

**Polyethyl Substituted Weakly Coordinating Carborane Anions: A Sequential  
Dehydrogenative Borylation/Hydrogenation Route**

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**Supporting Information**

Full experimental and spectroscopic data for complexes **1 – 6**

X-ray crystallographic data for **4** and **5**

## Experimental Data

**General.** All manipulations were carried out under an atmosphere of argon, using standard Schlenk- line and glove box techniques, unless otherwise stated. Glassware was pre-dried in an oven at 130°C and flamed with a blowtorch under vacuum prior to use. Solvents were dried over activated alumina, copper and molecular sieve columns using a MBraun solvent purification system. CD<sub>2</sub>Cl<sub>2</sub> was distilled under vacuum from CaH<sub>2</sub>. [(PPh<sub>3</sub>)<sub>2</sub>Rh(*closo*-CB<sub>11</sub>H<sub>12</sub>)] and [(PPh<sub>3</sub>)<sub>2</sub>Rh(1-Me-*closo*-CB<sub>11</sub>H<sub>11</sub>)] were prepared by the published literature routes or slight variations thereof.<sup>1</sup> All other chemicals were used as received from Aldrich. Microanalyses were performed by Mr. Alan Carver (University of Bath Microanalytical Service). Mass spectroscopy of the anions was performed in the FAB- mode using a NOBA matrix using a FISON S Autosoc Mass Spectrometer.

<sup>1</sup> A. Rifat, N. J. Patmore, M. F. Mahon, and A. S. Weller, *Organometallics*, 2002, **21**, 2856

### NMR spectroscopy

<sup>1</sup>H, <sup>1</sup>H{<sup>11</sup>B}, <sup>11</sup>B{<sup>1</sup>H}, <sup>11</sup>B and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on Bruker Avance 300MHz or 400MHz spectrometers. Residual protio solvent was used as reference for <sup>1</sup>H and <sup>1</sup>H{<sup>11</sup>B} NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>: δ = 5.33). <sup>11</sup>B, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} spectra were referenced against BF<sub>3</sub>.OEt<sub>2</sub> (external) and 85% H<sub>3</sub>PO<sub>4</sub> (external) respectively. Values are quoted in ppm. Coupling constants are quoted in Hz.

### Rh(PPh<sub>3</sub>)<sub>2</sub>(7 or 12-(CH=CH<sub>2</sub>)-*closo*-CB<sub>11</sub>H<sub>11</sub>), 1-12 and 1-7

(PPh<sub>3</sub>)<sub>2</sub>Rh(1-H-*closo*-CB<sub>11</sub>H<sub>11</sub>) (45 mg, 0.058 mmol) was placed in a 15 cm<sup>3</sup> Young's ampoule and CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added *via* cannula. The solution was freeze-pump-thawed three times. On the third cycle the solution was charged with ethene (0.500 g) the ampoule closed and then allowed to warm to room temperature with stirring. After 15 hours, the solvent was evaporated under vacuum to afford a dark orange product. Yield – quantitative by NMR spectroscopy.

<sup>1</sup>H NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.81-7.06 (m, 30H, PPh<sub>3</sub>), 4.95 [d, 1H, B-CH=CH<sub>2</sub>, *J*(HH) 16, 7 isomer], 4.83 [d, 1H, B-CH=CH<sub>2</sub>, *J*(HH) 16, 12 isomer], 4.15 [d, 1H, B-CH=CH<sub>2</sub>, *J*(HH) 9, 7 isomer], 4.10 [d, 1H, B-CH=CH<sub>2</sub>, *J*(HH) 9, 12 isomer], 2.67 [dd, 1H, B-CH=CH<sub>2</sub>, *J*(HH) 16, <sup>3</sup>*J*(H-H) 9 Hz, 7 isomer], 2.56 [dd, 1H, B-CH=CH<sub>2</sub>, *J*(HH) 16, *J*(H-H) 9, 12 isomer], 2.37 (s, 1H, C<sub>cage</sub>-H, 7 isomer), 2.22 (s, 1H, C<sub>cage</sub>-H, 12 isomer).

selected - <sup>1</sup>H{<sup>11</sup>B} NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 1.86 (br s, B-H, 7 isomer), 1.80 (br s, B-H, 7 isomer), 1.64 (br s, B-H, 7 isomer), 1.52 (br, B-H, 12 isomer), 1.24 (br s, B-H, 7 isomer), 0.18 (br s, B-H, 7 isomer), 0.56 (br, B-H, 12 isomer), -0.80 (br s, B-H-Rh, 7 isomer), -1.72 (br, B-H-Rh, 12 isomer), -2.15 (br s, B-H-Rh, 7 isomer).

<sup>11</sup>B NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 2.71 (s, B-C), -2.18 (s, B-C), -14.93 (br, overlapping signals).

<sup>31</sup>P{<sup>1</sup>H} NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>, 298 K): 40.7 (br).

**[Rh(PPh<sub>3</sub>)<sub>2</sub>(7 or 12-(CH<sub>2</sub>CH<sub>3</sub>)-*closo*-CB<sub>11</sub>H<sub>11</sub>)], 2-12 and 2-7**

[(PPh<sub>3</sub>)<sub>2</sub>Rh(1-*H-closo*-CB<sub>11</sub>H<sub>11</sub>)] (45 mg, 0.058 mmol) was placed in a 15 cm<sup>3</sup> Young's ampoule and CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added *via* cannula. The solution was freeze-pump-thawed three times. On the third cycle the solution was charged with ethene (1.012 g) and allowed to warm to room temperature with stirring. After 15 hours, excess of ethene was removed under vacuum and replaced with hydrogen (1 atm). After one hour, the solvent was evaporated under vacuum to afford a red product. Yield – quantitative by NMR spectroscopy.

<sup>1</sup>H NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.80-7.06 (m, 30H, PPh<sub>3</sub>), 2.51 (br s, 1H, C<sub>cage</sub>-H, 12 isomer), 2.46 (s, 1H, C<sub>cage</sub>-H, 7 isomer), 0.95-0.30 (m, B-Et), -0.84 (br q, B-H-Rh), -2.11 (br q, B-H-Rh).

**Selected-<sup>1</sup>H{<sup>11</sup>B} NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 2.51 (br s, 1H, C<sub>cage</sub>-H, 12 isomer), 2.46 (s, 1H, C<sub>cage</sub>-H, 7 isomer), 1.98 (br s, B-H), 1.64 (br s, B-H), 1.55 (br s, B-H), 1.44 (br s, B-H), 0.95-0.30 (m, B-Et), -0.84 (br s, B-H-Rh), -2.11 (br s, B<sub>12</sub>-H-Rh).

<sup>11</sup>B{<sup>1</sup>H} NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 8.51 (s, B-H), 5.04 (s, B-H), 2.67 (s, B-H), 0.89 (s, B-H), -12.00 (s, B-H), -14.18 (s, B-H), -16.12 (s, B-H), -16.89 (s, B-H).

<sup>31</sup>P{<sup>1</sup>H} NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>, 298 K): 12 isomer: 46.0 [d, J(RhP) 194]; 7 isomer: 45.8 [d, J(RhP) 189].

**[Rh(PPh<sub>3</sub>)<sub>2</sub>(nbd)][7 or 12-(CH=CH<sub>2</sub>)-*closo*-CB<sub>11</sub>H<sub>11</sub>]**

[(PPh<sub>3</sub>)<sub>2</sub>Rh(CB<sub>11</sub>H<sub>12</sub>)] (45 mg, 0.058 mmol) was placed in a 15 cm<sup>3</sup> Young's ampoule and CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added *via* cannula. The solution was freeze-pump-thawed three times. On the third cycle the solution was charged with ethene (0.500 g), the ampoule closed and then allowed to warm to room temperature with stirring. After 15 hours, the solvent was evaporated under vacuum and the residue redissolved with CH<sub>2</sub>Cl<sub>2</sub>. Norbornadiene (0.5 cm<sup>3</sup>, 4.63 mmol) was added to the CH<sub>2</sub>Cl<sub>2</sub> solution and stirred for 3 hours. The solvent was evaporated under vacuum and the residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 cm<sup>3</sup>) and precipitated with pentane (15 cm<sup>3</sup>) to afford an orange precipitate. The solvent was decanted *via* cannula and the product dried under vacuum. Mass 47 mg, yield 92 %. FAB- (NOBA matrix), m/z: 169.2 showing the correct isotope pattern for B<sub>11</sub>C<sub>3</sub>H<sub>14</sub>. P<sub>2</sub>RhB<sub>11</sub>C<sub>46</sub>H<sub>5</sub> requires %C 62.1 %H 5.89. Found %C 61.8 %H 5.75.

