

## Experimental Section.

**General Considerations.**  $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{CrCO}^1$ ,  $\text{B}(\text{C}_6\text{F}_5)_3^2$  and complex **3**<sup>3</sup> were prepared as described in the literature. Benzene, tetrahydrofuran and pentane were dried over and distilled from sodium/benzophenone immediately prior to use. 2,6-dimethylphenyl isocyanide (Fluka) was used without further purification. Air and moisture sensitive compounds were handled and stored in a nitrogen-filled glovebox and were manipulated using argon and vacuum Schlenk techniques. Magnetic susceptibility measurements on the compounds were performed using a Johnson Matthey Magnetic Susceptibility Balance (solid state) or using the Evans' NMR method<sup>4</sup> (solutions) on Bruker AMX 300 (300 MHz <sup>1</sup>H) or Bruker AVANCE 500 (500 MHz <sup>1</sup>H) spectrometers. IR spectra of the compounds were recorded as nujol mulls between NaCl discs or in solution (0.1 mm path length with NaCl windows) on a Perkin Elmer Spectrum 1000 spectrophotometer. Element analyses were performed by Desert Analytics (Tucson, AZ).

*Synthesis of  $[\text{C}_5\text{H}_4(\text{CMe}_2)_2\text{C}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3]\text{CrCN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)(\text{C}_6\text{H}_6)$  (**4**).* A dark green solution of **3** (154.1 mg, 0.1987 mmol) in 1 mL of benzene was added to 25.5 mg (0.1944 mmol) of CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). The solution immediately turned dark brown. After 6 h crystals of **4** began to form. To stimulate the crystallization, a few drops of pet-ether was added occasionally to the solution. After 3 days, the crystals were isolated, washed with a few mL of pentane, and dried in vacuum. A crystal was selected for X-ray diffraction. Yield: 136.0 mg (71%).  $\mu_{\text{eff}} = 1.75$  B.M.  $\nu(\text{CN}) = 2100$  cm<sup>-1</sup>. Anal. Found (calcd) for **4**•C<sub>6</sub>H<sub>6</sub>, C<sub>49</sub>H<sub>34</sub>BCrF<sub>15</sub>N: C, 60.02(59.77); N, 1.20 (1.42); H, 3.36(3.48).

*Synthesis of  $[\eta^5\text{-C}_5\text{H}_4(\text{CMe}_2)_2\eta^5\text{-C}_5\text{H}_3\text{B}(\text{C}_6\text{F}_5)_3]\text{Cr}(\text{CN})\text{CN}-(2,6\text{-Me}_2\text{C}_6\text{H}_3)$  (**5**).*

**Method A** (oxidation of **4** (generated *in situ*) with AgCN). A Schlenk vessel was charged with **3** (346.5 mg, 0.4469 mmol), CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (60.0 mg, 0.4574 mmol), and AgCN (67.0 mg, 0.5004 mmol) and the vessel was evacuated. THF (40 mL) was condensed onto the mixture, which was cooled in liq N<sub>2</sub>. Upon thawing the solution was dark-green, and it turned yellow-brown upon warming to room temperature (RT) and red-brown upon refluxing for 16 h. After cooling to RT, the clear red-brown solution was filtered. The solution was concentrated to 5 mL under vacuum, at which point crystallization began. Then the solution was heated until all material was dissolved. Pentane was diffused into the THF solution, and over the course of 2 days orange-red crystals formed along with some orange-red precipitate. The solvent was decanted from the solids and the solids were dried under vacuum (yield: 0.33 g (73%). X-ray quality crystals were grown by cooling a hot benzene solution of **5**. The <sup>1</sup>H NMR spectrum of **5** showed one THF molecule per molecule of **5**. IR (NaCl/nujol): 2159 cm<sup>-1</sup> (s), 2112 cm<sup>-1</sup> (m). <sup>1</sup>H NMR (500,13 MHz, THF-*d*<sub>8</sub>, -16 °C):  $\delta$  7.23 (t, <sup>3</sup>J<sub>HH</sub> = 7.59 Hz, 1H, *p*-xylyl); 7.12 (d, <sup>3</sup>J<sub>HH</sub> = 7.59 Hz, 2H, *m*-xylyl); 5.98 (m, 1H, C<sub>5</sub>H<sub>3</sub>); 5.92 (m, 1H, C<sub>5</sub>H<sub>3</sub>); 5.859 (m, 1H, C<sub>5</sub>H<sub>3</sub>); 5.83 (m, 1H, C<sub>5</sub>H<sub>4</sub>); 5.76 (m, 1H, C<sub>5</sub>H<sub>4</sub>); 5.38 (m, 1H, C<sub>5</sub>H<sub>4</sub>); 4.92 (m, 1H, C<sub>5</sub>H<sub>4</sub>); 3.62 (m, 4H, THF); 2.46 (s, 6H, 2 x Me of xylyl); 1.78 (m, 4H, THF); 1.32 (s, 3H, (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 1.28 (s, 3H, (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 1.22 (s, 3H, (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 1.12 (s, 3H, (CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>). <sup>13</sup>C NMR (125.75 MHz, THF-*d*<sub>8</sub>, 25 °C):  $\delta$  178.87 (s, CN-xylyl); 149.14 (d, <sup>1</sup>J<sub>CF</sub> = 240 Hz, *o*-C<sub>6</sub>F<sub>5</sub>); 139.53 (d, <sup>1</sup>J<sub>CF</sub> = 248 Hz, *p*-C<sub>6</sub>F<sub>5</sub>); 138.19 (s, CN); 137.59 (d, <sup>1</sup>J<sub>CF</sub> = 238 Hz, *m*-C<sub>6</sub>F<sub>5</sub>); 136.97 (s, *o*-xylyl); 133.21 (s, *ipso*-xylyl); 131.01 (*p*-xylyl); 129.53 (*ipso*-Cp to C<sub>2</sub> bridge); 128.88

