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## Oxidative Addition and C-H Activation Chemistry with a PNP Pincer Ligated Cobalt Complex.

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Supporting Information

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**I. General Considerations.** All air- and moisture-sensitive manipulations were carried out using standard high vacuum line, Schlenk or cannula techniques or in an M. Braun inert atmosphere drybox containing an atmosphere of purified nitrogen. The M. Braun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.<sup>1</sup> Deuterated solvents for NMR spectroscopy were distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves. The ligand 2,6-(CH<sub>2</sub>P(<sup>i</sup>Pr)<sub>2</sub>)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (<sup>iPr</sup>PNP) and the corresponding cobalt dichloride complex, (<sup>iPr</sup>PNP)CoCl<sub>2</sub> were prepared according to literature procedures.<sup>2,3</sup>

<sup>1</sup>H NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 399.860 MHz. All chemical shifts are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) chemical shifts of the solvent as a secondary standard. <sup>13</sup>C NMR spectra were recorded on a Bruker 500 spectrometer operating at 125.71 MHz. <sup>13</sup>C chemical shifts are reported relative to SiMe<sub>4</sub> using chemical shifts of the solvent as a secondary standard where applicable. <sup>31</sup>P NMR spectra were collected on a Bruker 300 AVANCE spectrometer operating at 299.763 MHz and were referenced to 85 % H<sub>3</sub>PO<sub>4</sub> as an external standard. All coupling constants are reported in Hertz (Hz). Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

Solution magnetic moments were determined by the method of Evans at 22 °C using a ferrocene standard unless otherwise noted. Gouy magnetic susceptibility balance measurements were performed with a Johnson Matthey instrument that was calibrated with HgCo(SCN)<sub>4</sub>.

S3

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with molybdenum and copper X-ray tubes ( $\lambda = 0.71073$  and 1.54184 Å respectively). Preliminary data revealed the crystal system. The data collection strategy was optimized for completeness and redundancy using the Bruker COSMO software suite. The space group was identified, and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

#### **II.** Preparation and Characterization of Cobalt Compounds.

**Preparation of (<sup>iPr</sup>PNP)CoCI**. A 100 mL round bottom flask was charged with 0.500 g (1.07 mmol) of (<sup>iPr</sup>PNP)CoCI<sub>2</sub> and 30 mL of toluene. The purple suspension was frozen in the cold well and 1.07 mL of a 1.0M NaEt<sub>3</sub>BH solution (1.07 mmol) in toluene was added via microsyringe to the thawing solution. The resulting reaction mixture was stirred overnight and a color change to brownish-purple was observed after 2 hours. The precipitate was removed by filtration through Celite and the volatiles were removed in vacuo. Recrystallization of the dark residue from a 1:7 toluene-pentane mixture at -35 °C for 18 hours furnished 0.350 g (0.808 mmol, 75 % yield) of pure dark purple analytically pure crystals suitable for X-ray diffraction. Anal Calcd for C<sub>19</sub>H<sub>35</sub>ClCoNP<sub>2</sub>: C, 52.60; H, 8.13; N, 3.23. Found: C, 52.63; H, 7.97; N, 3.06. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C): δ -4.33 (bs, Δv<sub>1/2</sub> = 165 Hz), -2.66 (bs, Δv<sub>1/2</sub> = 165 Hz), 2.88 (bs, Δv<sub>1/2</sub> = 201 Hz P-CH*Me*<sub>2</sub>), 27.2 (bs, Δv<sub>1/2</sub> = 167 Hz), 50.5 (bs Δv<sub>1/2</sub> = 1073 Hz), 55.9 (bs Δv<sub>1/2</sub> = 304 Hz). Magnetic Susceptibility: (benzene-*d*<sub>6</sub>, 23 °C) μ<sub>eff</sub> = 2.4(3) μ<sub>B</sub>.