<sup>1</sup>H NMR (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.50-7.26 (m, 30H, PPh<sub>3</sub>), 6.35 [dd, B-CH=CH<sub>2</sub>, J(HH) 19, J(HH) 13, 7 isomer], 6.23 [dd, B-CH=CH<sub>2</sub>, J(HH) 19, J(HH) 13, 12 isomer], 5.53 (br s, B-CH=CH<sub>2</sub>, 12 isomer), 5.37 (br s, B-CH=CH<sub>2</sub>, 7 and 12 isomers), 5.32 (br s, B-CH=CH<sub>2</sub>, 7 and 12 isomers), 5.18 (br s, B-CH=CH<sub>2</sub>, 12 isomer), 4.50 (br s, 4H, C<sub>7</sub>H<sub>8</sub>), 4.08 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 2.44 (br s, C<sub>cage</sub>-H, 7 isomer), 2.31 (br s, 1H, C<sub>cage</sub>-H, 12 isomer), 1.56 (s, 2H, C<sub>7</sub>H<sub>8</sub>).

**$^{11}\text{B}\{^1\text{H}\}$  NMR** ( $\delta/\text{ppm}$   $\text{CD}_2\text{Cl}_2$ ), assignments from  $^{11}\text{B}$ - $^{11}\text{B}$  COSY and  $^{11}\text{B}$  NMR, primed numbers indicate 7 isomer: 1.2 (*B12*-CH=CH<sub>2</sub>), -4.6 (*B7'*-CH=CH<sub>2</sub>), -5.8 (*B12'*-H), -12.4 (*B7-11,8',11'*-H, coincident signal), -13.4 (*B9',10'*-H), -15.6 (*B2',3'*-H), -16.4 (*B2-6,4',6'*-H, coincident signal), -18.5 (*B5'*-H).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** ( $\delta/\text{ppm}$   $\text{CD}_2\text{Cl}_2$ , 298 K): 29.6 [d, *J*(RhP) 156].

**[Rh(PPh<sub>3</sub>)<sub>2</sub>(nbd)][7 or 12-(CH<sub>2</sub>CH<sub>3</sub>)-*closo*-CB<sub>11</sub>H<sub>11</sub>]**

[(PPh<sub>3</sub>)<sub>2</sub>Rh(CB<sub>11</sub>H<sub>12</sub>)] (45 mg, 0.058 mmol) was placed in a 15 cm<sup>3</sup> Young's ampoule and CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>) was added *via* cannula. The solution was freeze-pump-thawed three times. On the third cycle the solution was charged with ethene (1.012 g) and allowed to warm to room temperature with stirring. After 15 hours, excess of ethene was removed under vacuum and replaced with hydrogen (1 atm). After one hour, the solvent was evaporated under vacuum. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> and norbornadiene (0.5 cm<sup>3</sup>, 4.63 mmol) was added. After stirring for 3 hours, the solvent was evaporated under vacuum and the orange residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) and precipitated with pentane (15 ml). The solvent was decanted *via* cannula and the product dried under vacuum. Mass 44 mg, yield 87 %. FAB- (NOBA matrix), *m/z*: 171.1 showing the correct isotope pattern for B<sub>11</sub>C<sub>3</sub>H<sub>16</sub>. P<sub>2</sub>RhB<sub>11</sub>C<sub>46</sub>H<sub>54</sub> requires %C 62.0 %H 6.11. Found %C 61.9 %H 6.23.

**$^1\text{H}$  NMR** ( $\delta/\text{ppm}$   $\text{CD}_2\text{Cl}_2$ ): 7.37-7.27 (m, 30H, PPh<sub>3</sub>), 4.47 (br s, 4H, C<sub>7</sub>H<sub>8</sub>), 3.99 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 2.26 (br s, C<sub>cage</sub>-H), 2.16 (br s, C<sub>cage</sub>-H), 1.59 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 1.06-0.70 (m, B-Et).

**$^1\text{H}\{^{11}\text{B}\}$  NMR** ( $\delta/\text{ppm}$   $\text{CD}_2\text{Cl}_2$ ): 7.37-7.27 (m, 30H, PPh<sub>3</sub>), 4.47 (br s, 4H, C<sub>7</sub>H<sub>8</sub>), 3.99 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 2.26 (br s, C<sub>cage</sub>-H), 2.16 (br s, C<sub>cage</sub>-H), 1.63 (br s, B-H), 1.61 (br s, B-H), 1.59 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 1.55 (br s, B-H), 1.06-0.70 (m, B-Et).

**$^{11}\text{B}$  NMR** ( $\delta/\text{ppm}$   $\text{CD}_2\text{Cl}_2$ ) assignments from  $^{11}\text{B}$ - $^{11}\text{B}$  COSY, primed numbers indicate 7 isomer:: 4.13 (s, *B12*-Et), -1.78 (s, *B7'*-Et), -6.20 [d, *B12'*-H, *J*(BH) 133], -12.77 [d, *B7-11,8',11'*-H, *J*(BH) 136], -14.03 (d br, *B9',10'*-H), -16.00 (d br, *B2',3'*-H), -16.90 [d, *B2-6,4',6'*-H, *J*(BH) 147], -19.81 [d, *B5'*-H, *J*(BH) 149].

**$^{31}\text{P}\{^1\text{H}\}$  NMR** ( $\delta/\text{ppm}$   $\text{CD}_2\text{Cl}_2$ , 298 K): 29.4 [d, *J*(RhP) 155].

**Rh(PPh<sub>3</sub>)<sub>2</sub>{1-H-(CH<sub>2</sub>CH<sub>3</sub>)<sub>5</sub>CB<sub>11</sub>H<sub>6</sub>} 3**

A solution of [(PPh<sub>3</sub>)<sub>2</sub>Rh(1-H-*closo*-CB<sub>11</sub>H<sub>11</sub>)] (179 mg, 0.232 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) was freeze-pump-thawed three times. On the third cycle ethene (~ 0.600 g) was added to the solution and warmed up to room temperature. After stirring for 24 hours, the solution was degassed again and hydrogen was placed in the Young's ampoule and the solution stirred for 2 hours. This sequential treatment with ethene / hydrogen was repeated a total of 6 times. The final dark pink-red solution was reduced *in vacuo* to dryness. In our hands analytically pure material as could not be obtained. Addition of nbd to compound **3** (see below) results in compound **4** that can be produced in a analytically pure form.

**<sup>1</sup>H NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.45-7.00 (m, 30 H, PPh<sub>3</sub>), 2.31 (br s, C<sub>cage-H</sub>), 0.86-0.14 (m, 26H, B-Et), -4.95 (br q, B-H-Rh).

**<sup>11</sup>B NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.8 (br s, 1B, B-Et), -4.3 (br s, 2B, B-Et), -9.2 (br s, 2B, B-Et), -12.8 (vbr d, 2B, B-H), -17.9 [d, 3B, B-H, *J*(HB) 93 Hz], -19.9 [d, 1B, B-H, *J*(HB) 95].

