hz, 2H), 7.30 (t, $J = 7.8$ Hz, 1H), 6.65 (d, $J = 7.5$ Hz, 2H), 2.8-1.4 (bs, 21H), 1.38 (dd, $J = 5.4, 12.6$ Hz, 18H), 1.21 (bs, 18H), 0.50 (bs, 6H). ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6 , 121.4 MHz): δ 79 (bs). Anal. Calcd for $\text{C}_{37}\text{H}_{68}\text{BCoNP}_3$: C, 64.44; H, 9.94; N, 2.03. Found: C, 64.25; H, 9.95; N, 2.08.

[PhBP^{*i*Pr}]₃Fe(N₂Me) (3.14): A solution of **2.2** (75 mg, 0.131 mmol) in THF (2 mL) was added to a stirring suspension of Mg^0 powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature to generate **3.2** *in situ*. After stirring for 12 h, the resulting orange-amber solution was filtered (filter-paper/pipet) to remove excess Mg powder and insolubles. A solution of methyl tosylate (24.4 mg, 0.131 mmol) in THF (2 mL) was added in two portions to the stirring solution of “[FeN₂--Mg]” at room temperature. The combined solution was stirred for 6 h, then the solution was filtered (filter-paper/pipet) and evaporated to dryness in vacuo. The resulting oily brown solid was extracted into benzene and filtered (filter-paper/pipet) to yield a gold solution. The benzene was removed in vacuo to afford a tan brown solid. The solids were washed with petroleum ether (2 x 3 mL) and dried in vacuo to afford analytically pure material (38 mg, 56%). ^1H NMR (C_6D_6 , 300 MHz): δ 34, 19.2, 18.5, 3.2 (bs), 2.0 (bs), -14 (bs), -30 (bs). Evans Method (C_6D_6): 4.93 μB . IR: (THF/KBr) $\nu_{\text{NN}} = 1597$ cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{56}\text{BFeN}_2\text{P}_3$: C, 57.95; H, 9.73; N, 4.83. Found: C, 58.65; H, 9.98; N, 4.78. *Note*: An isolated sample of **3.3** also reacted with stoichiometric MeOTs in THF to form **3.14**.

[PhBP^{iPr}₃]Fe(¹⁵N₂Me) (3.14-¹⁵N₂): A solution of methyl tosylate (24.1 mg, 0.131 mmol) in THF (2 mL) was added in two portions to the stirring solution of **3.2-¹⁵N₂** (50 mg, 0.065 mmol) in THF (2 mL) under a blanket of Argon in a 25 mL round-bottom Schlenk flask. The reaction was stirred for 2 h at room temperature and worked up in a similar fashion to **3.14**. The product was analyzed and proved identical to **3.14** according to its ¹H NMR. IR: (THF/KBr) $\nu_{\text{NN}} = 1538 \text{ cm}^{-1}$.

[PhBP^{iPr}₃]Co(N₂Me) (3.15): A solution of **2.4** (100 mg, 0.15 mmol) in THF (2 mL) was added to a stirring suspension of Mg⁰ powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature to generate **3.4** *in situ*. After stirring for 12 h, the resulting red solution was filtered (filter-paper/pipet). A solution of methyl tosylate (27.9 mg, 0.15 mmol) in THF (2 mL) was added dropwise to the stirring solution of “[CoN₂)₂--Mg]” at room temperature. The solution was stirred for 5 h where the color changed from cherry-red to brown. Then, the solution was filtered (filter-paper/pipet) and evaporated to dryness under vacuum. The resulting brown solid was extracted into benzene and filtered (filter-paper/pipet) to yield a tan solution. The benzene was removed in vacuo to afford a tan solid. The solids were washed with petroleum ether (2 x 3 mL) and dried in vacuo to afford analytically pure material (60 mg, 68%). ¹H NMR (C₆D₆, 300 MHz): δ 23.9 (bs), 12.8, 3.22 (bs), 1.04 (bs). Evans Method (C₆D₆): 1.92 μ_{B} . IR: (THF/KBr) $\nu_{\text{NN}} = 1599 \text{ cm}^{-1}$. Anal. Calcd for C₂₈H₅₆BCoN₂P₃: C, 57.64; H, 9.67; N, 4.80. Found: C, 57.75; H, 9.72; N, 4.69. *Note:* An isolated sample of **3.4** also reacted with stoichiometric MeOTs in THF to form **3.15**.