S4

**Preparation of (**<sup>iPr</sup>**PNP)CoCH**<sub>3</sub>. A 20 mL scintillation vial was charged with 0.068 g (0.157 mmol) of (<sup>iPr</sup>PNP)CoCl and 10 mL of toluene. The purple solution was frozen in the cold well. A separate vial was charged with 103  $\mu$ L of a 1.6 M LiCH<sub>3</sub> solution (0.157) mmol) in diethyl ether, which was further diluted with 5 mL of diethyl ether. The alkyllithium solution was added dropwise to the thawing toluene solution by pipette over the course of one minute. An immediate color change to dark brown was observed and the solution was warmed to ambient temperature and stirred for two minutes before being filtered through a pad of Celite. Removal of the volatiles in vacuo and trituration with pentane afforded 0.063 g (0.152 mmol, 97 % yield) of an analytically pure dark brown powder identified as (<sup>iPr</sup>PNP)CoCH<sub>3</sub>. Anal Calcd for C<sub>20</sub>H<sub>38</sub>CoNP<sub>2</sub>: C, 58.11; H, 9.27; N, 3.39. Found: C, 57.60; H, 8.82; N, 3.21. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 23 °C): δ -1.22 (t, <sup>3</sup>J<sub>PH</sub> = 10.1, 3H, Co-C*H*<sub>3</sub>), 1.23 (pq, J<sub>PH</sub> = 6.8, 12H, P-CH*Me*<sub>2</sub>), 1.37 (pq, J<sub>PH</sub> = 6.8, 12H, P-CH*Me*<sub>2</sub>), 1.58 (t,  $J_{PH} = 4.9$ , 4H, P-C*H*<sub>2</sub>), 2.37 (m, 4H, P-C*H*Me<sub>2</sub>), 5.64 (d,  ${}^{3}J_{HH} = 7.4$ , 2H, meta pyridine CH), 8.64 (t,  ${}^{3}J_{HH} = 7.4$ , 1H, para pyridine CH). { ${}^{1}H$ } ${}^{13}C$  NMR (benzene- $d_{6}$  23 °C): δ -26.8 (t,  ${}^{2}J_{PC}$  = 24.8, Co- $CH_{3}$ ), 18.4 (P-CH $Me_{2}$ ), 19.8 (t,  ${}^{2}J_{PC}$  = 3.0, P-CH*Me*<sub>2</sub>), 22.8 (t, <sup>1</sup>J<sub>PC</sub> = 8.5 Hz, P-*C*HMe<sub>2</sub>), 36.6 (t, <sup>1</sup>J<sub>PC</sub> = 6.7 Hz, P-*C*H<sub>2</sub>), 109.5 (meta pyridine *C*H), 123.9 (t,  $J_{PC} = 7.5$ , para pyridine *C*H), 154.9 (t,  ${}^{2}J_{PC} = 7.1$ , ipso pyridine *C*). {<sup>1</sup>H}<sup>31</sup>P NMR (benzene-*d*<sub>6</sub>, 23 °C): δ 48.5 (br s, *P*-CHMe<sub>2</sub>).

**Preparation of (**<sup>iPr</sup>**PNP)CoH**<sub>3</sub>**.** A thick walled glass vessel was charged with 0.200 g (0.484 mmol) of (<sup>iPr</sup>PNP)CoCH<sub>3</sub> and 7 mL of diethyl ether. At the high vacuum line, the solution was frozen and degassed and 1 atm of H<sub>2</sub> gas was admitted at 77 K. The solution was thawed and shaken vigorously and a color change from dark brown to yellow-orange was observed. Recrystallization under an H<sub>2</sub> atmosphere at -35 °C for 2 days afforded yellow crystals suitable for X-ray diffraction. Analytically pure bulk material

was obtained by performing the above reaction using 0.100 g (0.242 mmol) of (<sup>Pr</sup>PNP)CoCH<sub>3</sub> in 5 mL of pentane. Upon addition of dihydrogen and thawing a vellow precipitate was formed which was isolated by filtration and washed with cold pentane, yielding 0.054 g (0.134 mmol, 54 % yield) of (<sup>iPr</sup>PNP)CoH<sub>3</sub> as a yellow solid. Anal Calcd for C<sub>19</sub>H<sub>38</sub>CoNP<sub>2</sub>: C, 56.85; H, 9.54; N, 3.49. Found: C, 56.49; H, 9.23; N, 3.16. <sup>1</sup>H NMR (benzene- $d_6$ , 23 °C):  $\delta$  -14.1 (br s, 3H, Co- $H_3$ ), 1.19 (dd,  ${}^{3}J_{PH} = 13.5$ ,  ${}^{3}J_{HH} = 6.5$ , 12H, P-CH*Me*<sub>2</sub>), 1.30 (dd, <sup>3</sup>J<sub>PH</sub> = 13.5, <sup>3</sup>J<sub>HH</sub> = 6.5, 12H, P-CH*Me*<sub>2</sub>), 1.99 (m, 4H, P-C*H*Me<sub>2</sub>), 3.01  $(pt, {}^{2}J_{PH} = 3.4, 4H, P-CH_{2}), 6.44 (d, {}^{3}J_{HH} = 7.3, 2H, meta pyridine CH), 6.66 (t, {}^{3}J_{HH} = 7.3, 2H)$ 1H, para pyridine C*H*). <sup>1</sup>H NMR (toluene- $d_8$ , -75 °C):  $\delta$  -22.90 (br s, 1H, Co-*H*), -9.64 (br s, 2H, Co-*H*), 1.23 (br s, 12H, P-CH*Me*<sub>2</sub>), 1.37 (br s, 12H, P-CH*Me*<sub>2</sub>), 1.99 (br s, 4H, P-CHMe<sub>2</sub>), 2.77 (br s, 4H, P-CH<sub>2</sub>), 6.44 (br s, 2H, meta pyridine CH), 6.72 (br s, 1H, para pyridine CH). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene-d<sub>6</sub> 23 °C): δ 19.2 (P-CHMe<sub>2</sub>), 19.8 (P-CHMe<sub>2</sub>), 27.4 (t, <sup>1</sup>J<sub>PC</sub> = 11.9 Hz, P-CHMe<sub>2</sub>), 41.0 (t, <sup>1</sup>J<sub>PC</sub> = 7.3 Hz, P-CH<sub>2</sub>), 118.1 (t, <sup>3</sup>J<sub>PC</sub> = 4.6 Hz, meta pyridine CH), 131.1 (para pyridine CH), 162.6 (t,  ${}^{2}J_{PC} = 6.9$ , ipso pyridine C). {<sup>1</sup>H}<sup>31</sup>P NMR (benzene-*d<sub>6</sub>*, 23 °C): δ 109.9 (br s, *P*-CHMe<sub>2</sub>). IR (KBr): *v*<sub>Co-H</sub> = 1886, 1640 cm<sup>-1</sup>.