**<sup>31</sup>P{<sup>1</sup>H} NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>, 298 K): 45.1 (br).

#### **[Rh(PPh<sub>3</sub>)<sub>2</sub>(nbd)][1-H-*closo*-(CH<sub>2</sub>CH<sub>3</sub>)<sub>5</sub>CB<sub>11</sub>H<sub>6</sub>] 4**

A solution of [(PPh<sub>3</sub>)<sub>2</sub>Rh(CB<sub>11</sub>H<sub>12</sub>)] (179 mg, 0.232 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was freeze-pump-thawed three times. On the third cycle ethene (~ 0.600 g) was added to the solution, the ampoule closed and warmed up to room temperature. After stirring for 24 hours, the solution was degassed again and hydrogen was placed in the Young's ampoule and the solution stirred for 2 hours. This sequential treatment with ethene / hydrogen was repeated a total of 6 times. Following the last hydrogenation the solvent was degassed and norbornadiene (1 ml, 9.27 mmol) added. After stirring overnight, the solvent was evaporated under vacuum, the orange residue redissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 ml) and precipitated with hexane (20 ml). The solvent was decanted via cannula and the product dried under vacuum. Mass 175 mg, yield 75 %. Crystals suitable for an X-ray diffraction study were grown from CH<sub>2</sub>Cl<sub>2</sub>/pentane solutions. RhP<sub>2</sub>B<sub>11</sub>C<sub>54</sub>H<sub>70</sub> requires %C 64.67 %H 7.04, found %C 64.5 %H 7.23. FAB- (NOBA matrix), m/z: 283.3. This preparation has been successfully scaled up to 1.5 g of material with only a small overall loss in yield (~70%).

**<sup>1</sup>H NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.49-7.20 (m, 30H, PPh<sub>3</sub>), 4.44 (br s, 4H, C<sub>7</sub>H<sub>8</sub>), 3.96 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 2.02 (br s, C<sub>cage-H</sub>), 1.55 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 0.96-0.36 (m, 25H, B-Et).

**<sup>1</sup>H{<sup>11</sup>B} NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 7.49-7.20 (m, 30H, PPh<sub>3</sub>), 4.44 (br s, 4H, C<sub>7</sub>H<sub>8</sub>), 3.96 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 2.02 (br s, C<sub>cage-H</sub>), 1.55 (br s, 2H, C<sub>7</sub>H<sub>8</sub>), 1.48 (br s, B-H), 1.40 (br s, B-H), 1.36 (br s, B-H), 1.29 (br s, B-H), 1.21 (br s, B-H), 1.08 (br s, B-H), 0.96-0.36 (m, 25H, B-Et).

**<sup>11</sup>B NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>): 4.6 (br s, 1B, B-Et), -2.5 (br s, 2B, B-Et), -3.3 (br s, 1B, B-Et), -7.0 (br s, 1B, B-Et), -8.4 (br d, 1B, B-H) -12.5 (br d, 1B B-H), -13.7 (br d, 1B B-H), -14.6 (br d, B-H, 1B), -17.3 (br d, B-H, 2B overlapping coincidence).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (δ/ppm CD<sub>2</sub>Cl<sub>2</sub>, 298 K): 30.5 [d, *J*(RhP) 155].

#### **[Rh(PPh<sub>3</sub>)<sub>2</sub>(1-Me-(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>-CB<sub>11</sub>H<sub>8</sub>)] 5**

[(PPh<sub>3</sub>)<sub>2</sub>Rh(nbd)][1-Me-*closo*-CB<sub>11</sub>H<sub>11</sub>] (50 mg, 0.057 mmol) was placed in a 15 cm<sup>3</sup> Young's ampoule and CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was added *via* cannula. The solution was freeze-pump-thawed three times. On the third cycle the solution was allowed to warm to room temperature with stirring under an atmosphere of hydrogen to obtain [(PPh<sub>3</sub>)<sub>2</sub>Rh(1-Me-CB<sub>11</sub>H<sub>11</sub>)]. After 30 minutes excess of hydrogen was removed with vacuum and replaced with ethene. After 24 hours, the solution was degassed again and hydrogen was placed in the Young's ampoule and the solution stirred for 2 hours. This procedure was repeated a total of six times. The solution was then reduced *in vacuo* to dryness to afford a dark red residue. Crystals suitable for an X-ray diffraction experiment were grown from CH<sub>2</sub>Cl<sub>2</sub>/pentane solutions. Mass 12 mg, Yield 25%. FAB- (NOBA matrix), m/z:

241.2 that shows the correct isotope patten for  $B_{11}C_8H_{26}$ . Compound **5** was always formed with a small (~ 10%) of another carborane anion that could not be removed by bulk purification methods. Mass spectroscopy suggests that the identity of this may be  $[1-H-closo-(C_2H_5)_4-CB_{11}H_7]^-$ .

$^1H$  NMR ( $\delta$ /ppm  $CD_2Cl_2$ ): 7.52-7.10 (m, 30H,  $PPh_3$ ), 1.64 (s, 3H,  $C_{cage}-CH_3$ ), 1.02-0.11 (m, 15H,  $B-CH_2CH_3$ ), -4.64 (br q, 2H,  $B-H-Rh$ ).

$^{11}B$  NMR ( $\delta$ /ppm  $CD_2Cl_2$ ): -2.1 (vbr, 3B), -12.7 (vbr, 3B), -16.3 (vbr, 3B), -18.8 [d, 2B  $B-H$ ,  $J(HB)$  94].

$^{31}P\{^1H\}$  NMR ( $\delta$ /ppm  $CD_2Cl_2$ , 298 K): 45.0 [d,  $J(RhP)$  193].

**[Rh( $PPh_3$ ) $_2$ (NCMe) $_x$ ][1-Me-( $CH_2CH_3$ ) $_3$ - $CB_{11}H_8$ )] (x = 2,3) 6.**

Acetonitrile (1  $cm^3$ ) was added to a solution of compound **5** in  $CH_2Cl_2$  to afford a yellow solution, which by NMR spectroscopy was shown to be a well separated ion pair.

$^1H$  NMR ( $\delta$ /ppm  $CD_3CN$ ): 7.75-7.17 (m, 30H,  $PPh_3$ ), 1.53 (s, 3H,  $C_{cage}-CH_3$ ), 0.97-0.34 (m, 15H,  $B-CH_2CH_3$ ).

$^1H\{^{11}B\}$  NMR ( $\delta$ /ppm  $CD_3CN$ ): 7.75-7.17 (m, 30H,  $PPh_3$ ), 1.63 (br s,  $B-H$ ), 1.43 (br s,  $B-H$ ), 1.37 (br s,  $B-H$ ), 1.33 (br s,  $B-H$ ), 1.53 (s, 3H,  $C_{cage}-CH_3$ ), 1.02-0.11 (m, 15H,  $B-Et$ ).

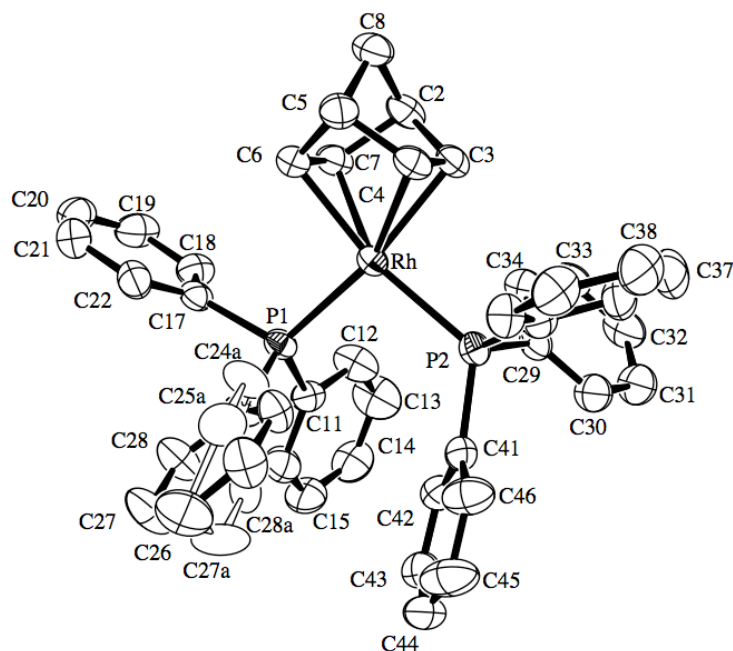
$^{11}B$  NMR ( $\delta$ /ppm  $CD_3CN$ ): 0.58 (br s, 1B,  $B-Et$ ), -1.72 (br s, 2B,  $B-Et$ ), -7.83 (br d, 1B,  $B-H$ ), -11.82 (br d, 2B,  $B-H$ ), -13.01 (br d, 3B,  $B-H$ ), -15.15 (br d, 2B,  $B-H$ ).

