

**Chapter 6: A structurally characterized homobimetallic  
bridging  $\mu_2$ -nitride complex of cobalt**

## 6.1 Introduction

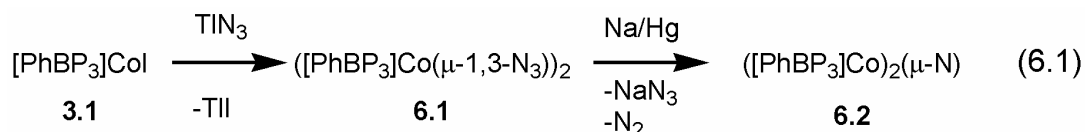
Bridging  $\mu_2$ -nitrides have been shown to be the final product of the chemical splitting of  $N_2$  in molybdenum<sup>1</sup> and niobium<sup>2</sup> systems. Furthermore, the potential for a bridging nitride to be part of the catalytic cycle for biological nitrogen fixation is intriguing in light of the recent X-ray structure of the MoFe-cofactor of nitrogenase, which features an interstitial  $\mu_6$ -ligand, possibly a nitride.<sup>3</sup> Previously, homobimetallic bridging  $\mu_2$ -nitrides of many early to mid-transition metals in high oxidation states have been synthesized.<sup>4,5</sup> Examples of this type of complex featuring late metals are limited to examples on Fe,<sup>6,7</sup> Ru,<sup>8</sup> and Os,<sup>9</sup> even though they are monomeric terminal nitride or imido late metal complexes,<sup>10,11</sup> and bridging nitride complexes of higher nuclearity (three or more metal atoms)<sup>12</sup> have been reported. The scarcity of homobimetallic bridging  $\mu_2$ -nitride complexes for late metals is all the more striking in light of the fact that the related mono-<sup>13</sup> and bis- $\mu_2$ -oxo complexes<sup>14</sup> are well-established for groups 9 through 12. Herein we report the first example of a homobimetallic bridging  $\mu_2$ -nitride complex of cobalt.

## 6.2 Results and discussion

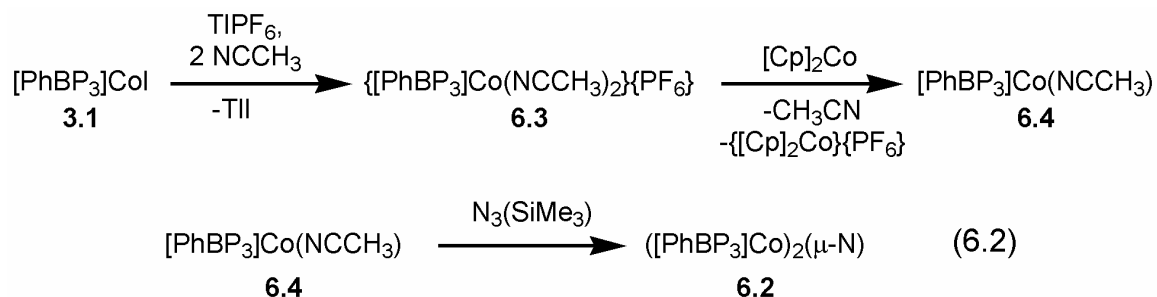
### 6.2.1 Synthesis of $([PhBP_3]Co)_2(\mu-N)$

The synthesis of the bridged nitride can be accomplished by the two routes shown in Eq. 6.1 and Eq. 6.2. The bridged azide complex  $([PhBP_3]Co(\mu-1,3-N_3))_2$  (**6.1**) ( $[PhBP_3] = [PhB(CH_2PPh_2)_3]$ ) is prepared by reacting the previously described  $[PhBP_3]CoI$  (**3.1**)<sup>15</sup> with excess  $TiN_3$  in THF (Eq. 6.1). Complex **6.1** is isolated in 66% yield and characterized by IR, UV-vis, and NMR spectroscopy, as well as single crystal X-ray diffraction. The addition of one equivalent of Na/Hg amalgam to **6.1** in THF gives

the desired bridged nitride,  $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$  (**6.2**), in 90% yield. Complex **6.2** is formally a mixed valent  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  species. This route to the  $\mu_2$ -bridging nitride manifold is similar to that employed in our laboratory for the preparation of the low valent  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$   $\mu_2$ -nitride,  $\{([\text{PhBP}_3]\text{Fe})_2(\mu\text{-N})\} \{\text{Na}(\text{THF})_5\}$ . The bridged nitride complex, **6.2**, is deep red in color and has two charge transfer bands in its UV-vis spectrum at 395 ( $\epsilon = 21800 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 549 ( $\epsilon = 8800 \text{ M}^{-1} \text{ cm}^{-1}$ ) nm; the near-IR region of the spectrum shows no additional bands, in contrast to the NIR bands of related  $\{([\text{PhBP}_3]\text{Fe})_2(\mu\text{-N})\} \{\text{Na}(\text{THF})_5\}$ .