**Preparation of (<sup>iPr</sup>PNP)CoC**<sub>6</sub>**H**<sub>5</sub> **or (<sup>iPr</sup>PNP)CoC**<sub>6</sub>**D**<sub>5</sub>. **Method 1**: A J. Young NMR tube was charged with 0.015 g (0.036 mmol) of (<sup>iPr</sup>PNP)CoCH<sub>3</sub> and 0.500 g of benzene-*d*<sub>6</sub>. The sealed tube was heated to 80 °C whereupon complete conversion to (<sup>iPr</sup>PNP)CoC<sub>6</sub>D<sub>5</sub> was observed after 10 hours. **Method 2**: A 20 mL scintillation vial was charged with 0.065 g (0.150 mmol) of (<sup>iPr</sup>PNP)CoCl and 5 mL of toluene. A separate vial was charged with 0.014 g (0.150 mmol) of phenyllithium and 3 mL of toluene. Both vials were chilled to -35 °C before the aryl lithium solution was added dropwise over the course of one minute to the deep purple cobalt solution. An immediate color change to

red-brown was observed. The solution was allowed to warm to room temperature and stirred for 1 h before being filtered through a pad of Celite. The volatiles were removed in vacuo and the red-brown residue washed with cold pentane to afford 0.035 g (0.099 mmol, 66 % yield) of (<sup>iPr</sup>PNP)CoC<sub>6</sub>H<sub>5</sub>. Anal Calcd for C<sub>25</sub>H<sub>40</sub>CoNP<sub>2</sub>: C, 63.15; H, 8.48; N, 2.95. Found: C, 62.96; H, 8.41; N, 2.81. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C):  $\delta$  1.18 (m overlapped, 24H, P-CH*M*e<sub>2</sub>), 1.95 (t, <sup>2</sup>J<sub>PH</sub> = 4.2, 4H, P-C*H*<sub>2</sub>), 2.20 (m, 4H, P-C*H*Me<sub>2</sub>), 5.83 (d, <sup>3</sup>J<sub>HH</sub> = 7.4, 2H, meta pyridine *CH*), 6.75 (t, <sup>3</sup>J<sub>HH</sub> = 7.0, 1H, para aryl *CH*), 6.98 (m, 2H, meta aryl *CH*), 7.09 (d, <sup>3</sup>J<sub>HH</sub> = 7.0, 2H, ortho aryl *CH*), 7.90 (t, <sup>3</sup>J<sub>HH</sub> = 7.4, 1H, para pyridine *CH*). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 23 °C):  $\delta$  18.3 (P-CH*M*e<sub>2</sub>), 19.2 (P-CH*M*e<sub>2</sub>), 23.3 (t, <sup>1</sup>J<sub>PC</sub> = 9.5 Hz, P-*C*HMe<sub>2</sub>), 36.1 (t, <sup>1</sup>J<sub>PC</sub> = 6.0 Hz, P-*C*H<sub>2</sub>), 116.6 (pyridine meta *C*H), 118.9 (aryl *C*H), 121.8 (t, <sup>3</sup>J<sub>PC</sub> = 6.7 Hz, para pyridine *C*H), 124.8 (aryl *C*H), 138.9 (aryl *C*H), 157.6 (t, <sup>2</sup>J<sub>PC</sub> = 8.3, pyridine ortho *C*). {<sup>1</sup>H}<sup>31</sup>P NMR (benzene-*d*<sub>6</sub>, 23 °C):  $\delta$  46.0 (br s, *P*-CHMe<sub>2</sub>).