**[Rh( $PPh_3$ ) $_2$ (NCMe) $_x$ ][1-Me-( $CH_2CH_2CH_2CH_2CH_2CH_3$ ) $_3$ - $CB_{11}H_8$ )] (x = 2,3) 7.**

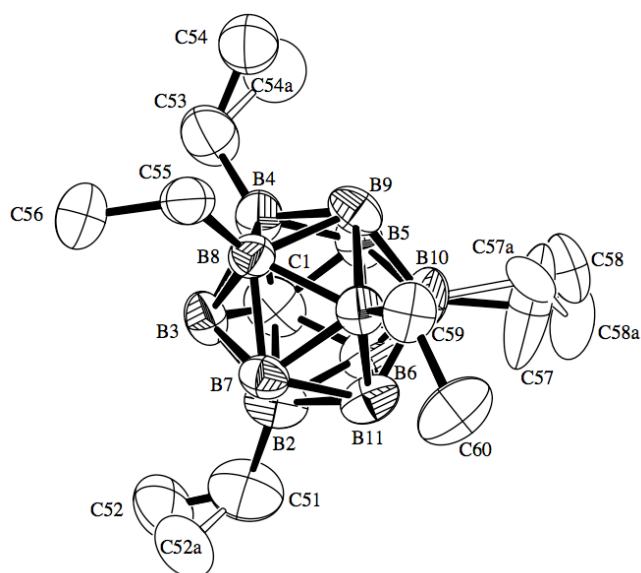
$^1H$  NMR ( $\delta$ /ppm  $CD_3CN$ ): 7.75-7.17 (m, 30H,  $PPh_3$ ), 1.40 (s, 3H,  $C_{cage}-CH_3$ ), 1.20-0.30 (m, 39H,  $B-CH_2CH_3$ ).

$^{11}B$  NMR ( $\delta$ /ppm  $CD_3CN$ ): 0.1 (br s, 1B,  $B-Et$ ), -2.0 (br s, 2B,  $B-Et$ ), -12.4 (br d, 8B,  $B-H$ )

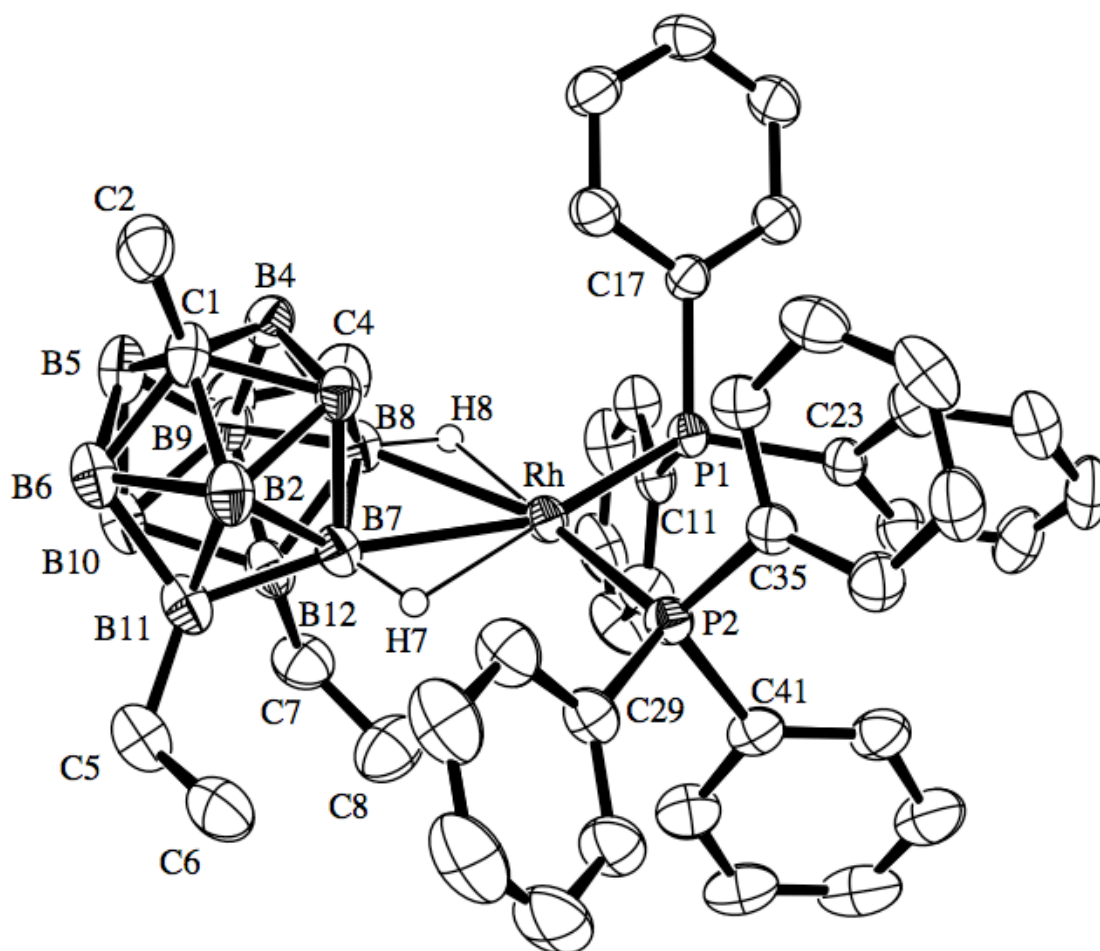
FAB- (NOBA matrix), m/z: 409.6 that shows the correct isotope patten for  $B_{11}C_{20}H_{50}$



**Figure S1.** View of the cationic portion of complex **4** showing the numbering scheme and the  $[\text{Rh}(\text{PPh}_3)_2(\text{nbd})]^+$  cation. Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity. The phenyl ring C23-C28 is disordered between two sites.



**Figure S2.** View of the anionic portion of complex **4** showing the numbering scheme and the  $[(\text{C}_2\text{H}_5)_5\text{CB}_{11}\text{H}_7]^-$  anion. Three of the ethyl groups are disordered in the solid-state with the major disordered component shown in full (C52:C52a 70:30; C54:C54a 86:14; C57/C58:C57a/C58a 56:44). Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity.



**Figure S3.** View of the complex **5** showing the numbering scheme. Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms, apart from H7 and H8, are omitted for clarity.



Table S1. Crystal data and structure refinement for Compound 4.

Identification code	k05asw1	
Empirical formula	C54 H70 B11 P2 Rh	
Formula weight	1002.86	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
space group	P 2 <sub>1</sub> /c	
Unit cell dimensions	a = 16.7380(2) Å	alpha = 90 deg.
	b = 18.0910(2) Å	beta = 111.6180(10) deg.
	c = 18.5710(2) Å	gamma = 90 deg.
Volume	5227.88(10) Å <sup>3</sup>	
Z, Calculated density	4, 1.274 Mg/m <sup>3</sup>	
Absorption coefficient	0.424 mm <sup>-1</sup>	
F(000)	2096	
Crystal size	0.20 x 0.10 x 0.05 mm	
Theta range for data collection	3.45 to 27.49 deg.	
Limiting indices	-21<=h<=21, -23<=k<=23, -24<=l<=24	
Reflections collected / unique	76466 / 11940 [R(int) = 0.0545]	
Completeness to theta = 27.49	99.5 %	
Max. and min. transmission	0.9791 and 0.9199	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	11940 / 0 / 677	
Goodness-of-fit on F <sup>2</sup>	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1095	
R indices (all data)	R1 = 0.0664, wR2 = 0.1173	
Largest diff. peak and hole	0.645 and -0.476 e.Å <sup>-3</sup>	

Table S2. Bond lengths [Å] for Compound 2.