An alternate route (Eq. 6.2) proceeds via the addition of  $\text{TIPF}_6$  and acetonitrile to a THF solution of **3.1** to give the green cationic bis-acetonitrile complex,  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\} \{\text{PF}_6\}$ , **6.3**, in 95% yield. Complex **6.3** can be reduced with  $[\text{Cp}]_2\text{Co}$  in THF to give the neutral paramagnetic mono-acetonitrile adduct,  $[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)$  **6.4** in 78% yield.

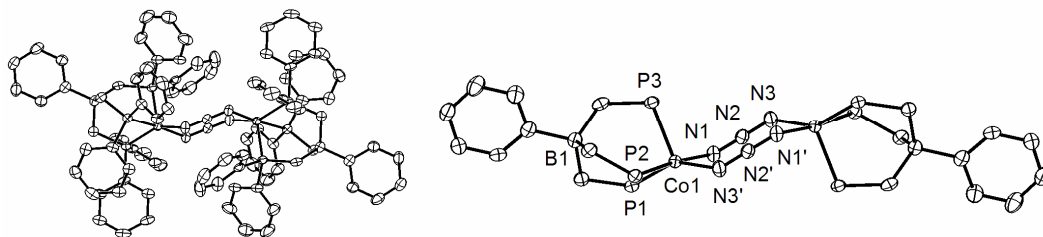


Addition of 20 equivalents of  $(\text{Me}_3\text{Si})\text{N}_3$  ( $\text{Me}_3\text{Si} = \text{TMS}$ ) to a THF solution of **6.4** turns the solution from brown to dark red characteristic of **6.2**. Pure **6.2** was obtained in 17% yield by crystallization of the reaction mixture upon standing for one day.

Trimethylsilylazide has previously been shown to be an effective nitrogen transfer agent to give terminal nitride complexes.<sup>16</sup> Notably, the reactivity of **6.4** with (Me<sub>3</sub>Si)N<sub>3</sub> is very different from the reactivity of the [Tp<sup>R,R</sup>]CoN<sub>2</sub> ([Tp] = hydro-tris(pyrazolyl)borate, R = <sup>i</sup>Pr or <sup>t</sup>Bu) complexes reported by Theopold and co-workers, which undergo intramolecular C-H bond activation to form amides.<sup>17</sup>

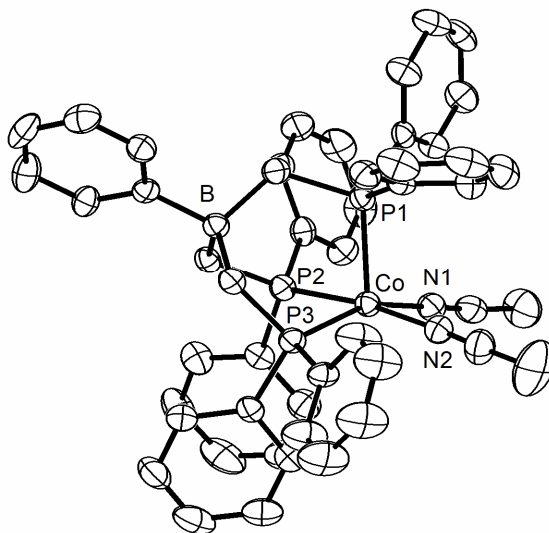
### 6.2.2 Structural characterization and magnetic studies of precursors

The solid-state structures of the precursor compounds are of interest. Both **6.1** and **6.3** were studied by X-ray diffraction. The coordination geometry for each metal center within **6.1** is best described as a distorted square pyramidal with a crystallographic inversion center present (Figure 6.1). A small amount (< 3%) of [PhBP<sub>3</sub>]Tl co-crystallized in the sample leading to some disorder in the structure. The bond lengths and angles of **6.1** are similar to those of its cationic analogue [(H<sub>3</sub>CC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>)Co(μ<sub>2</sub>-1,3-N<sub>3</sub>)]<sub>2</sub>[BPh<sub>4</sub>]<sub>2</sub>, (H<sub>3</sub>CC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub> = triphos).<sup>18</sup> Notably, the structure differs somewhat from ([PhBP<sub>3</sub>]Co(μ-Br))<sub>2</sub> (**3.2**) and ([PhBP<sub>3</sub>]Co(μ-Cl))<sub>2</sub> (**3.3**) as **6.1** has shorter Co-P bonds. In addition, one of the P-Co-N bond angles is nearly linear (N1-Co1-P2, 174.01(10)).



