

# **Photolysis and Thermolysis of Bis(imino)pyridine Cobalt Azides: C-H Activation from Putative Cobalt Nitrido Complexes.**

Crisita Carmen Hojilla Atienza, Amanda C. Bowman, Emil Lobkovsky, and Paul J. Chirik\*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York, U. S. A. 14850

Supporting Information

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## Experimental Section

### A. General Considerations.

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.<sup>1</sup> Argon and dihydrogen gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Benzene-*d*<sub>6</sub> was purchased from Cambridge Isotope Laboratories and distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves or sodium metal. The complexes (<sup>i</sup>PrPDI)CoCl<sub>2</sub>, (<sup>i</sup>PrBPDI)CoCl<sub>2</sub>, (<sup>Mes</sup>BPDI)CoCl<sub>2</sub> and (<sup>t</sup>BuBPDI)CoCl<sub>2</sub> were prepared according to literature procedures.<sup>2</sup>

<sup>1</sup>H NMR spectra were recorded on Varian Mercury 300, Inova 400 and 500 spectrometers operating at 299.763, 399.780 and 500.62 MHz, respectively. 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.

### B. Preparation of Bis(imino)pyridine Cobalt Compounds.

**Preparation of (<sup>i</sup>PrPDI)CoCl.** A 100 mL round-bottom flask was charged with 1.068 g (1.746 mmol) of (<sup>i</sup>PrPDI)CoCl<sub>2</sub>, approximately 50 mL of toluene and a magnetic stir bar. The contents of the flask were cooled in a liquid nitrogen-chilled cold well and 1.660 μL (1.660 mmol, 0.95 equiv) of a 1.0 M NaEt<sub>3</sub>BH solution in toluene was added dropwise with stirring. The reaction was warmed to room temperature and stirred for three hours. The resulting dark pink solution was filtered through Celite and the volatiles were

removed from the filtrate in vacuo. Recrystallization of the resulting residue from a toluene/pentane (~1:3 v/v) mixture afforded 0.766 g (80 %) of dark pink crystals identified as (<sup>i</sup>PrPDI)CoCl.<sup>3</sup>

**Preparation of (<sup>i</sup>PrBPDI)CoCl.** This compound was prepared in a manner similar to (<sup>i</sup>PrPDI)CoCl with 1.440 g (1.957 mmol) of (<sup>i</sup>PrBPDI)CoCl<sub>2</sub> and 1.860 μL (1.860 mmol, 0.95 equiv) of a 1.0 M NaEt<sub>3</sub>BH solution in toluene and yielded 1.031 g (79 % yield) of dark red crystals identified as (<sup>i</sup>PrBPDI)CoCl.<sup>3</sup>

**Preparation of (<sup>Mes</sup>BPDI)CoCl.** A 100 mL round-bottom flask was charged with 1.004 g (1.541 mmol) of (<sup>Mes</sup>BPDI)CoCl<sub>2</sub>, 0.036 g (1.6 mmol, 1.0 equiv) of sodium metal, 0.010 g (0.078 mmol, 0.051 equiv) of naphthalene, and approximately 20 mL of THF. After stirring the mixture for six hours, the THF was removed in vacuo. The resulting solid was dissolved in toluene and filtered through Celite. Removing the volatiles from the filtrate in vacuo yielded a dark pink solid which, after recrystallization from a toluene/pentane (~1:3 v/v) mixture, afforded 0.588 g (62 %) of dark pink crystals identified as (<sup>Mes</sup>BPDI)CoCl. Anal. Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>3</sub>ClCo: C, 72.13; H, 5.73; N, 6.82. Found: C, 71.92; H, 5.55; N, 6.58. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 2.05 (s, 6H, *p*-CH<sub>3</sub>), 2.35 (s, 12H, *o*-CH<sub>3</sub>), 6.79 (s, 4H, *m*-aryl), 6.98 (t, 4H, *m*-phenyl), 7.14 (d, 2H, *m*-pyridine), 7.20 (t, 2H, *p*-phenyl), 7.82 (d, 4H, *o*-phenyl), 9.39 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 20.66 (*o*-CH<sub>3</sub>), 21.63 (*p*-CH<sub>3</sub>), 117.76 (*p*-pyridine), 122.63 (*o*-phenyl), 127.87 (*m*-pyridine), 128.26 (*p*-phenyl), 128.50 (*m*-phenyl), 129.52 (*m*-aryl), 130.83 (*o*-aryl), 135.25 (*p*-aryl), 140.94 (*i*-phenyl), 153.32 (*i*-aryl), 155.50 (*o*-pyridine), 168.34 (C=N).