[PhBP^{iPr}₃]Co(¹⁵N₂Me) (12-¹⁵N₂): A solution of methyl tosylate (7.7 mg, 0.041 mmol) in THF (2 mL) was added in two portions to a stirring solution of **3.4-¹⁵N₂** (50 mg,

0.034 mmol) in THF (2 mL) under a blanket of Argon in a 25 mL round-bottom Schlenk flask. The reaction was stirred for 4 h at room temperature and worked up in a similar fashion to **3.15**. The spectroscopic features in the ^1H NMR were identical for those reported for **3.15**. IR: (THF/KBr) $\nu_{\text{NN}} = 1542\text{ cm}^{-1}$.

[PhBP^{iPr}₃]Co(N₂SiMe₃) (3.16): A solution of **2.4** (100 mg, 0.15 mmol) in THF (2 mL) was added to a stirring suspension of Mg⁰ powder (100 mg, 4.1 mmol) in THF (2 mL) at room temperature to generate **3.4** *in situ*. After stirring for 12 h, the resulting red solution was filtered (filter-paper/pipet). A solution of chlorotrimethylsilane (16.3 mg, 0.15 mmol) in THF (2 mL) was added dropwise to the stirring solution at room temperature. The resulting solution was stirred for 5 h, during which time the color changed from cherry-red to brown. The solution was then filtered and evaporated to dryness under vacuum. The resulting brown solid was extracted into benzene and filtered to provide a brown filtrate. The volatiles were removed in vacuo to afford brown solids that were washed with petroleum ether (2 x 3 mL) and then dried in vacuo to afford analytically pure material (76 mg, 79%). ^1H NMR (C₆D₆, 300 MHz): δ 24.1 (bs), 13.1, 3.22 (bs), 0.15 (bs). Evans Method (C₆D₆): 2.08 μ_{B} . IR: (THF/KBr) $\nu_{\text{NN}} = 1654\text{ cm}^{-1}$. Anal. Calcd for C₃₀H₆₂BCoN₂P₃Si: C, 56.16; H, 9.74; N, 4.37. Found: C, 56.45; H, 9.83; N, 4.22.

Alternative synthesis of 3.16: A 0.5 weight % Na/Hg amalgam (8.3 mg, 0.36 mmol of sodium dissolved in 1.66 mg of mercury) was stirred in THF (3 mL). Chlorotrimethylsilane (39 mg, 0.36 mmol) was added directly to the stirring solution of amalgam prior to the addition of **2.4**. A solution of **2.4** (40 mg, 0.060 mmol) in THF (1 mL) was added to the amalgam/Me₃SiCl solution at room temperature. The combined

solutions were stirred for 5 h, after which time the solution was filtered to remove mercury and precipitates. The silyldiazenido product **3.16** was identified by IR and ^1H NMR spectroscopies, and the dinuclear, N_2 -bridged product **3.8** was also identified. The ratio of **3.16** to **3.8** was 85:15 according to integration of a ^1H NMR spectrum of the crude product mixture.

[PhBP^{*i*Pr}₃]Co($^{15}\text{N}_2\text{SiMe}_3$) (3.16- $^{15}\text{N}_2$): A solution of chlorotrimethylsilane (3.6 mg, 0.034 mmol) in THF (2 mL) was added in two portions to a stirring solution of **3.4- $^{15}\text{N}_2$** (25 mg, 0.017 mmol) in THF (2 mL) under a blanket of Argon in a 25 mL round-bottom Schlenk flask. The reaction was stirred for 4 h at room temperature and worked up in a similar fashion to **3.16**. The product was analyzed and proved identical to **3.16** according to its ^1H NMR. IR: (THF/KBr) $\nu_{\text{NN}} = 1596 \text{ cm}^{-1}$.

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