**Figure 6.1.** Displacement ellipsoids are represented at 50%. The structure on the right is shown without aryl carbon atoms for clarity. Selected interatomic distances (Å) and angles (deg) for  $[(\text{PhBP}_3)\text{Co}(\mu\text{-}1,3\text{-N}_3)]_2$ , (**6.1**): Co1-P1, 2.232(1); Co1-P2, 2.203(1); Co1-P3, 2.255(1); Co1-N1, 1.977(3); Co1-N3', 1.955(3). P1-Co1-P2, 89.32(5); P1-Co1-P3, 95.97(5); P2-Co1-P3, 91.45(5); N1-Co1-P1, 90.85(11); N1-Co1-P2, 174.01(10); N1-Co1-P3, 94.48(10); N3'-Co1-P1, 149.44(11); N3'-Co1-P2, 88.44(10); N3'-Co1-P3, 114.55(11); N3'-Co1-N1, 88.36(14).

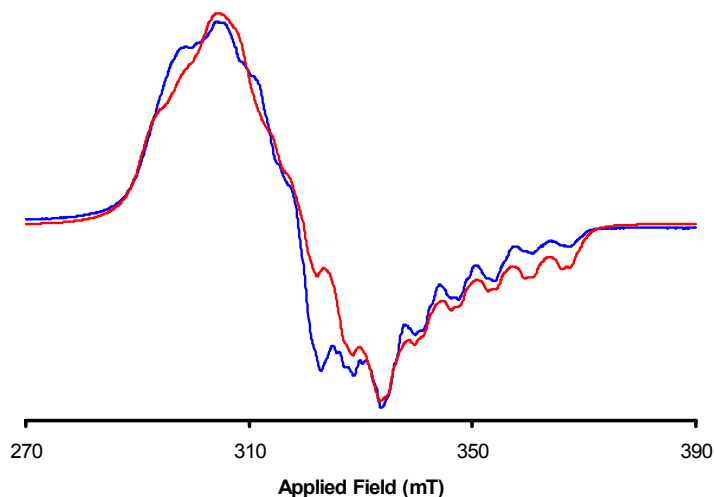
The solid-state structure determined for **6.3** reveals a square pyramidal geometry about Co, similar to what is observed for dicationic  $[(\text{triphos})\text{Co}(\text{NCCH}_2\text{CH}_3)_2][\text{BF}_4]_2$  (Figure 6.2).<sup>19</sup> This contrasts to a similar five-coordinate “[PhBP<sub>3</sub>]Co” species, namely, [PhBP<sub>3</sub>]CoI(PMe<sub>3</sub>), which features a trigonal bipyramidal geometry. The geometry difference for these species is also observed in solution by EPR (see below). The axial Co-P bond (Co-P1, 2.331(1)) is elongated compared to the other two equatorial Co-P bonds (2.238(1) and 2.253(1)).



**Figure 6.2.** Displacement ellipsoid representation (50%) for  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\}^+$  (**6.3**) with the anion omitted for clarity. Selected interatomic distances ( $\text{\AA}$ ) and angles (deg): Co-P1, 2.331(1); Co-P2, 2.238(1); Co-P3, 2.253(1); Co-N1, 1.947(3); Co-N2, 1.914(2). P1-Co-P2, 90.01(3); P1-Co-P3, 96.11(3); P2-Co-P3, 87.90(3); N1-Co-P1, 105.92(7); N1-Co-P2, 91.45(7); N1-Co-P3, 157.96(7); N2-Co-P1, 97.34(7); N2-Co-P2, 172.54(7); N2-Co-P3, 90.02(7); N1-Co-N2, 87.79(10).