**Preparation of (<sup>t</sup>BuBPDI)CoCl.** This compound was prepared in a manner similar to (<sup>i</sup>PrPDI)CoCl with 0.702 g (1.03 mmol) of (<sup>t</sup>BuBPDI)CoCl<sub>2</sub> and 0.985 μL (0.985 mmol, 0.96

equiv) of a 1.0 M NaEt<sub>3</sub>BH solution in toluene and yielded 0.448 g (73 % yield) of red-brown crystals identified as a 1:1 mixture of the *rac*- and *meso*-isomers of (<sup>t</sup>BuBPDI)CoCl. Anal. Calcd for C<sub>39</sub>H<sub>39</sub>N<sub>3</sub>ClCo: C, 72.72; H, 6.10; N, 6.52. Found: C, 72.53; H, 6.23; N, 6.38. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>; Integration of peaks is based on the mixture and not on each isomer.): δ = 1.21 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.25 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.96 (t, 4H, *m*-phenyl), 6.97 (t, 4H, *m*-phenyl), 6.99 (t, 4H, *aryl-H*<sup>4</sup>), 7.02 (d, 4H, *m*-pyridine), 7.13 (d, 4H, *aryl-H*<sup>3</sup>), 7.18 (t, 2H, *p*-phenyl), 7.20 (d, 2H, *p*-phenyl), 7.35 (d, 4H, *aryl-H*<sup>5</sup>), 7.71 (d, 4H, *o*-phenyl), 7.81 (d, 4H, *o*-phenyl), 8.17 (d, 4H, *aryl-H*<sup>6</sup>), 9.56 (t, 2H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 33.43 (C(CH<sub>3</sub>)<sub>3</sub>), 33.48 (C(CH<sub>3</sub>)<sub>3</sub>), 37.90 (C(CH<sub>3</sub>)<sub>3</sub>), 37.92 (C(CH<sub>3</sub>)<sub>3</sub>), 117.12 (*p*-pyridine), 124.36 (*aryl-C*<sup>4</sup>), 126.55 (*aryl-C*<sup>6</sup>), 126.75 (*aryl-C*<sup>3</sup>), 130.35 (*aryl-C*<sup>5</sup>), 142.63 (*i*-phenyl), 142.90 (*i*-phenyl), 143.47 (*aryl-C*<sup>2</sup>), 151.90 (*i*-aryl), 155.15 (*o*-pyridine), 155.25 (*o*-pyridine), 160.62 (C=N), 126.03, 128.28, 128.30, 128.69, 128.90, 129.66, 129.87 and 129.96 (*o*-phenyl, *m*-phenyl, *p*-phenyl, *m*-pyridine).

**Preparation of (<sup>Cl</sup><sup>2</sup>BPDI)CoCl.** A 100 mL round-bottom flask was charged with 0.212 g (0.301 mmol) of (<sup>Cl</sup><sup>2</sup>BPDI)CoCl, approximately 30 mL of toluene and a magnetic stir bar. The contents of the flask were cooled in a liquid nitrogen chilled cold well and 180 μL (0.288 mmol, 0.96 equiv) of a 1.6 M LiCH<sub>3</sub> solution in diethyl ether was added dropwise with stirring. The reaction was warmed to room temperature and stirred for overnight. The resulting dark red solution was filtered through Celite and the volatiles were removed from the filtrate in vacuo. Recrystallization of the resulting residue from a toluene/pentane (~1:3 v/v) mixture afforded 0.152 g (75 %) of dark pink crystals identified as (<sup>Cl</sup><sup>2</sup>BPDI)CoCl. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 6.60 (t, 2H, *p*-aryl), 7.01 (t, 4H, *m*-phenyl), 7.02 (d, 4H, *m*-aryl), 7.13 (d, 2H, *m*-pyridine), 7.28 (t, 2H, *p*-phenyl), 8.23 (d, 4H, *o*-phenyl), 9.49 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 119.02 (*p*-pyridine), 120.34 (*o*-phenyl), 127.23 (*p*-aryl), 128.31 (*m*-aryl), 128.35 (*m*-phenyl), 128.49 (*m*-

*pyridine*), 128.82 (*p-phenyl*), 129.11 (*o-aryl*), 141.56 (*i-phenyl*), 153.83 (*i-aryl*), 156.40 (*o-pyridine*), 169.93 (C=N).

**Preparation of (<sup>i</sup>PrPDI)CoN<sub>3</sub>.** A 100 mL round-bottom flask was charged with 0.419 g (0.703 mmol) of (<sup>i</sup>PrPDI)CoCl, 0.052 g (0.80 mmol, 1.1 equiv) of NaN<sub>3</sub> and approximately 50 mL of THF. After stirring for 48 hours, the THF was removed in vacuo. The resulting residue was dissolved in 50 mL of toluene/diethyl ether (~1:2 v/v) and filtered through Celite. Removing the solvent from the filtrate in vacuo yielded a dark pink solid which, after recrystallization from a toluene/pentane (~1:3 v/v) mixture, afforded 0.318 g (75 %) of dark pink crystals identified as (<sup>i</sup>PrPDI)CoN<sub>3</sub>. Anal. Calcd for C<sub>33</sub>H<sub>43</sub>N<sub>6</sub>Co: C, 68.03; H, 7.44; N, 14.42. Found: C, 68.25; H, 7.41; N, 13.99. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 0.17 (s, 6H, C(CH<sub>3</sub>)), 1.07 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.25 (septet, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.98 (d, 2H, *m-pyridine*), 7.33 (d, 4H, *m-aryl*), 7.43 (t, 2H, *p-aryl*), 9.15 (t, 1H, *p-pyridine*). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 20.48 (C(CH<sub>3</sub>)), 23.53 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.93 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.15 (CH(CH<sub>3</sub>)<sub>2</sub>), 115.59 (*p-pyridine*), 124.39 (*m-aryl*), 127.53 (*m-pyridine* or *p-aryl*), 140.64 (*o-aryl*), 149.37 (*i-aryl*), 152.67 (*o-pyridine*), 165.63 (C=N), one resonance not located. IR (toluene): ν<sub>N3</sub> = 2055 cm<sup>-1</sup>.