**Preparation of (<sup>iPr</sup>PNP)Co(CCToI)**<sub>2</sub>**H.** A 20 mL scintillation vial was charged with 0.037 g (0.089 mmol) of (<sup>iPr</sup>PNP)CoCH<sub>3</sub> and 2 mL of diethyl ether. To the rapidly stirring solution was added 0.021 g (0.178 mmol) of p-tolylacetylene via microsyringe. An immediate lightening of the solution to yellow with concomitant formation of a yellow precipitate was observed upon addition of the alkyne. The suspension was stirred for 30 min at room temperature after which time a yellow solid was collected on a sintered glass frit and washed with cold pentane (2 x 2 mL) to afford analytically pure material (0.047 g, 0.075 mmol, 84 % yield). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a concentrated tetrahydrofuran solution stored at -35 °C for 3 days. Anal Calcd for C<sub>37</sub>H<sub>50</sub>CoNP<sub>2</sub>: C, 70.57; H, 8.00; N, 2.22. Found: C, 70.35; H, 7.87; N, 2.14. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C): δ -19.0 (t, <sup>2</sup>J<sub>PH</sub> = 51 Hz, 1H, Co-*H*), 1.34 (pq,

J<sub>HH</sub> = 6.4, 12H, P-CH*Me*<sub>2</sub>), 1.46 (pq, J<sub>HH</sub> = 6.4, 12H, P-CH*Me*<sub>2</sub>), 2.07 (s, 6H, tolyl *Me*), 2.79 (m, 4H, P-C*H*Me<sub>2</sub>), 3.50 (br s, 4H, P-C*H*<sub>2</sub>), 6.49 (m, 2H, meta pyridine *CH*), 6.77 (m, 1H, para pyridine *CH*), 6.96 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 4H, tolyl aryl *CH*), 7.38 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 4H, tolyl aryl *CH*). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene- $d_6$ , 23 °C): δ 18.9 (P-CH*Me*<sub>2</sub>), 20.7 (P-CH*Me*<sub>2</sub>), 21.6 (tolyl *Me*), 26.1 (t, J<sub>PC</sub> = 11.6, P-*C*HMe<sub>2</sub>), 42.8 (t, J<sub>PC</sub> = 10.5, P-*C*H<sub>2</sub>), 115.7 (acetylene *C*), 119.8 (meta pyridine *C*H), 128.4 (tolyl ipso *C* overlapped), 129.3 (tolyl *C*H), 130.9 (tolyl *C*H), 133.5 (acetylene *C*), 135.9 (para pyridine *C*H), 162.3 (ortho pyridine *C*). {<sup>1</sup>H}<sup>31</sup>P NMR (benzene- $d_6$ , 23 °C): δ 83.4 (br s, *P*-CHMe<sub>2</sub>). IR (KBr):  $v_{CC}$  = 2076 cm<sup>-1</sup>,  $v_{Co-H}$  = 1922 cm<sup>-1</sup>.

**Preparation of (<sup>IP</sup>rPNP)Co(H)(PH<sup>I</sup>Pr<sub>2</sub>).** A thick walled glass vessel was charged with 0.070 g (0.169 mmol) of (<sup>IP</sup>rPNP)CoCH<sub>3</sub> and 3 mL of diethyl ether. The vessel was degassed and 1 atmosphere of H<sub>2</sub> gas was admitted at 77 K. Upon thawing and vigorous shaking, a color change from dark brown to yellow was observed. The vessel was degassed and immediately transferred to the glovebox, whereupon the solution was transferred into a 20 mL scintillation vial and stirred for 18 hours. A gradual color change from light yellow to dark brown was observed after 3 hours. The contents of the vial were concentrated in vacuo and filtered through Celite on a small glass frit. Recrystallization of the dark residue from diethyl ether at -35 °C yielded 0.035 g (0.068 mmol, 40 % yield based on starting Co) of an analytically pure dark brown microcrystalline solid identified as (<sup>IP</sup>rPNP)Co(H)(PH<sup>I</sup>Pr)<sub>2</sub>). Crystals suitable for X-ray diffraction were obtained from slow evaporation of a diethyl ether solution at -35 °C over the course of 3 days. Anal Calcd for C<sub>25</sub>H<sub>51</sub>CoNP<sub>3</sub>: C, 58.02; H, 9.93; N, 2.71. Found: C, 57.62; H, 9.56; N, 2.65. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C): δ -25.0 (td, <sup>2</sup>J<sub>PH</sub> = 59.6, 28.7, 1H, Co-*H*), 0.93 (m, 6H, P-CH*Me*<sub>2</sub>), 0.99 (dd, <sup>3</sup>J<sub>PH</sub> = 11.4, <sup>3</sup>J<sub>HH</sub> = 6.8, 6H, P-*H*(CH*Me*<sub>2</sub>)<sub>2</sub>), 1.11 (dd, <sup>3</sup>J<sub>PH</sub> = 14.7, <sup>3</sup>J<sub>HH</sub> = 7.0, 6H,