Complex **6.3** was determined to be low spin by SQUID magnetometry with an average magnetic moment ( $\chi_m T_{\text{av}}$ , 10 to 300 K) of  $0.60 \text{ cm}^3 \text{ K mol}^{-1}$ . The complex obeys the Curie-Weiss law. The EPR spectrum of **6.3**, taken in a mixture of benzene and acetonitrile, shows well-defined hyperfine ( $I_{\text{Co}} = 7/2$ ) and superhyperfine ( $3 \times I_{\text{P}} = 1/2$ ) coupling. The coupling parameters were successfully simulated, and the experimental and simulated spectra are shown in Figure 6.3. The spectrum shows an axial signal ( $g_{\perp} > g_{\parallel}$ ) typical of low spin Co(II) square pyramidal structures.<sup>20</sup> This confirms that the

species maintains its solid-state geometry in solution and contrasts with  $[\text{PhBP}_3]\text{CoI}(\text{PMe}_3)$ , which shows an axial EPR spectrum with  $g_{\parallel} > g_{\perp}$ .



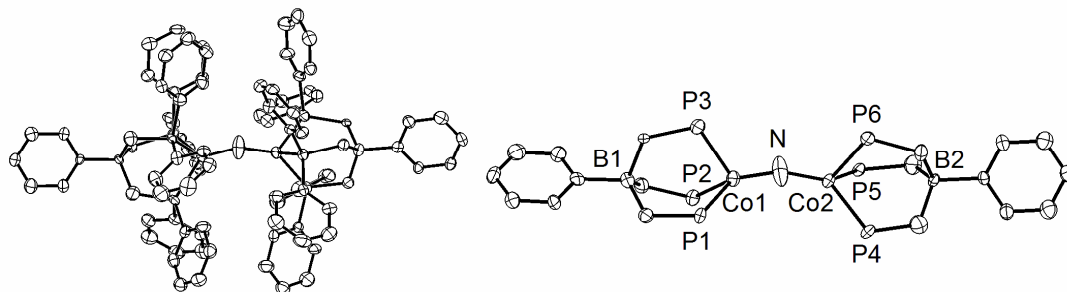
**Figure 6.3.** EPR spectrum of  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\} \{\text{PF}_6\}$  (**6.3**) in a mixture of benzene and acetonitrile at 77 K. The blue line (—) is the experimental spectrum, and the red line (—) is the simulated spectrum. Simulated Parameters:  $g_x = 2.150$ ,  $a_{x(\text{Co})} = 22$  gauss,  $a_{x(\text{P})} = 26$  gauss;  $g_y = 2.176$ ,  $a_{y(\text{Co})} = 54$  gauss,  $a_{y(\text{P})} = 15$  gauss;  $g_z = 1.974$ ,  $a_{z(\text{Co})} = 65$  gauss,  $a_{z(\text{P})} = 17$  gauss. See Experimental Section for instrumental parameters.

### 6.2.3 Structural characterization of $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$

The solid state structure of **6.2** is of significant interest, and suitable crystals for X-ray diffraction were grown from methylene chloride and petroleum ether (Figure 6.4). The solid-state structure obtained includes disorder of the phosphine ligands coordinated to  $\text{Co}_2$  (approximately 9% of the lattice features molecules with phosphines in the second, chemically equivalent, position). In addition, the crystal suffers from racemic

twinning in the orthorhombic space group  $Pna2_1$ . The structure of **6.2** presented herein is the best data set obtained from X-ray diffraction studies of a number of different crystalline samples derived from different recrystallization attempts. The molecular structures obtained for the other crystals all indicated similar metrics for the cobalt complex, and therefore the identity of **6.2** is not in question. The Co1-N and Co2-N bonds are quite short, 1.623(8) Å and 1.648(8) Å respectively, suggesting significant metal-ligand multiple bond character. Recently published terminal cobalt imides have Co-N bond distances of 1.658(2) Å for  $[\text{PhBP}_3]\text{Co}\equiv\text{N}(p\text{-tolyl})$  and 1.624(4) Å for a  $\beta$ -diketiminato supported terminal imide.<sup>21</sup> These short Co-N bonds compare well to bridging  $\mu_2$ -nitrides of iron, although it should be noted that in the latter cases the iron centers are high valent  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{IV}}$  or  $\text{Fe}^{\text{IV}}/\text{Fe}^{\text{IV}}$ .<sup>4,7</sup> These bond distances are also significantly shorter than in the published bridged  $\mu_2$ -imides of Co ( $\text{Co-N(R)-Co}$ ), which have Co-N bond distances between 1.97 and 2.05 Å.<sup>21,22</sup> The Co-P distances of **6.2** shown are within 0.02 Å of 2.25 Å, which is characteristic of low spin cobalt complexes previously studied, and likewise the P-Co-P angles are barely greater than 90°. Interestingly, the Co1-N-Co2 angle is slightly bent at 155.3(6)°, making this angle more acute than previously examined iron  $\mu_2$ -nitrides, which typically have Fe-N-Fe bond angles between 170 and 180°. <sup>4,7</sup> The exception to this trend is  $\{([\text{PhBP}_3]\text{Fe})_2(\mu\text{-N})\}\{\text{Na}(\text{THF})_5\}$ , which has an Fe1-N-Fe2 bond angle of 135.9(3).