**Preparation of (<sup>i</sup>PrBPDI)CoN<sub>3</sub>.** This compound was prepared in a manner similar to (<sup>i</sup>PrPDI)CoN<sub>3</sub> with 0.403 g (0.576 mmol) of (<sup>i</sup>PrBPDI)CoCl and 0.044 g (0.68 mmol, 1.2 equiv) NaN<sub>3</sub> and yielded 0.368 g (90 % yield) of dark red crystals identified as (<sup>i</sup>PrBPDI)CoN<sub>3</sub>. Anal. Calcd for C<sub>43</sub>H<sub>47</sub>N<sub>6</sub>Co: C, 73.07; H, 6.70; N, 11.89. Found: C, 73.28; H, 6.45; N, 11.86. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 1.07 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.53 (septet, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.95 (t, 4H, *m-phenyl*), 7.20 (d, 4H, *m-aryl*), 7.21 (t, 2H, *p-phenyl*), 7.26 (d, 2H, *m-pyridine*), 7.38 (t, 2H, *p-aryl*), 7.68 (d, 4H, *o-phenyl*), 9.00 (t, 1H, *p-pyridine*). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 23.66 (CH(CH<sub>3</sub>)<sub>2</sub>),

24.66 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.78 (CH(CH<sub>3</sub>)<sub>2</sub>), 118.55 (*p*-pyridine), 124.57 (*m*-aryl), 124.62 (*o*-phenyl), 127.56 (*m*-pyridine), 127.90 (*p*-aryl), 128.69 (*m*-phenyl), 128.66 (*p*-phenyl), 139.76 (*i*-phenyl), 141.21 (*o*-aryl), 150.58 (*i*-aryl), 155.33 (*o*-pyridine), 166.43 (C=N). IR (toluene):  $\nu_{\text{N}_3} = 2055 \text{ cm}^{-1}$ .

**Preparation of (<sup>Mes</sup>BPDI)CoN<sub>3</sub>.** This compound was prepared in a manner similar to (<sup>iPr</sup>PDI)CoN<sub>3</sub> with 0.413 g (0.670 mmol) of (<sup>Mes</sup>BPDI)CoCl and 0.066 g (1.0 mmol, 1.5 equiv) of NaN<sub>3</sub> and yielded 0.335 g (80 %) of dark pink crystals identified as (<sup>Mes</sup>BPDI)CoN<sub>3</sub>. Anal. Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>6</sub>Co: C, 71.37; H, 5.67; N, 13.50. Found: C, 71.69; H, 5.51; N, 13.62. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta = 2.07$  (s, 6H, *p*-CH<sub>3</sub>), 2.28 (s, 12H, *o*-CH<sub>3</sub>), 6.81 (s, 4H, *m*-aryl), 6.97 (t, 4H, *m*-phenyl), 7.18 (t, 2H, *p*-phenyl), 7.24 (d, 2H, *m*-pyridine), 7.74 (d, 4H, *o*-phenyl), 9.00 (t, 1H, *p*-pyridine). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>):  $\delta = 20.21$  (*o*-CH<sub>3</sub>), 22.62 (*p*-CH<sub>3</sub>), 115.91 (*p*-pyridine), 123.69 (*o*-phenyl), 126.28 (*m*-pyridine), 128.96 (*p*-phenyl), 129.01 (*m*-phenyl), 130.26 (*m*-aryl), 130.30 (*o*-aryl), 135.68 (*p*-aryl), 140.61 (*i*-phenyl), 151.66 (*i*-aryl), 155.56 (*o*-pyridine), 166.69 (C=N). IR (toluene):  $\nu_{\text{N}_3} = 2053 \text{ cm}^{-1}$ .

**Preparation of (<sup>tBu</sup>BPDI)CoN<sub>3</sub>.** This compound was prepared in a manner similar to (<sup>iPr</sup>PDI)CoN<sub>3</sub> with 0.395 g (0.613 mmol) of (<sup>tBu</sup>BPDI)CoCl and 0.044 g (0.68 mmol, 1.1 equiv) of NaN<sub>3</sub> and yielded 0.269 g (67 % yield) of dark pink crystals identified as a mixture of the *rac*- and *meso*-isomers of (<sup>tBu</sup>BPDI)CoN<sub>3</sub>. Anal. Calcd for C<sub>39</sub>H<sub>39</sub>N<sub>6</sub>Co: C, 71.99; H, 6.04; N, 12.92. Found: C, 71.82; H, 6.06; N, 12.68. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): *Major isomer* -  $\delta = 1.29$  (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.98 (t, 4H, *m*-phenyl), 7.06 (t, 2H, aryl-*H*<sup>4</sup> or aryl-*H*<sup>5</sup>), 7.14-7.20 (2H, *m*-pyridine; 2H, *p*-phenyl; 2H, aryl-*H*<sup>3</sup> or aryl-*H*<sup>6</sup>), 7.41 (t, 2H, aryl-*H*<sup>4</sup> or aryl-*H*<sup>5</sup>), 7.75 (d, 4H, *o*-phenyl), 7.94 (d, 2H, aryl-*H*<sup>3</sup> or aryl-*H*<sup>6</sup>), 9.07 (t, 1H, *p*-pyridine); *Minor isomer* -  $\delta = 1.23$  (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 6.96 (t, 4H, *m*-phenyl), 7.05 (t, 2H,