P-*H*(CH*Me*<sub>2</sub>)<sub>2</sub>), 1.24 (m overlapped, 12H, P-CH*Me*<sub>2</sub>), 1.36 (dd,  ${}^{3}J_{PH} = 14.7$ ,  ${}^{3}J_{HH} = 7.4$ , 6H, P-CH*Me*<sub>2</sub>), 1.92 (m, 2H, P-C*H*Me<sub>2</sub>), 2.06 (m, 2H, P-H(C*H*Me<sub>2</sub>)<sub>2</sub>), 2.29 (m, 2H, P-C*H*Me<sub>2</sub>), 2.94 (m, 4H, P-C*H*<sub>2</sub>), 4.57 (dtt,  ${}^{1}J_{PH} = 252.4$ ,  ${}^{3}J_{PH} = 12.5$ ,  ${}^{3}J_{HH} = 6.4$ , 1H, P-*H*(CHMe<sub>2</sub>)<sub>2</sub>), 6.28 (d,  ${}^{3}J_{HH} = 7.3$ , 2H, meta pyridine *CH*), 6.60 (td,  ${}^{3}J_{HH} = 7.3$ ,  ${}^{5}J_{PH} = 3.3$ , 1H, para pyridine *CH*). { ${}^{1}H$ }{}^{13}C NMR (benzene-*d*<sub>6</sub>, 23 °C): δ 19.1 (s, P-CH*Me*<sub>2</sub>), 19.2 (t, J<sub>PC</sub> = 3.0, P-CH*Me*<sub>2</sub>), 20.7 (t, J<sub>PC</sub> = 5.9, P-CH*Me*<sub>2</sub>), 21.5 (d, J<sub>PC</sub> = 7.5, P-CH*Me*<sub>2</sub>), 21.9 (t, J<sub>PC</sub> = 3.8, P-CH*Me*<sub>2</sub>), 22.1 (s, P-CH*Me*<sub>2</sub>), 24.9 (s, P-*C*HMe<sub>2</sub>), 25.1 (s, P-*C*HMe<sub>2</sub>), 26.5 (t, J<sub>PC</sub> = 3.4, P-H(*C*HMe<sub>2</sub>)<sub>2</sub>), 26.6 (t, J<sub>PC</sub> = 3.4, P-H(*C*HMe<sub>2</sub>)<sub>2</sub>), 30.6 (t, J<sub>PC</sub> = 12.7, P-*C*HMe<sub>2</sub>), 44.4 (t, J<sub>PC</sub> = 4.8, P-*C*H<sub>2</sub>), 117.9 (d, J<sub>PC</sub> = 3.6, meta pyridine *C*H), 125.6 (d, J = 5.0, para pyridine *C*H), 161.6 (td, J<sub>PC</sub> = 9.1, 4.4, ortho pyridine *C*). { ${}^{1}H$ }<sup>31</sup>P NMR (benzene-*d*<sub>6</sub>, 23 °C): δ 43.2 (t,  ${}^{2}J_{PP} = 91.7$ , *P*-H(CHMe<sub>2</sub>)<sub>2</sub>), 93.6 (d,  ${}^{2}J_{PP} = 91.7$ , *P*-CHMe<sub>2</sub>).