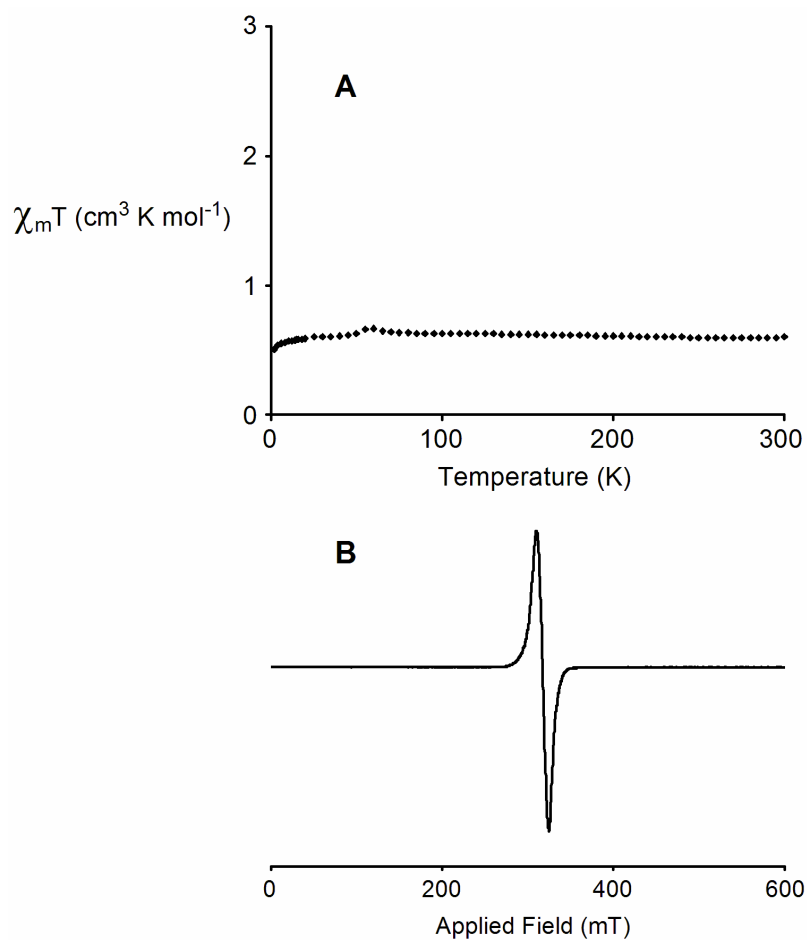


**Figure 6.4.** Displacement ellipsoids are represented at 50%. The structure on the right is shown without aryl carbon atoms for clarity. Selected interatomic distances (Å) and angles (deg) for ([PhBP<sub>3</sub>]Co)<sub>2</sub>(μ-N) (**6.2**): Co1-P2, 2.238(2); Co1-P3, 2.258(2); Co1-P1, 2.259(2); Co1-N, 1.623(8); Co2-P6, 2.243(3); Co2-P5, 2.249(2); Co2-P4, 2.254(2); Co2-N, 1.648(8). Co1-N-Co2, 155.3(6).

#### 6.2.4 Magnetic characterization of ([PhBP<sub>3</sub>]Co)<sub>2</sub>(μ-N)

Since **6.2** is a paramagnetic complex, we decided to investigate its magnetic properties using variable temperature SQUID magnetization measurements. The complex was determined to have only one unpaired electron with  $\chi_m T_{av}$  (10 K to 300 K) equaling 0.60 cm<sup>3</sup> K mol<sup>-1</sup>, obeying the Curie-Weiss law (Figure 6.5A). This result rules out the possibility of strong anti-ferromagnetic coupling to give one unpaired electron at low temperature. Variable temperature EPR studies performed in glassy toluene show only one signal in the temperature range of 5 to 60 K. The spectrum shows no well-resolved coupling or anisotropy, and the signal is centered at  $g \approx 2.11$  (Figure 6.5B). This result corroborates the SQUID assignment of one unpaired electron for the molecule since no low field signals indicative of high spin cobalt are observed.<sup>23</sup> These combined results

suggest that the species may be a valence localized  $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$  species wherein both metal ions are low spin.