*aryl-H<sup>4</sup>* or *aryl-H<sup>5</sup>*), 7.14-7.20 (2H, *m*-pyridine; 2H, *p*-phenyl; 2H, *aryl-H<sup>3</sup>* or *aryl-H<sup>6</sup>*), 7.42 (t, 2H, *aryl-H<sup>4</sup>* or *aryl-H<sup>5</sup>*), 7.66 (d, 4H, *o*-phenyl), 8.04 (d, 2H, *aryl-H<sup>3</sup>* or *aryl-H<sup>6</sup>*), 9.05 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): *Major isomer* - δ = 33.23 (C(CH<sub>3</sub>)<sub>3</sub>), 37.80 (C(CH<sub>3</sub>)<sub>3</sub>), 118.14 (*p*-pyridine), 125.58 (*aryl-C<sup>4</sup>* or *aryl-C<sup>5</sup>*), 126.62 (*aryl-C<sup>3</sup>* or *aryl-C<sup>6</sup>*), 128.68 (*m*-phenyl), 130.64 (*aryl-C<sup>4</sup>* or *aryl-C<sup>5</sup>*), 140.18 (*aryl-C<sup>2</sup>* or *i*-phenyl), 141.72 (*aryl-C<sup>2</sup>* or *i*-phenyl), 153.09 (*i*-aryl), 155.16 (*o*-pyridine), 164.89 (N=C), 124.77, 124.74, 126.90 and 127.61 (*o*-phenyl, *p*-phenyl, *m*-pyridine, *aryl-C<sup>3</sup>/C<sup>6</sup>*); *Minor isomer* - δ = 33.25 (C(CH<sub>3</sub>)<sub>3</sub>), 37.87 (C(CH<sub>3</sub>)<sub>3</sub>), 118.24 (*p*-pyridine), 125.66 (*aryl-C<sup>4</sup>* or *aryl-C<sup>5</sup>*), 126.05 (*aryl-C<sup>3</sup>* or *aryl-C<sup>6</sup>*), 128.52 (*m*-phenyl), 130.88 (*aryl-C<sup>4</sup>* or *aryl-C<sup>5</sup>*), 140.03 (*aryl-C<sup>2</sup>* or *i*-phenyl), 141.98 (*aryl-C<sup>2</sup>* or *i*-phenyl), 153.14 (*i*-aryl), 155.28 (*o*-pyridine), 165.38 (N=C), 124.87, 124.85, 126.86 and 127.37 (*o*-phenyl, *p*-phenyl, *m*-pyridine, *aryl-C<sup>3</sup>/C<sup>6</sup>*). IR (toluene): ν<sub>N3</sub> = 2055 cm<sup>-1</sup>.

**Preparation of (<sup>Cl2</sup>BPDI)CoN<sub>3</sub>.** This compound was prepared in a manner similar to (<sup>iPr</sup>PDI)CoN<sub>3</sub> with 0.098 g (0.146 mmol) of (<sup>Cl2</sup>BPDI)CoCl and 0.012 g (0.185 mmol, 1.3 equiv) NaN<sub>3</sub> and yielded 0.084 g (85 % yield) of dark red crystals identified as (<sup>Cl2</sup>BPDI)CoN<sub>3</sub>. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 6.60 (t, 2H, *p*-aryl), 6.99 (tt, 4H, *m*-phenyl), 7.03 (d, 4H, *m*-aryl), 7.24 (tt, 2H, *p*-phenyl), 7.26 (d, 2H, *m*-pyridine), 8.11 (dd, 4H, *o*-phenyl), 9.05 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 119.57 (*p*-pyridine), 121.20 (*o*-phenyl), 127.56 (*p*-aryl), 127.64 (*m*-pyridine), 128.35 (*m*-phenyl), 128.50 (*m*-aryl), 128.57 (*p*-phenyl), 129.01 (*o*-aryl), 141.07 (*i*-phenyl), 151.87 (*i*-aryl), 155.95 (*o*-pyridine), 167.88 (C=N). IR (toluene): ν<sub>N3</sub> = 2054 cm<sup>-1</sup>.

**Independent Synthesis of (<sup>iPr</sup>BPDI)CoNCO.** A 100 mL round-bottom flask was charged with 0.171 g (0.244 mmol) of (<sup>iPr</sup>BPDI)CoCl, 0.045 g (0.55 mmol, 2.3 equiv) of KOCN and approximately 50 mL of THF. After stirring for 72 hours, the THF was removed in