**Preparation of (**<sup>iPr</sup>**PNP)Co(H)(PMe**<sub>3</sub>**).** A thick walled glass vessel was charged with 0.107 g (0.259 mmol) of (<sup>iPr</sup>PNP)CoCH<sub>3</sub> and 5 mL of benzene. The vessel was degassed and 1 atm of H<sub>2</sub> was admitted at 77 K. Upon thawing and vigorous shaking, a color change from dark brown to light yellow-orange was observed. The vessel was immediately degassed and 60 torr of PMe<sub>3</sub> (0.330 mmol) was added from a 100.1 mL calibrated gas bulb. The contents of the vessel were again thawed and an immediate color change to dark red was observed. The solution was stirred for 15 min at room temperature before the volatiles were removed in vacuo. Washing the residue with cold pentane afforded 0.117 g (95%) of an analytically pure red solid. Recrystallization of the crude reaction mixture from diethyl ether afforded crystals suitable for X-ray diffraction. Anal Calcd for C<sub>22</sub>H<sub>45</sub>CoNP<sub>3</sub>: C, 55.58; H, 9.54; N, 2.95. Found: C, 55.62; H, 9.39; N, 2.82. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C): δ -25.4 (td, <sup>2</sup>J<sub>PH</sub> = 56.7, 41.3, 1H, Co-*H*), 0.91 (m, 6H, P-CH*Me*<sub>2</sub>), 1.18 (d, <sup>2</sup>J<sub>PH</sub> = 4.6, 9H, P*Me*<sub>3</sub>), 1.21 (m, 6H, P-CH*Me*<sub>2</sub>), 1.30 (m, 6H, P-

CH*Me*<sub>2</sub>), 1.46 (m, 6H, P-CH*Me*<sub>2</sub>), 1.96 (m, 2H, P-C*H*Me<sub>2</sub>), 2.07 (m, 2H, P-C*H*Me<sub>2</sub>), 2.70 (d, <sup>2</sup>J<sub>HH</sub> = 15.9, 2H, P-C*H*<sub>2</sub>), 2.99 (dd, <sup>2</sup>J<sub>HH</sub> = 15.9, <sup>2</sup>J<sub>PH</sub> = 4.5, 2H, P-C*H*<sub>2</sub>), 6.30 (d, <sup>3</sup>J<sub>HH</sub> = 7.5, 2H, meta pyridine *CH*), 6.62 (td, <sup>3</sup>J<sub>HH</sub> = 7.5, <sup>5</sup>J<sub>PH</sub> = 3.2, 1H, para pyridine *CH*). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 23 °C): δ 19.0 (s, P-CH*Me*<sub>2</sub>), 19.2 (t, J<sub>PC</sub> = 3.8, P-CH*Me*<sub>2</sub>), 20.5 (t, J<sub>PC</sub> = 6.1, P-CH*Me*<sub>2</sub>), 22.8 (t, J<sub>PC</sub> = 5.8, P-CH*Me*<sub>2</sub>), 24.6 (m overlapped, P-*C*HMe<sub>2</sub>), 24.7 (m overlapped, P-CH*Me*<sub>2</sub>), 25.3 (d, <sup>1</sup>J<sub>PC</sub> = 24.5, P*Me*<sub>3</sub>), 33.1 (t, J<sub>PC</sub> = 12.9, P-*C*HMe<sub>2</sub>), 45.1 (t, J<sub>PC</sub> = 4.8, P-*C*H<sub>2</sub>), 117.7 (q, J<sub>PC</sub> = 3.6, meta pyridine *C*H), 126.4 (d, J = 5.5, para pyridine *C*H), 161.8 (td, J<sub>PC</sub> = 9.2, 5.0 ortho pyridine *C*). {<sup>1</sup>H}<sup>31</sup>P NMR (benzene-*d*<sub>6</sub>, 23 °C): δ -8.7 (t, <sup>2</sup>J<sub>PP</sub> = 98.7, *P*Me<sub>3</sub>), 91.2 (d, <sup>2</sup>J<sub>PP</sub> = 98.7, *P*-CHMe<sub>2</sub>). IR (KBr):  $v_{Co-H} = 1818 \text{ cm}^{-1}$ .