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Rh-C (7)	2.173 (3)
Rh-C (6)	2.194 (3)
Rh-C (3)	2.210 (3)
Rh-C (4)	2.221 (3)
Rh-P (1)	2.3229 (7)
Rh-P (2)	2.3458 (8)
P (1)-C (23)	1.824 (3)
P (1)-C (11)	1.831 (3)
P (1)-C (17)	1.833 (3)
P (2)-C (35)	1.824 (3)
P (2)-C (41)	1.827 (3)
P (2)-C (29)	1.828 (3)
C (2)-C (3)	1.532 (4)
C (2)-C (7)	1.542 (4)
C (2)-C (8)	1.544 (5)
C (3)-C (4)	1.365 (4)
C (4)-C (5)	1.523 (4)
C (5)-C (6)	1.537 (4)
C (5)-C (8)	1.545 (5)
C (6)-C (7)	1.366 (4)
C (11)-C (12)	1.377 (4)
C (11)-C (16)	1.382 (4)
C (12)-C (13)	1.390 (5)
C (13)-C (14)	1.360 (6)
C (14)-C (15)	1.368 (6)
C (15)-C (16)	1.397 (5)
C (17)-C (22)	1.393 (4)
C (17)-C (18)	1.398 (4)
C (18)-C (19)	1.390 (5)
C (19)-C (20)	1.380 (6)
C (20)-C (21)	1.380 (6)
C (21)-C (22)	1.388 (5)
C (23)-C (24A)	1.32 (3)
C (23)-C (24)	1.379 (6)
C (23)-C (28A)	1.40 (2)
C (23)-C (28)	1.412 (5)
C (26)-C (25)	1.317 (7)
C (26)-C (27A)	1.35 (3)
C (26)-C (27)	1.413 (6)
C (26)-C (25A)	1.58 (3)
C (24)-C (25)	1.390 (8)
C (27)-C (28)	1.382 (6)
C (24A)-C (25A)	1.31 (4)
C (27A)-C (28A)	1.42 (4)
C (29)-C (30)	1.386 (4)
C (29)-C (34)	1.395 (4)
C (30)-C (31)	1.385 (5)
C (31)-C (32)	1.377 (5)
C (32)-C (33)	1.382 (5)
C (33)-C (34)	1.387 (4)
C (35)-C (36)	1.388 (4)
C (35)-C (40)	1.409 (4)
C (36)-C (37)	1.392 (5)

C (37) -C (38)	1.378 (6)
C (38) -C (39)	1.383 (5)
C (39) -C (40)	1.382 (4)
C (41) -C (46)	1.389 (5)
C (41) -C (42)	1.391 (4)
C (42) -C (43)	1.392 (5)
C (43) -C (44)	1.379 (6)
C (44) -C (45)	1.354 (6)
C (45) -C (46)	1.394 (5)
C (1) -B (6)	1.681 (7)
C (1) -B (3)	1.722 (6)
C (1) -B (5)	1.732 (7)
C (1) -B (2)	1.743 (7)
C (1) -B (4)	1.744 (8)
B (2) -C (51)	1.630 (7)
B (2) -B (6)	1.723 (8)
B (2) -B (11)	1.753 (8)
B (2) -B (3)	1.754 (7)
B (2) -B (7)	1.779 (6)
B (3) -B (7)	1.768 (6)
B (3) -B (4)	1.782 (6)
B (3) -B (8)	1.790 (6)
B (4) -C (53)	1.572 (7)
B (4) -B (5)	1.730 (7)
B (4) -B (8)	1.791 (6)
B (4) -B (9)	1.800 (7)
B (5) -B (9)	1.735 (6)
B (5) -B (6)	1.746 (7)
B (5) -B (10)	1.776 (6)
B (6) -B (11)	1.709 (6)
B (6) -B (10)	1.718 (8)
B (7) -B (11)	1.752 (6)
B (7) -B (12)	1.769 (6)
B (7) -B (8)	1.782 (6)
B (8) -C (55)	1.589 (6)
B (8) -B (9)	1.791 (6)
B (8) -B (12)	1.802 (6)
B (9) -B (10)	1.764 (7)
B (9) -B (12)	1.776 (6)
B (10) -C (57)	1.588 (16)
B (10) -C (57A)	1.623 (16)
B (10) -B (11)	1.766 (7)
B (10) -B (12)	1.804 (6)
B (11) -B (12)	1.767 (6)
B (12) -C (59)	1.605 (5)
C (51) -C (52)	1.333 (14)
C (51) -C (52A)	1.461 (17)
C (53) -C (54A)	1.534 (15)
C (53) -C (54)	1.558 (11)
C (55) -C (56)	1.533 (5)
C (57) -C (58)	1.33 (2)
C (57A) -C (58A)	1.57 (2)
C (59) -C (60)	1.522 (6)

Table S3. Bond angles [deg] for Compound 4.

---

C (7) -Rh-C (6)	36.45 (12)
C (7) -Rh-C (3)	65.92 (11)
C (6) -Rh-C (3)	77.13 (11)
C (7) -Rh-C (4)	76.96 (11)
C (6) -Rh-C (4)	64.81 (11)
C (3) -Rh-C (4)	35.88 (11)
C (7) -Rh-P (1)	98.54 (8)
C (6) -Rh-P (1)	94.67 (8)
C (3) -Rh-P (1)	162.89 (8)
C (4) -Rh-P (1)	151.51 (8)
C (7) -Rh-P (2)	145.87 (9)
C (6) -Rh-P (2)	164.59 (8)
C (3) -Rh-P (2)	91.39 (8)
C (4) -Rh-P (2)	99.88 (8)
P (1) -Rh-P (2)	99.01 (3)
C (23) -P (1) -C (11)	109.65 (14)
C (23) -P (1) -C (17)	103.55 (14)
C (11) -P (1) -C (17)	102.41 (13)
C (23) -P (1) -Rh	111.36 (10)
C (11) -P (1) -Rh	116.03 (10)
C (17) -P (1) -Rh	112.81 (9)
C (35) -P (2) -C (41)	104.23 (14)
C (35) -P (2) -C (29)	104.39 (14)
C (41) -P (2) -C (29)	102.98 (14)
C (35) -P (2) -Rh	109.52 (10)
C (41) -P (2) -Rh	123.72 (9)
C (29) -P (2) -Rh	110.26 (10)
C (3) -C (2) -C (7)	101.8 (2)
C (3) -C (2) -C (8)	99.8 (3)
C (7) -C (2) -C (8)	99.7 (3)
C (4) -C (3) -C (2)	106.6 (3)
C (4) -C (3) -Rh	72.52 (16)
C (2) -C (3) -Rh	95.35 (17)
C (3) -C (4) -C (5)	107.3 (3)
C (3) -C (4) -Rh	71.60 (16)
C (5) -C (4) -Rh	96.52 (18)
C (4) -C (5) -C (6)	101.3 (2)
C (4) -C (5) -C (8)	100.0 (3)
C (6) -C (5) -C (8)	99.9 (3)
C (7) -C (6) -C (5)	106.8 (3)
C (7) -C (6) -Rh	70.92 (18)
C (5) -C (6) -Rh	97.19 (19)
C (6) -C (7) -C (2)	106.8 (3)
C (6) -C (7) -Rh	72.63 (18)
C (2) -C (7) -Rh	96.53 (19)
C (2) -C (8) -C (5)	93.8 (2)
C (12) -C (11) -C (16)	118.8 (3)
C (12) -C (11) -P (1)	117.0 (2)
C (16) -C (11) -P (1)	124.2 (3)
C (11) -C (12) -C (13)	120.6 (3)
C (14) -C (13) -C (12)	120.6 (4)
C (13) -C (14) -C (15)	119.4 (3)
C (14) -C (15) -C (16)	120.8 (3)