vacuo. The resulting residue was dissolved in 50 mL of toluene and filtered through Celite. Removing the solvent from the filtrate in vacuo yielded a dark pink solid which, after recrystallization from a toluene/pentane (~1:3 v/v) mixture, afforded 0.113 g (65 %) of dark red crystals identified as (<sup>i</sup>PrBPDI)CoNCO. Anal. Calcd for C<sub>44</sub>H<sub>47</sub>N<sub>4</sub>OCO: C, 74.77; H, 6.70; N, 7.93. Found: C, 74.75; H, 6.80; N, 7.90. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 1.03 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.07 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.49 (septet, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.95 (dd, 4H, *m*-phenyl), 7.11 (d, 2H, *m*-pyridine), 7.21 (d, 4H, *m*-aryl), 7.24 (tt, 2H, *p*-phenyl), 7.41 (t, 2H, *p*-aryl), 7.74 (dd, 4H, *o*-phenyl), 9.24 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 23.70 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.72 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.84 (CH(CH<sub>3</sub>)<sub>2</sub>), 118.44 (*p*-pyridine), 124.40 (*m*-aryl), 124.67 (*o*-phenyl), 127.79 (*p*-aryl), 128.31 (*m*-pyridine), 128.72 (*p*-phenyl), 128.80 (*m*-phenyl), 139.64 (*i*-phenyl), 141.04 (*o*-aryl), 151.67 (*i*-aryl), 155.77 (*o*-pyridine), 167.90 (C=N), IR (toluene): ν<sub>NCO</sub> = 2218 cm<sup>-1</sup>.

**Independent Synthesis of (<sup>i</sup>PrPDI)CoNCO.** This compound was prepared in a manner similar to (<sup>i</sup>PrBPDI)CoNCO with 0.112 g (0.194 mmol) of (<sup>i</sup>PrPDI)CoCl and 0.028 g (0.035 mmol, 1.8 equiv) of KOCN and yielded 0.055 g (49 %) of dark pink crystals identified as (<sup>i</sup>PrPDI)CoNCO. Anal. Calcd for C<sub>34</sub>H<sub>43</sub>N<sub>4</sub>OCO: C, 70.09; H, 7.44; N, 9.62. Found: C, 69.89; H, 7.40; N, 9.38. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 0.15 (s, 6H, C(CH<sub>3</sub>)), 1.10 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.24 (septet, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.85 (d, 2H, *m*-pyridine), 7.30 (d, 4H, *m*-aryl), 7.43 (t, 2H, *p*-aryl), 9.34 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>): δ = 20.89 (C(CH<sub>3</sub>)), 23.89 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.32 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.53 (CH(CH<sub>3</sub>)<sub>2</sub>), 115.92 (*p*-pyridine), 124.47 (*m*-aryl), 125.37 (*m*-pyridine), 127.75 (*p*-aryl), 140.91 (*o*-aryl), 150.50 (*i*-aryl), 153.40 (*o*-pyridine), 167.33 (C=N). IR (toluene): ν<sub>NCO</sub> = 2218 cm<sup>-1</sup>.



**Preparation of (<sup>Mes</sup>BPDI)CoN<sub>2</sub>.** A 100 mL round bottom flask was charged with 17.4 g (86.3 mmol) of Hg and approximately 40 mL of toluene. To the flask was added 0.087 g (3.78 mmol, 4.77 equiv) of Na in small pieces with vigorous stirring. After stirring the amalgam for 20 minutes, 0.517 g (0.793 mmol) of (<sup>Mes</sup>BPDI)CoCl<sub>2</sub> was added to the flask. A color change to dark red was initially observed followed by a gradual color change to olive green. The reaction was stirred for 24 hours then filtered through Celite. Removing the solvent from the filtrate in vacuo yielded an olive green powder which, after recrystallization from a toluene/pentane (~1:3 v/v) mixture, furnished 0.182 g (38 %) of olive green crystals identified as (<sup>Mes</sup>BPDI)CoN<sub>2</sub>. Anal. Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>5</sub>Co: C, 73.01; H, 5.80; N, 11.51. Found: C, 72.99; H, 6.13; N, 11.20. Magnetic susceptibility (Evans method):  $\mu_{\text{eff}} = 1.3(3) \mu_{\text{B}}$ . <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta = 4.52$  (198 Hz), 9.99 (296 Hz), 12.03 (317 Hz). IR (toluene):  $\nu_{\text{N}_2} = 2109 \text{ cm}^{-1}$ .

**Independent Synthesis of (<sup>Mes</sup>BPDI)CoNCO.** A 100 mL round bottom flask was charged with 0.053 g (0.087 mmol) of (<sup>Mes</sup>BPDI)CoN<sub>2</sub>, 0.013 g (0.087 mmol, 1.0 equiv) of AgOCN and approximately 40 mL of toluene/ether (1:1 v/v). The resulting reaction mixture was stirred for 72 hours then filtered through Celite. Removing the solvent from the filtrate in vacuo yielded a dark red solid which, after recrystallization from a toluene/pentane (~1:3 v/v) mixture, furnished 0.031 g (57 %) of dark red crystals identified as (<sup>Mes</sup>BPDI)CoNCO. Anal. Calcd for C<sub>38</sub>H<sub>35</sub>N<sub>4</sub>OCo: C, 73.30; H, 5.67; N, 9.00. Found: C, 73.57; H, 5.95; N, 8.71. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta = 2.07$  (s, 6H, *p*-CH<sub>3</sub>), 2.26 (s, 12H, *o*-CH<sub>3</sub>), 6.80 (s, 4H, *m*-aryl), 6.98 (dd, 4H, *m*-phenyl), 7.13 (d, 2H, *m*-pyridine), 7.21 (tt, 2H, *p*-phenyl), 7.81 (dd, 4H, *o*-phenyl), 9.22 (t, 1H, *p*-pyridine). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>):  $\delta = 20.27$  (*o*-CH<sub>3</sub>), 21.62 (*p*-CH<sub>3</sub>), 118.27 (*p*-pyridine), 123.29 (*o*-phenyl), 127.37 (*m*-pyridine), 128.90 (*p*-phenyl), 128.93 (*m*-phenyl), 139.85 (*m*-aryl), 130.45 (*o*-

*aryl*), 135.68 (*p-aryl*), 140.14 (*i-phenyl*), 152.40 (*i-aryl*), 155.53 (*o-pyridine*), 167.85 (C=N). IR (toluene):  $\nu_{\text{NCO}} = 2215 \text{ cm}^{-1}$ .