**Preparation of (<sup>Pr</sup>PNP)Co(CH<sub>3</sub>)<sub>3</sub>.** A 20 mL scintillation vial was charged with 0.062 g (0.150 mmol) of (<sup>iPr</sup>PNP)CoCH<sub>3</sub>, a stirbar, and 1 mL of diethyl ether. The solution was chilled to -35 °C and 0.014 g (0.100 mmol) of methyl iodide was added dropwise to the dark brown solution. An immediate color change to deep red was observed along with formation of a dark red precipitate. After warming to room temperature the red solution was filtered and the filtrate evaporated to dryness to afford 0.017 g (0.038 mmol, 77 % yield based on expected 1:2 ratio of products) of (<sup>iPr</sup>PNP)Co(CH<sub>3</sub>)<sub>3</sub>. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 23 °C): δ 0.22 (t, <sup>3</sup>J<sub>PH</sub> = 6.5, 6H, Co-*Me*), 0.50 (t, <sup>3</sup>J<sub>PH</sub> = 7.5, 3H, Co-*Me*), 1.06 (pq, J<sub>HH</sub> = 5.5, 12H, P-CH*Me*<sub>2</sub>), 2.62 (m, 4H, P-C*H*Me<sub>2</sub>), 3.02 (t, J<sub>PC</sub> = 3.7, 4H, P-C*H*<sub>2</sub>), 6.41 (d, <sup>3</sup>J<sub>HH</sub> = 7.6, 2H, meta pyridine *CH*), 6.68 (t, <sup>3</sup>J<sub>HH</sub> = 7.6, 1H, para pyridine *CH*). {<sup>1</sup>H}<sup>13</sup>C NMR (benzene-*d*<sub>6</sub>, 23 °C): δ -14.9 (t, <sup>2</sup>J<sub>PC</sub> = 27, Co-*C*H<sub>3</sub>), -5.4 (t, <sup>2</sup>J<sub>PC</sub> = 21, Co-*C*H<sub>3</sub>), 20.1 (P-CH*Me*<sub>2</sub>), 20.2 (P-CH*Me*<sub>2</sub>), 24.0 (t, <sup>1</sup>J<sub>PC</sub> = 7.0 Hz, P-*C*HMe<sub>2</sub>), 39.1 (t, <sup>1</sup>J<sub>PC</sub> = 8.3 Hz, P-*C*H<sub>2</sub>), 119.1 (t, <sup>3</sup>J<sub>PC</sub> = 4.2 Hz, meta pyridine *CH*), 133.3

(para pyridine *C*H), 162.2 (t,  ${}^{2}J_{PC} = 5.7$ , ortho pyridine *C*). { ${}^{1}H$ } ${}^{31}P$  NMR (benzene- $d_{6}$ , 23 °C):  $\delta$  57.0 (br s, *P*-CHMe<sub>2</sub>).

**Preparation of (**<sup>iPr</sup>**PNP)CoCH**<sub>3</sub>(**I**). A 20 mL scintillation vial was charged with 0.062 g (0.150 mmol) of (<sup>iPr</sup>**PNP**)CoCH<sub>3</sub>, a stirbar, and 1 mL of diethyl ether. The solution was chilled to -35 °C and 0.014 g (0.100 mmol) of methyl iodide was added dropwise to the dark brown solution. An immediate color change to deep red was observed along with formation of a dark red precipitate. After warming to room temperature the red solid was collected on a sintered glass frit, washed with diethyl ether (2 x 1 mL) and dried in vacuo to afford 0.053 (0.098 mmol, 98 % yield based on expected 1:2 ratio of products) of (<sup>iPr</sup>PNP)CoCH<sub>3</sub>(I). Crystals suitable for X-ray diffraction were obtained from a benzene solution left to stand at room temperature. Anal Calcd for C<sub>20</sub>H<sub>38</sub>CoINP<sub>2</sub>: C, 44.46; N, 7.09; N, 2.59. Found: C, 44.37; H, 6.88; N, 2.54. Magnetic susceptibility (MSB, 23 °C):  $\mu_{eff} = 2.1(1) \mu_{B}$ .

# III. Variable Temperature NMR Data for (<sup>iPr</sup>PNP)CoH<sub>3</sub>.



**Figure S1.** Variable temperature <sup>1</sup>H NMR spectra of ( $^{iPr}PNP$ )CoH<sub>3</sub> in toluene-*d*<sub>8</sub>. In descending order: 25 °C, -35 °C, -50 °C, -75 °C.

Table S1. Values of T1 as a func	tion of temperature. Re	corded in toluene- $d_8$ .
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Temp (°C)	T₁ (ms)	Temp (°C)	T₁ (ms)
25	333	-45	72
15	275	-50	72
5	217	-55	72
-5	181	-60	91
-15	145	-65	104
-25	109	-70	159
-35	65	-75	138

### IV. Additional Crystallographic Data



**Figure S2.** Molecular structure of (<sup>iPr</sup>PNP)CoH(PMe<sub>3</sub>) at 30% probability ellipsoids. Hydrogens, except those on the benzylic positions and cobalt, omitted for clarity.