**Figure 6.5.** (A) SQUID plot of  $\chi_m T$  ( $\text{cm}^3 \text{ K mol}^{-1}$ ) versus  $T$  for  $([\text{PhBP}_3]\text{Co})(\mu\text{-N})$ , **6.2**, ( $\blacklozenge$ ). (B) EPR spectrum of  $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$ , **6.2**, in toluene at 30 K. See Experimental Section for instrumental parameters.

### 6.3 Conclusion

In summary, we have expanded the family of homobimetallic bridging  $\mu_2$ -nitride complexes to include a Group 9 metal, cobalt. The bridged nitride exhibits short Co-N bond distances, typical of bridging nitride moieties, although the slightly bent

Co1-N-Co2 angle is unusual compared to most analogous bridging Fe  $\mu_2$ -nitride complexes. The species is a low spin complex ( $S = \frac{1}{2}$ ) with one unpaired electron.

## 6.4 Experimental section

### 6.4.1 General considerations

General procedures were performed according to Section 2.4.1 and 3.5.1. Magnetic measurements were conducted as described in Section 3.5.2. EPR measurements and simulations were conducted as described in Section 3.5.3.

### 6.4.2 EPR measurements

Instrumental parameters for the spectra shown:

For  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\}\{\text{PF}_6\}$  (**6.3**) in Figure 6.3: EPR spectrum of  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\}\{\text{PF}_6\}$  in a mixture (1:1) of benzene and acetonitrile at 77 K. Instrumental parameters:  $\nu$ , 9.509 GHz, Modulation frequency, 100 kHz, Modulation Amplitude, 4 G, Microwave Power, 12.755 mW, Conversion Time, 20.48 ms, Time Constant, 5.12 ms, Scans, 20.

For  $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$  (**6.2**) in Figure 6.5: EPR spectrum of  $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$  (**6.2**) in toluene at 30 K. Instrumental parameters:  $\nu$ , 9.379 GHz; Modulation frequency, 100 kHz; Modulation Amplitude, 2 G; Microwave Power, 0.638 mW; Conversion Time, 81.92 ms; Time Constant, 20.48 ms; Scans, 1.

### 6.4.3 Starting materials and reagents

The preparation of  $[\text{PhBP}_3]\text{CoI}$  (**3.1**) is described in Chapter 3. The reagent  $\text{TiN}_3$  was prepared according to a literature procedure.<sup>24</sup> The reagents  $\text{TiPF}_6$ ,  $[\text{Cp}]_2\text{Co}$ ,  $(\text{TMS})\text{N}_3$ , sodium, and mercury metal were purchased from commercial vendors and used without further purification.

#### 6.4.4 Synthesis of compounds

**Synthesis of  $[\text{PhBP}_3]\text{Co}(\mu_2\text{-1,3-N}_3)_2$ , **6.1**.** The reagents  $\text{TiN}_3$  (1.73 g, 7.03 mmol) and  $[\text{PhBP}_3]\text{CoI}$ , **3.1**, (0.613 g, 0.703 mmol) were mixed together as solids in a 250 mL Erlenmeyer flask, and THF (150 mL) was added. The reaction mixture was stirred for 24 h and then filtered over Celite. The THF was removed under reduced pressure, and the red powder was extracted with 100 mL of  $\text{CH}_2\text{Cl}_2$ . This solution was filtered over Celite and then the solvent was removed in vacuo (0.364 g, 66% yield). The red powder can be crystallized by vapor diffusion of petroleum ether into a  $\text{CH}_2\text{Cl}_2$  solution.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz):  $\delta$  8.06, 7.45 (d,  $J = 6.9$  Hz), 7.26 (t,  $J = 7.5$  Hz), 7.08 (t,  $J = 7.5$  Hz), 5.87, 3.28 (br s). UV-vis (THF)  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 375 (8600), 518 (3900). IR ( $\text{cm}^{-1}$ , THF): 2070. Anal. Calcd for  $\text{C}_{90}\text{H}_{82}\text{B}_2\text{Co}_2\text{N}_6\text{P}_6$ : C, 68.72; H, 5.25; N, 5.34. Found: C, 68.80; H, 5.52; N, 5.14.