**Preparation of 1 by Photolysis.** A thick walled quartz reaction vessel was charged with 0.010 g (0.014 mmol) of (<sup>i</sup>PrBPDI)CoN<sub>3</sub> and approximately 20 mL of cyclopentane. The resulting solution was irradiated for 2 hours at 15 °C (Rayonet Photochemical Chamber Reactor RPR-200, RPR-2537Å lamp) during which the dark pink solution turned bright green. The solvent was removed in vacuo and the bright green solid was collected. Analysis of the <sup>1</sup>H NMR spectrum of the product established approximately 90 % conversion to **1**. Anal. Calcd for C<sub>43</sub>H<sub>47</sub>N<sub>4</sub>Co: C, 76.08; H, 6.98; N, 8.25. Found: C, 75.88; H, 7.38; N, 7.91. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, *aryl'* = cyclometalated aryl):  $\delta$  = 0.68 (d, 3H, *aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 0.72 (d, 6H, *aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 0.72 (d, 3H, *aryl'*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (d, 3H, *aryl'*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (d, 3H, *aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (s, 3H, *aryl'*-C(CH<sub>3</sub>)<sub>2</sub>), 1.67 (s, 3H, *aryl'*-C(CH<sub>3</sub>)<sub>2</sub>), 2.78 (s, 1H, NH), 3.10 (septet, 1H, *aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 3.32 (septet, 1H, *aryl'*-CH(CH<sub>3</sub>)<sub>2</sub>), 3.81 (septet, 1H, *aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 6.95-7.31 (4H, *m-phenyl*; 2H, *p-phenyl*; 2H, *m-aryl*; 1H, *m-aryl'*; 1H, *p-aryl*; 1H, *p-aryl'*), 7.33 (dd, 1H, *m-aryl'*), 7.66 (t, 1H *p-pyridine*), 7.80 (dd, 2H, *o-phenyl*), 8.02 (dd, 2H, *o-phenyl*), 8.25 (d, 1H, *m-pyridine*), 8.33 (d, 1H, *p-pyridine*). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, *aryl'* = cyclometalated aryl):  $\delta$  = 20.79 (*aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 23.47 (*aryl'*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.21 (*aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 26.17(*aryl'*-CH(CH<sub>3</sub>)<sub>2</sub>), 26.52 (*aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 26.75 (*aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 28.69 (*aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 28.80 (*aryl'*-CH(CH<sub>3</sub>)<sub>2</sub>), 30.04 (*aryl*-CH(CH<sub>3</sub>)<sub>2</sub>), 34.90 (*aryl'*-C(CH<sub>3</sub>)<sub>2</sub>), 45.59 (*aryl'*-C(CH<sub>3</sub>)<sub>2</sub>), 57.89 (*aryl'*-C(CH<sub>3</sub>)<sub>2</sub>), 121.03 (*p-pyridine*), 121.33 (*m-pyridine*), 121.48 (*m-pyridine*), 123.48 (*m-aryl'*), 123.49 (*m-aryl*), 123.84 (*m-aryl'*), 124.72 (*m-aryl*, *p-aryl'*), 127.08 (*o-phenyl*), 127.28 (*o-phenyl*), 139.78 (*o-aryl*), 141.58 (*o-aryl*), 144.88 (*o-aryl'*), 144.97 (*o-aryl'*), 148.09 (*i-aryl'*), 148.17 (*i-aryl*), 151.53 (*o-pyridine*), 152.47 (*o-pyridine*), 155.22 (*i-phenyl*), 157.22 (*i-phenyl*),

169.83 (C=N); 125.49, 126.99, 127.02, 128.94 and 129.65 (*m*-phenyl, *p*-phenyl, *m*-aryl).

IR (toluene):  $\nu_{\text{NH}} = 3307 \text{ cm}^{-1}$ .

**Preparation of 1: Thermolysis.** A thick walled glass vessel was charged with 0.058 g (0.082 mmol) (<sup>i</sup>PrBPDl)CoN<sub>3</sub>. The glass vessel was degassed and the sample was heated to 215 °C for 1 hour. Analysis of the <sup>1</sup>H NMR spectrum of the resulting bright green product showed >95 % conversion of <sup>i</sup>PrBPDlCoN<sub>3</sub> to **1**.

**Toepler Pump Experiment: Solid State Thermolysis of (<sup>i</sup>PrBPDl)CoN<sub>3</sub>.** A thick walled glass vessel was charged with 0.059 g (0.083 mmol) of (<sup>i</sup>PrBPDl)CoN<sub>3</sub>. The vessel was degassed and heated to 245 °C for 15 minutes. A color change to bright green was observed. The liberated dinitrogen was collected with a Toepler pump into a volume of 15.9 mL. After 2 hours, 91 torr (93 %) of expected amount of dinitrogen was collected.