	( <sup>iPr</sup> PNP)CoH(PMe <sub>3</sub> )
Co(1)-N(1)	1.9499(14)
Co(1)-P(1)	2.1287(6)
Co(1)-P(2)	2.1396(7)
Co(1)-P(3)	2.1591(7)
Co(1)-H(1)	1.449(16)
C(2)-C(3)	1.390(2)
C(3)-C(4)	1.387(2)
C(4)-C(5)	1.390(2)
C(5)-C(6)	1.385(2)
N(1)-C(2)	1.3686(18)
N(1)-C(6)	1.3721(19)
C(1)-C(2)	1.505(2)
C(6)-C(7)	

**Table S2.** Selected bond distances (Å) and angles (deg) for (<sup>iPr</sup>PNP)CoH(PMe<sub>3</sub>).

	( <sup>iPr</sup> PNP)CoCl
Co(1)-Cl(1)	2.23338(9)
Co(1)-N(1)	2.035(3)
Co(1)-P(1)	2.2630(9)
Co(1)-P(2)	2.3057(9)
C(2)-C(3)	1.389(5)
C(3)-C(4)	1.389(5)
C(4)-C(5)	1.383(5)
C(5)-C(6)	1.385(5)
N(1)-C(2)	1.353(4)
N(1)-C(6)	1.358(4)
C(1)-C(2)	1.509(4)
C(6)-C(7)	1.502(4)
N(1)-Co(1)-Cl(1)	117.63(8)

**Table S3.** Selected bond distances (Å) and angles (deg) for (<sup>iPr</sup>PNP)CoCl.

**Table S4.** Selected bond distances (Å) and angles (deg) for  $({}^{iPr}PNP)CoH_3$  and  $({}^{iPr}PNP)CoH(HP^iPr_2)$ .

	( <sup>iPr</sup> PNP)CoH₃	( <sup>iPr</sup> PNP)CoH(HP <sup>i</sup> Pr <sub>2</sub> )
Co(1)-N(1)	1.9647(19)	1.9567(12)
Co(1)-P(1)	2.1150(6)	2.1355(5)
Co(1)-P(2)	2.1150(6)	2.1304(4)
Co(1)-P(3A)		2.1699(8)
C(2)-C(3)	1.389(2)	1.384(2)
C(3)-C(4)	1.3859(19)	1.382(2)
C(4)-C(5)	1.3859(19)	1.387(2)
C(5)-C(6)	1.389(2)	1.385(2)
N(1)-C(2)	1.3608(17)	1.3707(18)
N(1)-C(6)	1.3608(17)	1.3687(18)
C(1)-C(2)	1.503(2)	1.503(2)
C(6)-C(7)	1.503(2)	1.504(2)
P(1)-Co(1)-P(2)	173.82(2)	143.509(17)

	( <sup>iPr</sup> PNP)CoH(CCTol) <sub>2</sub>
Co(1)-N(1)	2.0831(13)
Co(1)-P(1)	2.2026(5)
Co(1)-P(2)	2.2069(4)
C(2)-C(3)	1.392(2)
C(3)-C(4)	1.389(3)
C(4)-C(5)	1.381(3)
C(5)-C(6)	1.388(2)
N(1)-C(2)	1.349(2)
N(1)-C(6)	1.350(2)
C(1)-C(2)	1.504(2)
C(6)-C(7)	1.502(2)
P(1)-Co(1)-P(2)	166.920(19)

**Table S5.** Selected bond distances (Å) and angles (deg) for (<sup>iPr</sup>PNP)CoH(CCTol)<sub>2</sub>H.

**Table S6.** Selected bond distances (Å) and angles (deg) for (<sup>iPr</sup>PNP)CoCH<sub>3</sub>(I).

	( <sup>iPr</sup> PNP)CoCl
Co(1)-C(20)	2.062(4)
Co(1)-N(1)	2.018(3)
Co(1)-P(1)	2.2025(11)
Co(1)-P(2)	2.1970(10)
Co(1)-I(1)	2.8319(6)
C(2)-C(3)	1.388(5)
C(3)-C(4)	1.386(5)
C(4)-C(5)	1.382(5)
C(5)-C(6)	1.385(5)
N(1)-C(2)	1.369(5)
N(1)-C(6)	1.363(5)
C(1)-C(2)	1.501(5)
C(6)-C(7)	1.505(5)
N(1)-Co(1)-C(20)	166.85(14)
P(1)-Co(1)-P(2)	167.57(4)

### V. Additional Spectroscopic Data



**Figure S3.** Benzene- $d_6^{-1}$ H NMR spectrum of (<sup>iPr</sup>PNP)Co(CH<sub>3</sub>)<sub>3</sub>.



**Figure S4.** X-band EPR spectrum of ( $^{iPr}PNP$ )CoCH<sub>3</sub>(I) recorded in toluene/diethyl ether glass at 10 K. Microwave frequency = 9.377 GHz, power = 0.20 mW, modulation amplitude = 0.8 mT/100 kHz.

### VI. References.

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