**Synthesis of  $[\text{PhBP}_3]\text{Co}_2(\mu\text{-N})$ , **6.2**.** Neat  $\text{N}_3(\text{TMS})$  (0.572 g, 4.96 mmol) was added to a THF solution (2 mL) of  $[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)$ , **6.4**, (0.195 g, 0.248 mmol) and mixed for one minute. The solution was allowed to stand for 24 h, and red crystals formed. The red crystals were washed with petroleum ether (3 x 3 mL) then dissolved in benzene (3 mL), which was frozen and lyophilized to remove solvent (0.032 g, 17% yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  9.4, 8.5, 7.9, 7.6, 3.3, 0.5. UV-vis ( $\text{C}_6\text{H}_6$ )  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 395 (21800), 549 (8800). SQUID (average from 10 – 310 K):  $\chi_{\text{m}}T = 0.60 \text{ cm}^3 \text{ K mol}^{-1}$ . Anal. Calcd for  $\text{C}_{90}\text{H}_{82}\text{B}_2\text{Co}_2\text{NP}_6$ : C, 71.92; H, 5.50; N, 0.93. Found: C, 70.42; H, 5.30; N, 1.05.

**Alternative Synthesis of  $[\text{PhBP}_3]\text{Co}_2(\mu\text{-N})$ , **6.2**.** A 0.52 % Na/Hg amalgam was prepared by dissolving 6.2 mg (0.27 mmol) of sodium into 1.2 g of mercury. A THF solution (15 mL) of  $[\text{PhBP}_3]\text{Co}(\mu_2\text{-1,3-N}_3)_2$ , **6.1**, (0.212 g, 0.270 mmol) was added to

the amalgam and allowed to stir for 14 h. The reaction mixture was then filtered through Celite to remove the amalgam, and the filtrate was dried in vacuo affording a fine red powder. The powder was dissolved in benzene (12 mL) and stirred vigorously. The solution was then filtered over Celite, and the solvent was removed under reduced pressure (0.183 g, 90% yield). The compound can be crystallized in  $\text{CH}_2\text{Cl}_2$  at  $-35\text{ }^\circ\text{C}$ . This preparation gave the same spectra as the above method.

**Synthesis of  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\}\{\text{PF}_6\}$ , 6.3.** A THF (3 mL) solution of  $\text{TiPF}_6$  (0.042 g, 0.12 mmol) was added to a THF (10 mL) solution of  $[\text{PhBP}_3]\text{CoI}$ , **3.1**, (0.101 g, 0.116 mmol) causing the green reaction mixture to become cloudy. An excess of acetonitrile (approximately 5 to 15 equivalents) was added to the mixture causing an instant color change to yellow. An orange solid precipitated after 4 h leaving a green supernatant. The solution was filtered over Celite and then concentrated to dryness under reduced pressure. The resulting powder was dissolved in benzene (8 mL), and vapor diffusion of petroleum ether afforded green crystals (0.107 g, 95.7% yield). Note: the crystals grown for the X-ray diffraction experiment contained the  $\{\text{BF}_4\}$  counteranion instead of  $\{\text{PF}_6\}$ .  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 300 MHz):  $\delta$  10.4 (br), 7.2, 7.0, 3.6, 3.1 (br), 1.7. UV-vis ( $\text{C}_6\text{H}_6$ )  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ): 740 (280). SQUID (average from 10 – 310 K):  $\chi_{\text{m}}T = 0.60\text{ cm}^3\text{ K mol}^{-1}$ . EPR (77 K, benzene/acetonitrile):  $g_x = 2.150$ ,  $a_{x(\text{Co})} = 22$  gauss,  $a_{x(\text{P})} = 26$  gauss;  $g_y = 2.176$ ,  $a_{y(\text{Co})} = 54$  gauss,  $a_{y(\text{P})} = 15$  gauss;  $g_z = 1.974$ ,  $a_z = 65$  gauss,  $a_{z(\text{P})} = 17$  gauss. Anal. Calcd for  $\text{C}_{49}\text{H}_{47}\text{BCoP}_4\text{N}_2\text{F}_6$ : C, 60.58; H, 4.87; N, 2.88. Found: C, 60.59; H, 5.39; N, 2.23.

**Synthesis of  $[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)$ , 6.4:** A THF solution (3 mL) of  $[\text{Cp}]_2\text{Co}$  (0.0789 g, 0.417 mmol) was added to a stirring THF solution (15 mL) of

$\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\} \{\text{PF}_6\}$ , **6.3**, (0.413 g, 0.426 mmol). The solution was stirred for 16 h and then filtered over Celite followed by removal of the solvent under reduced pressure. The powder was reconstituted in 12 mL of benzene and stirred followed by filtration over Celite. The solution was then frozen and lyophilized (0.255 g, 78% yield).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta$  16.0, 15.0, 13.7, 12.2, 10.4, 8.1, 7.2, 5.5. IR ( $\text{cm}^{-1}$ , THF): 2045. Anal. Calcd for  $\text{C}_{47}\text{H}_{44}\text{BCoNP}_3$ : C, 71.80; H, 5.65; N, 1.78. Found: C, 71.44; H, 5.82; N, 1.20.