**Preparation of 2: Solid State Thermolysis.** A thick walled glass vessel was charged with 0.120 g (0.193 mmol) (<sup>Mes</sup>BPDl)CoN<sub>3</sub>. The glass vessel was degassed and the sample was heated to 165 °C for 4 hours. Analysis of the <sup>1</sup>H NMR spectrum of the resulting bright green product established >95 % conversion of <sup>Mes</sup>BPDlCoN<sub>3</sub> to **2**. Anal. Calcd for C<sub>37</sub>H<sub>35</sub>N<sub>4</sub>Co: C, 74.73; H, 5.93; N, 9.42. Found: C, 74.33; H, 6.16; N, 9.89. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, aryl' = cyclometalated aryl): 1.97 (s, 3H, aryl' *p*-CH<sub>3</sub>), 2.12 (s, 3H, aryl *o*-CH<sub>3</sub>), 2.18 (s, 3H, aryl *o*-CH<sub>3</sub>), 2.34 (s, 3H, aryl *p*-CH<sub>3</sub>), 3.07 (s, 3H, aryl' *o*-CH<sub>3</sub>), 6.65 (s, 2H, *m*-aryl'), 6.76 (t, 2H, *m*-phenyl), 6.85 (t, 2H, *m*-phenyl), 7.06 (d, 1H, *m*-aryl), 7.08 (d, 1H, *m*-aryl), 7.12-7.21 (6H, *o*-phenyl, *p*-phenyl), 7.40 (t, 1H, *p*-py), 7.64 (d, 1H, *m*-py), 8.12 (t, 1H, aryl'-CH=NH), 8.68 (d, 1H, *m*-py), 9.15 (s, 1H, CH(py)(phenyl)(N-aryl)), 15.41 (d, 1H, aryl'-CH=NH). <sup>13</sup>C {<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, aryl' = cyclometalated aryl):  $\delta$  = 20.04 (aryl-*o*-CH<sub>3</sub>), 20.08 (aryl'-*p*-CH<sub>3</sub>), 20.18 (aryl-*o*-CH<sub>3</sub>), 21.80 (aryl-*p*-CH<sub>3</sub>), 26.47

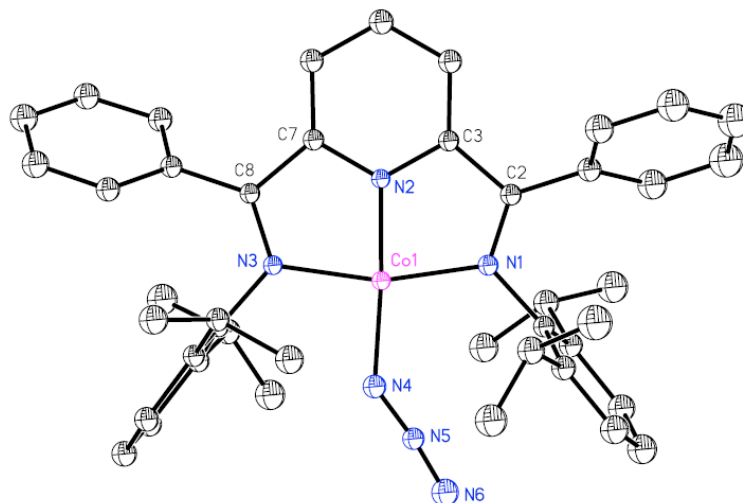
(*aryl'*-o-CH<sub>3</sub>), 83.75 (CH(py))(phenyl)(N-aryl)), 113.42 (*m-py*), 120.52 (*m-py*), 120.60 (*o-aryl'*), 124.43 (*p-aryl'*), 126.52 (*o-aryl'*), 129.38 (*m-aryl*), 129.62 (*m-aryl*), 130.63 (*o-aryl*), 131.21 (*m-aryl'*), 132.46 (*o-aryl*), 135.26 (*p-aryl*), 135.53 (*m-aryl'*), 142.87 (*i-phenyl*), 146.37 (*i-phenyl*), 148.44 (*i-aryl'*), 150.96 (*i-aryl*), 155.11 (*o-py*), 155.87 (C=N), 158.87 (*aryl'*-CH=NH), 174.52 (*o-py*); 125.09, 127.55, 127.72, 128.86, 129.16, 129.99 and 130.43 (*p-py* and *phenyl*-Cs). IR (toluene):  $\nu_{\text{NH}} = 3293 \text{ cm}^{-1}$ .

### C. Trapping Experiments

**Photolysis of (<sup>i</sup>PrPDI)CoN<sub>3</sub> under CO atmosphere.** A thick walled glass vessel was charged with 0.010 g (0.017 mmol) of (<sup>i</sup>PrPDI)CoN<sub>3</sub> and approximately 15 mL of cyclopentane. On a high vacuum line, the vessel was degassed and four atmospheres of CO was admitted at -196 °C. The reaction mixture was thawed and then irradiated for 2 hours at 15 °C (Rayonet Photochemical Chamber Reactor RPR-200, RPR-2537Å lamp). The volatiles were removed in vacuo and the resulting dark pink solid was collected. Analysis of the <sup>1</sup>H NMR spectrum of the product established approximately 50 % conversion of (<sup>i</sup>PrPDI)CoN<sub>3</sub> to (<sup>i</sup>PrPDI)CoNCO.