C(11)-C(16)-C(15)	119.8(3)
C(22)-C(17)-C(18)	118.9(3)
C(22)-C(17)-P(1)	120.6(2)
C(18)-C(17)-P(1)	120.3(2)
C(19)-C(18)-C(17)	120.2(3)
C(20)-C(19)-C(18)	120.4(3)
C(19)-C(20)-C(21)	119.7(3)
C(20)-C(21)-C(22)	120.6(4)
C(21)-C(22)-C(17)	120.2(3)
C(24A)-C(23)-C(24)	30.9(14)
C(24A)-C(23)-C(28A)	121.3(16)
C(24)-C(23)-C(28A)	96.5(9)
C(24A)-C(23)-C(28)	114.7(13)
C(24)-C(23)-C(28)	117.0(3)
C(28A)-C(23)-C(28)	53.7(8)
C(24A)-C(23)-P(1)	111.2(12)
C(24)-C(23)-P(1)	119.9(3)
C(28A)-C(23)-P(1)	121.9(9)
C(28)-C(23)-P(1)	122.9(2)
C(25)-C(26)-C(27A)	93.7(12)
C(25)-C(26)-C(27)	120.9(4)
C(27A)-C(26)-C(27)	56.0(11)
C(25)-C(26)-C(25A)	26.8(11)
C(27A)-C(26)-C(25A)	105.5(18)
C(27)-C(26)-C(25A)	107.5(11)
C(23)-C(24)-C(25)	122.4(5)
C(26)-C(25)-C(24)	119.9(5)
C(28)-C(27)-C(26)	119.4(4)
C(27)-C(28)-C(23)	120.2(4)
C(25A)-C(24A)-C(23)	118(3)
C(24A)-C(25A)-C(26)	122(3)
C(26)-C(27A)-C(28A)	124(2)
C(23)-C(28A)-C(27A)	115.3(19)
C(30)-C(29)-C(34)	119.4(3)
C(30)-C(29)-P(2)	121.1(2)
C(34)-C(29)-P(2)	119.6(2)
C(31)-C(30)-C(29)	120.2(3)
C(32)-C(31)-C(30)	120.2(3)
C(31)-C(32)-C(33)	120.2(3)
C(32)-C(33)-C(34)	120.0(3)
C(33)-C(34)-C(29)	120.0(3)
C(36)-C(35)-C(40)	118.5(3)
C(36)-C(35)-P(2)	123.2(2)
C(40)-C(35)-P(2)	118.2(2)
C(35)-C(36)-C(37)	120.4(3)
C(38)-C(37)-C(36)	120.4(3)
C(37)-C(38)-C(39)	120.0(3)
C(40)-C(39)-C(38)	120.2(3)
C(39)-C(40)-C(35)	120.5(3)
C(46)-C(41)-C(42)	118.5(3)
C(46)-C(41)-P(2)	123.3(3)
C(42)-C(41)-P(2)	118.2(2)
C(41)-C(42)-C(43)	120.4(3)
C(44)-C(43)-C(42)	120.1(4)
C(45)-C(44)-C(43)	119.8(4)

C (44) -C (45) -C (46)	120.9 (4)
C (41) -C (46) -C (45)	120.1 (4)
B (6) -C (1) -B (3)	108.4 (3)
B (6) -C (1) -B (5)	61.5 (3)
B (3) -C (1) -B (5)	109.7 (3)
B (6) -C (1) -B (2)	60.4 (3)
B (3) -C (1) -B (2)	60.8 (3)
B (5) -C (1) -B (2)	111.3 (4)
B (6) -C (1) -B (4)	109.2 (4)
B (3) -C (1) -B (4)	61.9 (3)
B (5) -C (1) -B (4)	59.7 (3)
B (2) -C (1) -B (4)	111.6 (3)
C (51) -B (2) -B (6)	120.5 (4)
C (51) -B (2) -C (1)	121.5 (4)
B (6) -B (2) -C (1)	58.0 (3)
C (51) -B (2) -B (11)	122.1 (4)
B (6) -B (2) -B (11)	58.9 (3)
C (1) -B (2) -B (11)	105.6 (4)
C (51) -B (2) -B (3)	124.7 (5)
B (6) -B (2) -B (3)	105.0 (3)
C (1) -B (2) -B (3)	59.0 (3)
B (11) -B (2) -B (3)	107.2 (3)
C (51) -B (2) -B (7)	125.9 (4)
B (6) -B (2) -B (7)	105.3 (3)
C (1) -B (2) -B (7)	106.0 (3)
B (11) -B (2) -B (7)	59.5 (2)
B (3) -B (2) -B (7)	60.1 (3)
C (1) -B (3) -B (2)	60.2 (3)
C (1) -B (3) -B (7)	107.5 (3)
B (2) -B (3) -B (7)	60.7 (3)
C (1) -B (3) -B (4)	59.7 (3)
B (2) -B (3) -B (4)	109.4 (3)
B (7) -B (3) -B (4)	108.4 (3)
C (1) -B (3) -B (8)	107.4 (3)
B (2) -B (3) -B (8)	109.4 (3)
B (7) -B (3) -B (8)	60.1 (2)
B (4) -B (3) -B (8)	60.2 (3)
C (53) -B (4) -B (5)	120.7 (4)
C (53) -B (4) -C (1)	122.3 (4)
B (5) -B (4) -C (1)	59.8 (3)
C (53) -B (4) -B (3)	123.0 (4)
B (5) -B (4) -B (3)	107.1 (4)
C (1) -B (4) -B (3)	58.4 (3)
C (53) -B (4) -B (8)	123.3 (4)
B (5) -B (4) -B (8)	107.6 (3)
C (1) -B (4) -B (8)	106.3 (3)
B (3) -B (4) -B (8)	60.1 (2)
C (53) -B (4) -B (9)	123.4 (4)
B (5) -B (4) -B (9)	58.8 (3)
C (1) -B (4) -B (9)	105.3 (3)
B (3) -B (4) -B (9)	106.6 (3)
B (8) -B (4) -B (9)	59.8 (2)
B (4) -B (5) -C (1)	60.5 (3)
B (4) -B (5) -B (9)	62.6 (3)
C (1) -B (5) -B (9)	108.8 (3)
B (4) -B (5) -B (6)	106.9 (3)
C (1) -B (5) -B (6)	57.8 (3)

B(9)-B(5)-B(6)	105.8(3)
B(4)-B(5)-B(10)	110.8(3)
C(1)-B(5)-B(10)	106.5(3)
B(9)-B(5)-B(10)	60.3(3)
B(6)-B(5)-B(10)	58.4(3)
C(1)-B(6)-B(11)	110.5(4)
C(1)-B(6)-B(10)	111.6(4)
B(11)-B(6)-B(10)	62.0(3)
C(1)-B(6)-B(2)	61.6(3)
B(11)-B(6)-B(2)	61.4(3)
B(10)-B(6)-B(2)	113.1(3)
C(1)-B(6)-B(5)	60.7(3)
B(11)-B(6)-B(5)	110.9(3)
B(10)-B(6)-B(5)	61.7(3)
B(2)-B(6)-B(5)	111.6(4)
B(11)-B(7)-B(3)	106.6(3)
B(11)-B(7)-B(12)	60.2(3)
B(3)-B(7)-B(12)	109.0(3)
B(11)-B(7)-B(2)	59.5(3)
B(3)-B(7)-B(2)	59.3(3)
B(12)-B(7)-B(2)	108.8(3)
B(11)-B(7)-B(8)	108.3(3)
B(3)-B(7)-B(8)	60.6(2)
B(12)-B(7)-B(8)	61.0(2)
B(2)-B(7)-B(8)	108.6(3)
C(55)-B(8)-B(7)	124.6(3)
C(55)-B(8)-B(3)	122.1(3)
B(7)-B(8)-B(3)	59.3(2)
C(55)-B(8)-B(9)	121.8(3)
B(7)-B(8)-B(9)	106.1(3)
B(3)-B(8)-B(9)	106.6(3)
C(55)-B(8)-B(4)	119.2(3)
B(7)-B(8)-B(4)	107.3(3)
B(3)-B(8)-B(4)	59.7(3)
B(9)-B(8)-B(4)	60.3(2)
C(55)-B(8)-B(12)	124.0(3)
B(7)-B(8)-B(12)	59.1(2)
B(3)-B(8)-B(12)	106.5(3)
B(9)-B(8)-B(12)	59.3(2)
B(4)-B(8)-B(12)	107.9(3)
B(5)-B(9)-B(10)	61.0(3)
B(5)-B(9)-B(12)	109.6(3)
B(10)-B(9)-B(12)	61.2(2)
B(5)-B(9)-B(8)	107.4(3)
B(10)-B(9)-B(8)	109.4(3)
B(12)-B(9)-B(8)	60.7(2)
B(5)-B(9)-B(4)	58.6(3)
B(10)-B(9)-B(4)	108.1(3)
B(12)-B(9)-B(4)	108.7(3)
B(8)-B(9)-B(4)	59.9(2)
C(57)-B(10)-C(57A)	15.5(13)
C(57)-B(10)-B(6)	116.1(10)
C(57A)-B(10)-B(6)	127.7(6)
C(57)-B(10)-B(9)	131.9(12)
C(57A)-B(10)-B(9)	116.5(6)
B(6)-B(10)-B(9)	105.7(3)
C(57)-B(10)-B(11)	114.6(11)