### 6.4.5 X-ray experimental information

The general X-ray experimental procedure was performed according to section 2.4.4. Crystallographic information is provided in Table 6.1.

**Table 6.1.** X-ray diffraction experimental details for  $([\text{PhBP}_3]\text{Co}(\mu_2\text{-1,3-N}_3))_2$  (**6.1**),  $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$ , (**6.2**), and  $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\} \{\text{BF}_4\}$  (**6.3**).

|                                           | $([\text{PhBP}_3]\text{Co}(\mu_2\text{-1,3-N}_3))_2$ ( <b>6.1</b> )                                        | $([\text{PhBP}_3]\text{Co})_2(\mu\text{-N})$ , ( <b>6.2</b> ) |
|-------------------------------------------|------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| Chemical formula                          | $\text{C}_{90}\text{H}_{84}\text{B}_2\text{Cl}_{0.76}\text{Co}_{1.95}\text{N}_6\text{P}_6\text{Tl}_{0.05}$ | $\text{C}_{90}\text{H}_{82}\text{B}_2\text{NP}_6\text{Co}_2$  |
| Formula weight                            | 1587.53                                                                                                    | 1502.87                                                       |
| T (°C)                                    | -177                                                                                                       | -177                                                          |
| $\lambda$ (Å)                             | 0.71073                                                                                                    | 0.71073                                                       |
| a (Å)                                     | 13.0507(12)                                                                                                | 40.978(4)                                                     |
| b (Å)                                     | 14.4544(13)                                                                                                | 13.3841(13)                                                   |
| c (Å)                                     | 14.6285(13)                                                                                                | 13.7861(14)                                                   |
| $\alpha$ (°)                              | 100.286(2)                                                                                                 | 90                                                            |
| $\beta$ (°)                               | 111.438(1)                                                                                                 | 90                                                            |
| $\gamma$ (°)                              | 114.974(1)                                                                                                 | 90                                                            |
| V (Å <sup>3</sup> )                       | 2139.6(3)                                                                                                  | 7560.9(13)                                                    |
| Space group                               | $\text{P}\bar{1}$                                                                                          | $\text{Pna}2_1$                                               |
| Z                                         | 1                                                                                                          | 4                                                             |
| D <sub>calc</sub> (g/cm <sup>3</sup> )    | 1.551                                                                                                      | 1.320                                                         |
| $\mu$ (cm <sup>-1</sup> )                 | 43.6                                                                                                       | 6.14                                                          |
| R1, wR2 ( $I > 2\sigma(I)$ ) <sup>a</sup> | 0.0704, 0.1306                                                                                             | 0.0814, 0.1070                                                |

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$

**Table 6.1. (cont.)**

| $\{[\text{PhBP}_3]\text{Co}(\text{NCCH}_3)_2\} \{\text{BF}_4\}$ <b>(6.3)</b> |                                                                              |
|------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| Chemical formula                                                             | $\text{C}_{49}\text{H}_{47}\text{BN}_2\text{P}_3\text{Co} \cdot \text{BF}_4$ |
| Formula weight                                                               | 913.35                                                                       |
| T (°C)                                                                       | -177                                                                         |
| $\lambda$ (Å)                                                                | 0.71073                                                                      |
| a (Å)                                                                        | 19.2341(13)                                                                  |
| b (Å)                                                                        | 13.1806(9)                                                                   |
| c (Å)                                                                        | 19.6043(13)                                                                  |
| $\alpha$ (°)                                                                 | 90                                                                           |
| $\beta$ (°)                                                                  | 115.234(1)                                                                   |
| $\gamma$ (°)                                                                 | 90                                                                           |
| V (Å <sup>3</sup> )                                                          | 4495.8(5)                                                                    |
| Space group                                                                  | P2 <sub>1</sub> /c                                                           |
| Z                                                                            | 4                                                                            |
| D <sub>calcd</sub> (g/cm <sup>3</sup> )                                      | 1.349                                                                        |
| $\mu$ (cm <sup>-1</sup> )                                                    | 5.42                                                                         |
| R1, wR2 (I>2 $\sigma$ (I)) <sup>a</sup>                                      | 0.0531, 0.0819                                                               |

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