**Thermolysis of (<sup>i</sup>PrBPDI)CoN<sub>3</sub> under CO atmosphere.** A thick walled glass vessel was charged with 0.011 g (0.016 mmol) of (<sup>i</sup>PrBPDI)CoN<sub>3</sub> and approximately 20 mL of toluene. On a high vacuum line, the vessel was degassed and four atmospheres of CO was admitted at -196 °C. The reaction mixture was thawed and heated to 100 °C for 4 hours. The volatiles were removed in vacuo and the resulting dark pink solid was collected. Analysis of the <sup>1</sup>H NMR spectrum of the product established approximately 60 % conversion of (<sup>i</sup>PrBPDI)CoN<sub>3</sub> to (<sup>i</sup>PrBPDI)CoNCO.

**Reaction of (<sup>Mes</sup>BPDI)CoN<sub>3</sub> with CO gas.** A thick walled glass vessel was charged with 0.011 g (0.018 mmol) of (<sup>Mes</sup>BPDI)CoN<sub>3</sub> and approximately 10 mL of toluene. On a high vacuum line, the vessel was degassed and four atmospheres of CO was admitted at -196 °C. The reaction mixture was thawed and stirred for 2 hours at room temperature. The volatiles were removed in vacuo and the resulting red solid was collected. Analysis of the <sup>1</sup>H NMR spectrum of the product established full conversion of (<sup>Mes</sup>BPDI)CoN<sub>3</sub> to (<sup>Mes</sup>BPDI)CoNCO.

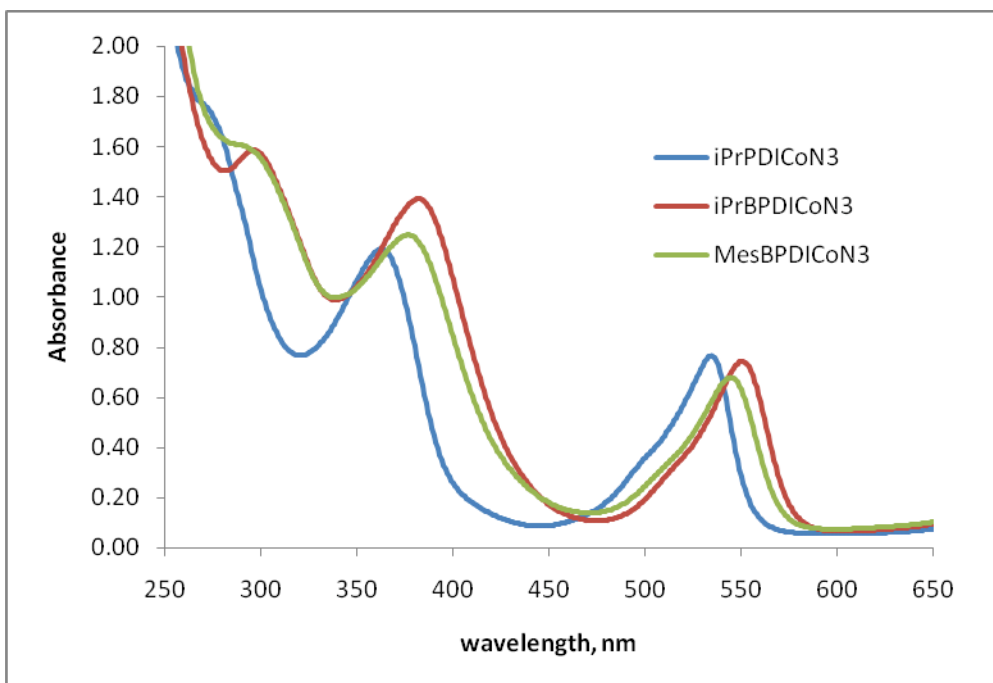


**Figure S1.** Molecular structure of (*i*PrBPDI)CoN<sub>3</sub> at 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

**Table S1.** Selected bond distances (Å) and angles (deg).

Co(1)-N(1)	1.8966(13)
Co(1)-N(2)	1.7867(12)
Co(1)-N(3)	1.9114(13)
Co(1)-N(4)	1.8582(13)
N(1)-C(2)	1.3263(19)
N(3)-C(8)	1.3222(19)
C(2)-C(3)	1.440(2)
C(7)-C(8)	1.445(2)
N(4)-N(5)	1.1964(18)
N(5)-N(6)	1.1449(19)
Co(1)-N(4)-N(5)	139.07(12)
N(4)-N(5)-N(6)	174.15(17)

## Electronic Spectra.



**Figure S2.** Electronic absorption spectra of bis(imino)pyridine cobalt azide compounds in diethyl ether.

	$\lambda_{\text{max}}$ , nm	$\epsilon$ , $\text{cm}^{-1}\text{M}^{-1}$
	550	6373
(iPrPDI)CoN <sub>3</sub>	382	9950
	534	8833
(iPrBPDI)CoN <sub>3</sub>	363	16600
	544	6168
	377	11281
(MesBPDI)CoN <sub>3</sub>		

## References.

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