C (57A) -B (10) -B (11)	128.1 (7)
B (6) -B (10) -B (11)	58.7 (3)
B (9) -B (10) -B (11)	106.6 (3)
C (57) -B (10) -B (5)	125.4 (8)
C (57A) -B (10) -B (5)	119.3 (7)
B (6) -B (10) -B (5)	59.9 (3)
B (9) -B (10) -B (5)	58.7 (3)
B (11) -B (10) -B (5)	107.0 (4)
C (57) -B (10) -B (12)	124.4 (7)
C (57A) -B (10) -B (12)	121.4 (7)
B (6) -B (10) -B (12)	105.6 (3)
B (9) -B (10) -B (12)	59.7 (2)
B (11) -B (10) -B (12)	59.3 (2)
B (5) -B (10) -B (12)	106.5 (3)
B (6) -B (11) -B (7)	107.1 (3)
B (6) -B (11) -B (2)	59.7 (3)
B (7) -B (11) -B (2)	61.0 (3)
B (6) -B (11) -B (10)	59.3 (3)
B (7) -B (11) -B (10)	109.5 (3)
B (2) -B (11) -B (10)	109.5 (3)
B (6) -B (11) -B (12)	107.6 (3)
B (7) -B (11) -B (12)	60.3 (2)
B (2) -B (11) -B (12)	110.1 (3)
B (10) -B (11) -B (12)	61.4 (3)
C (59) -B (12) -B (11)	122.9 (3)
C (59) -B (12) -B (7)	123.1 (3)
B (11) -B (12) -B (7)	59.4 (3)
C (59) -B (12) -B (9)	121.9 (3)
B (11) -B (12) -B (9)	106.1 (3)
B (7) -B (12) -B (9)	107.3 (3)
C (59) -B (12) -B (8)	122.6 (3)
B (11) -B (12) -B (8)	106.8 (3)
B (7) -B (12) -B (8)	59.9 (2)
B (9) -B (12) -B (8)	60.1 (2)
C (59) -B (12) -B (10)	121.4 (3)
B (11) -B (12) -B (10)	59.3 (3)
B (7) -B (12) -B (10)	107.1 (3)
B (9) -B (12) -B (10)	59.1 (3)
B (8) -B (12) -B (10)	107.2 (3)
C (52) -C (51) -C (52A)	43.5 (9)
C (52) -C (51) -B (2)	118.3 (8)
C (52A) -C (51) -B (2)	115.9 (7)
C (54A) -C (53) -C (54)	36.0 (6)
C (54A) -C (53) -B (4)	109.5 (7)
C (54) -C (53) -B (4)	117.7 (5)
C (56) -C (55) -B (8)	115.7 (3)
C (58) -C (57) -B (10)	119.2 (14)
C (58A) -C (57A) -B (10)	111.3 (10)
C (60) -C (59) -B (12)	115.2 (4)

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Table S4. Crystal data and structure refinement for Compound 5.

Identification code	k04asw21
Empirical formula	C44 H56 B11 P2 Rh
Formula weight	868.65
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.8660(2) Å    alpha = 83.5920(10) deg. b = 13.3420(4) Å    beta = 75.7420(10) deg. c = 17.7310(6) Å    gamma = 78.438(2) deg.
Volume	2211.41(11) Å <sup>3</sup>
Z, Calculated density	2, 1.305 Mg/m <sup>3</sup>
Absorption coefficient	0.491 mm <sup>-1</sup>
F(000)	900
Crystal size	0.20 x 0.13 x 0.03 mm
Theta range for data collection	5.57 to 27.44 deg.
Limiting indices	-12<=h<=12, -17<=k<=17, -22<=l<=22
Reflections collected / unique	26014 / 9894 [R(int) = 0.0741]
Completeness to theta = 27.44	98.0 %
Max. and min. transmission	0.9854 and 0.9083
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	9894 / 0 / 532
Goodness-of-fit on F <sup>2</sup>	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.0905
R indices (all data)	R1 = 0.0813, wR2 = 0.1028
Largest diff. peak and hole	0.452 and -0.678 e.Å <sup>-3</sup>

Table S5. Bond lengths [Å] for Compound 5.

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Rh-P(2)	2.2129(9)
Rh-P(1)	2.2457(8)
Rh-B(7)	2.401(4)
Rh-B(8)	2.405(4)
Rh-H(7)	1.93(3)
Rh-H(8)	1.93(3)
P(1)-C(17)	1.822(3)
P(1)-C(11)	1.825(3)
P(1)-C(23)	1.832(3)
P(2)-C(35)	1.824(3)
P(2)-C(41)	1.825(3)
P(2)-C(29)	1.834(3)
C(11)-C(12)	1.397(5)
C(11)-C(16)	1.400(5)
C(12)-C(13)	1.404(5)
C(13)-C(14)	1.370(7)
C(14)-C(15)	1.372(6)
C(15)-C(16)	1.382(5)
C(17)-C(18)	1.401(4)
C(17)-C(22)	1.403(5)
C(18)-C(19)	1.388(5)
C(19)-C(20)	1.372(5)
C(20)-C(21)	1.378(5)
C(21)-C(22)	1.385(5)
C(23)-C(24)	1.398(4)
C(23)-C(28)	1.402(5)
C(24)-C(25)	1.388(5)
C(25)-C(26)	1.378(6)
C(26)-C(27)	1.376(6)
C(27)-C(28)	1.383(5)
C(29)-C(34)	1.389(5)
C(29)-C(30)	1.410(5)
C(30)-C(31)	1.388(5)
C(31)-C(32)	1.387(7)
C(32)-C(33)	1.377(7)
C(33)-C(34)	1.400(6)
C(35)-C(36)	1.393(5)
C(35)-C(40)	1.399(5)
C(36)-C(37)	1.386(5)
C(37)-C(38)	1.378(6)
C(38)-C(39)	1.380(6)
C(39)-C(40)	1.391(5)
C(41)-C(42)	1.390(5)
C(41)-C(46)	1.403(5)
C(42)-C(43)	1.407(6)
C(43)-C(44)	1.370(7)
C(44)-C(45)	1.370(7)
C(45)-C(46)	1.377(5)
C(1)-C(2)	1.518(5)
C(1)-B(6)	1.693(6)
C(1)-B(3)	1.702(5)
C(1)-B(5)	1.705(5)
C(1)-B(2)	1.723(6)