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(*m*-xylyl); 127.49 (s, *ipso*-Cp to C<sub>2</sub> bridge); 124.4 (br, coincided resonances of *ipso*-C<sub>6</sub>F<sub>5</sub> and *ipso*-Cp to boron); 105.95 (C<sub>5</sub>H<sub>3</sub>); 104.03 (C<sub>5</sub>H<sub>4</sub>); 103.11 (C<sub>5</sub>H<sub>3</sub>); 98.40 (C<sub>5</sub>H<sub>3</sub>); 97.23 (C<sub>5</sub>H<sub>4</sub>); 93.09 (C<sub>5</sub>H<sub>4</sub>); 91.39 (C<sub>5</sub>H<sub>4</sub>); 47.54 (Me<sub>4</sub>C<sub>2</sub>); 45.27 (Me<sub>4</sub>C<sub>2</sub>); 29.31 ((CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 28.20 ((CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 26.90 ((CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 24.95 ((CH<sub>3</sub>)<sub>4</sub>C<sub>2</sub>); 18.54 (xylyl CH<sub>3</sub>). <sup>11</sup>B NMR (160.46 MHz, THF-*d*<sub>8</sub>, 25 °C, vs. BF<sub>3</sub>(OEt<sub>2</sub>) external reference): δ -11.70. <sup>19</sup>F NMR (470.59 MHz, THF-*d*<sub>8</sub>, -99 °C): δ -118.93 (*o*-F); -129.27 (*o*-F); -131.85 (*o*-F); -133.51 (*o*-F); -135.35 (*o*-F); -135.53 (*o*-F); -160.41 (*p*-F); -162.42 (*p*-F); -164.24 (*p*-F); -167.30 (*m*-F); -167.59 (*m*-F); -168.18 (*m*-F); -168.75 (*m*-F); -168.86 (*m*-F); -169.18 (*m*-F). X-ray quality crystals were grown by cooling a hot benzene solution of **4**. Anal. Found (calcd) for **5**•THF, C<sub>48</sub>H<sub>36</sub>BCrF<sub>15</sub>N<sub>2</sub>O: C, 57.18(57.39); N, 2.74 (2.79); H, 3.79(3.61).

**Method B:** (oxidation of **3** with AgCN and subsequent reaction with CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)). A Schlenk vessel equipped with a solid dispenser was charged with **3** (299.5 mg, 0.3863 mmol) and AgCN (52.4 mg, 0.3914 mmol). The solid dispenser was charged with CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (53.2 mg, 0.4055 mmol). To avoid sublimation of the isocyanide while evacuating the vessel, the dispenser was frozen in liq N<sub>2</sub>. THF (40 mL) was distilled into the evacuated vessel. After complete thawing of the mixture a clear bright green solution of **3** was obtained. Stirring the mixture for 16 h at room temperature yielded a dark purple-brown solution with finely-divided silver powder. Addition of the xylyl isocyanide resulted in an immediate color change of the solution from purple-brown to red-brown. The mixture was stirred for an additional 30 min. Then the solids were allowed to settle for an hour, after which time the red-brown solution was filtered. The clear red-brown solution was concentrated to about 10 mL. Diffusion of pentane into the solution afforded orange red crystals of **5**•THF. The solvent was decanted and the crystals were dried in vacuum (yield: 211 mg, 54%). The <sup>1</sup>H NMR and IR spectra of the product were identical with the spectra of the product obtained by method A.

*Crystal Structure Determinations.* Crystals of **4** and of **5** were removed from their flasks and covered with a layer of hydrocarbon oil. A suitable crystal of each compound was selected, attached to a glass fiber and placed in the low-temperature nitrogen stream.<sup>5</sup> Data for **4** and **5** were collected at 203(2) K and 83(2) K respectively using a Bruker/Siemens SMART APEX instrument (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3 ° per frame for 5 seconds, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.77 Å for **4** and 0.71 Å for **5**. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART<sup>6</sup> software and refined using SAINTPlus<sup>7</sup> on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS.<sup>8</sup> The structures were solved by direct methods and refined by least squares method on F<sup>2</sup> using the SHELXTL program package.<sup>9</sup> The structures of **4** and **5** were solved in the space groups P-1 (#2) and P2(1)/n (#14), respectively, by analysis of systematic absences. In both cases all atoms were refined anisotropically. No decomposition was observed during data collection.

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<sup>2</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was prepared from the reaction of C<sub>6</sub>F<sub>5</sub>MgBr with BF<sub>3</sub>(Et<sub>2</sub>O) in ether.  
The product was purified by vacuum sublimation (120 °C, 0.1 torr). See: Eur. Pat.  
Appl. 728760, 1996.  
<sup>3</sup> P.-J. Sinnema, D. M. J. Foo, B. Twamley and P.J. Shapiro, *J. Am. Chem. Soc.*  
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<sup>4</sup> Evans, D. F. *J. Am. Chem. Soc.* **1959**, *92*, 2003-2005.  
<sup>5</sup> Hope, H. *Prog. Inorg. Chem.*, **1995**, *41*, 1.  
<sup>6</sup> SMART: v.5.626, Bruker Molecular Analysis Research Tool, Bruker AXS,  
Madison, WI, **2002**.  
<sup>7</sup> SAINTPlus: v. 6.22, Data Reduction and Correction Program, Bruker AXS,  
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<sup>8</sup> SADABS: v.2.01, an empirical absorption correction program, Sheldrick, G.M.,  
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<sup>9</sup> SHELXTL: v. 6.10, Structure Determination Software Suite, Sheldrick, G.M.,  
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