C (1) -B (4)	1.728 (5)
B (2) -B (3)	1.757 (6)
B (2) -B (6)	1.759 (6)
B (2) -B (7)	1.766 (5)
B (2) -B (11)	1.805 (6)
B (3) -B (7)	1.777 (6)
B (3) -B (4)	1.778 (6)
B (3) -B (8)	1.779 (5)
B (4) -B (5)	1.756 (6)
B (4) -B (8)	1.769 (6)
B (4) -B (9)	1.785 (6)
B (5) -B (10)	1.754 (7)
B (5) -B (6)	1.767 (7)
B (5) -B (9)	1.783 (6)
B (6) -B (10)	1.755 (6)
B (6) -B (11)	1.779 (7)
B (7) -B (8)	1.732 (6)
B (7) -H (7)	1.08 (3)
B (8) -H (8)	1.15 (3)
B (7) -B (11)	1.787 (5)
B (7) -B (12)	1.792 (5)
B (8) -B (12)	1.783 (6)
B (8) -B (9)	1.786 (5)
B (9) -C (3)	1.596 (5)
B (9) -B (10)	1.794 (6)
B (9) -B (12)	1.804 (7)
C (3) -C (4)	1.512 (5)
B (10) -B (12)	1.774 (6)
B (10) -B (11)	1.796 (7)
B (11) -C (5)	1.590 (6)
B (11) -B (12)	1.813 (6)
C (5) -C (6)	1.505 (6)
B (12) -C (7)	1.597 (5)
C (7) -C (8)	1.481 (6)

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Table S6. Bond angles [deg] for Compound 5.

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P(2)-Rh-P(1)	95.77(3)
P(2)-Rh-B(7)	111.71(10)
P(1)-Rh-B(7)	152.43(10)
P(2)-Rh-B(8)	153.47(9)
P(1)-Rh-B(8)	110.20(10)
B(7)-Rh-B(8)	42.24(14)
P(2)-Rh-H(7)	86.7(10)
P(1)-Rh-H(7)	174.7(8)
B(7)-Rh-H(7)	25.9(10)
B(8)-Rh-H(7)	67.9(10)
P(2)-Rh-H(8)	178.0(8)
P(1)-Rh-H(8)	82.9(9)
B(7)-Rh-H(8)	69.7(9)
B(8)-Rh-H(8)	28.1(8)
H(7)-Rh-H(8)	94.5(13)
C(17)-P(1)-C(11)	104.90(15)
C(17)-P(1)-C(23)	100.16(15)
C(11)-P(1)-C(23)	102.81(14)
C(17)-P(1)-Rh	115.69(10)
C(11)-P(1)-Rh	104.50(10)
C(23)-P(1)-Rh	126.47(11)
C(35)-P(2)-C(41)	110.38(16)
C(35)-P(2)-C(29)	98.12(15)
C(41)-P(2)-C(29)	103.07(16)
C(35)-P(2)-Rh	116.58(11)
C(41)-P(2)-Rh	112.29(11)
C(29)-P(2)-Rh	114.82(12)
C(12)-C(11)-C(16)	118.9(3)
C(12)-C(11)-P(1)	123.7(3)
C(16)-C(11)-P(1)	117.4(3)
C(11)-C(12)-C(13)	119.4(4)
C(14)-C(13)-C(12)	120.4(4)
C(13)-C(14)-C(15)	120.6(4)
C(14)-C(15)-C(16)	120.1(4)
C(15)-C(16)-C(11)	120.6(4)
C(18)-C(17)-C(22)	118.3(3)
C(18)-C(17)-P(1)	120.6(3)
C(22)-C(17)-P(1)	121.0(2)
C(19)-C(18)-C(17)	120.6(3)
C(20)-C(19)-C(18)	120.1(3)
C(19)-C(20)-C(21)	120.3(4)
C(20)-C(21)-C(22)	120.5(3)
C(21)-C(22)-C(17)	120.2(3)
C(24)-C(23)-C(28)	118.0(3)
C(24)-C(23)-P(1)	119.0(2)
C(28)-C(23)-P(1)	123.0(2)
C(25)-C(24)-C(23)	120.7(3)
C(26)-C(25)-C(24)	120.2(3)
C(27)-C(26)-C(25)	119.8(3)
C(26)-C(27)-C(28)	120.7(4)
C(27)-C(28)-C(23)	120.5(3)
C(34)-C(29)-C(30)	118.7(3)

C (34) -C (29) -P (2)	124.0 (3)
C (30) -C (29) -P (2)	117.2 (3)
C (31) -C (30) -C (29)	120.3 (4)
C (32) -C (31) -C (30)	119.8 (4)
C (33) -C (32) -C (31)	121.0 (4)
C (32) -C (33) -C (34)	119.3 (5)
C (29) -C (34) -C (33)	120.9 (4)
C (36) -C (35) -C (40)	118.9 (3)
C (36) -C (35) -P (2)	118.3 (3)
C (40) -C (35) -P (2)	122.5 (3)
C (37) -C (36) -C (35)	120.3 (3)
C (38) -C (37) -C (36)	120.3 (4)
C (37) -C (38) -C (39)	120.2 (3)
C (38) -C (39) -C (40)	120.1 (4)
C (39) -C (40) -C (35)	120.1 (4)
C (42) -C (41) -C (46)	118.7 (3)
C (42) -C (41) -P (2)	125.6 (3)
C (46) -C (41) -P (2)	115.6 (3)
C (41) -C (42) -C (43)	119.3 (4)
C (44) -C (43) -C (42)	120.4 (4)
C (45) -C (44) -C (43)	120.8 (4)
C (44) -C (45) -C (46)	119.6 (4)
C (45) -C (46) -C (41)	121.2 (4)
C (2) -C (1) -B (6)	119.0 (3)
C (2) -C (1) -B (3)	118.3 (3)
B (6) -C (1) -B (3)	112.7 (3)
C (2) -C (1) -B (5)	119.0 (3)
B (6) -C (1) -B (5)	62.7 (3)
B (3) -C (1) -B (5)	113.1 (3)
C (2) -C (1) -B (2)	118.3 (3)
B (6) -C (1) -B (2)	62.0 (3)
B (3) -C (1) -B (2)	61.7 (2)
B (5) -C (1) -B (2)	113.6 (3)
C (2) -C (1) -B (4)	118.9 (3)
B (6) -C (1) -B (4)	112.9 (3)
B (3) -C (1) -B (4)	62.4 (2)
B (5) -C (1) -B (4)	61.5 (2)
B (2) -C (1) -B (4)	113.1 (3)
C (1) -B (2) -B (3)	58.6 (2)
C (1) -B (2) -B (6)	58.2 (2)
B (3) -B (2) -B (6)	107.0 (3)
C (1) -B (2) -B (7)	104.7 (3)
B (3) -B (2) -B (7)	60.6 (2)
B (6) -B (2) -B (7)	106.4 (3)
C (1) -B (2) -B (11)	105.7 (3)
B (3) -B (2) -B (11)	109.4 (3)
B (6) -B (2) -B (11)	59.9 (2)
B (7) -B (2) -B (11)	60.1 (2)
C (1) -B (3) -B (2)	59.7 (2)
C (1) -B (3) -B (7)	105.0 (3)
B (2) -B (3) -B (7)	59.9 (2)
C (1) -B (3) -B (4)	59.5 (2)
B (2) -B (3) -B (4)	109.0 (3)
B (7) -B (3) -B (4)	106.6 (3)
C (1) -B (3) -B (8)	104.9 (3)
B (2) -B (3) -B (8)	107.0 (3)

B(7)-B(3)-B(8)	58.3(2)
B(4)-B(3)-B(8)	59.6(2)
C(1)-B(4)-B(5)	58.6(2)
C(1)-B(4)-B(8)	104.3(3)
B(5)-B(4)-B(8)	107.1(3)
C(1)-B(4)-B(3)	58.1(2)
B(5)-B(4)-B(3)	107.1(3)
B(8)-B(4)-B(3)	60.2(2)
C(1)-B(4)-B(9)	106.2(3)
B(5)-B(4)-B(9)	60.5(2)
B(8)-B(4)-B(9)	60.3(2)
B(3)-B(4)-B(9)	109.4(3)
C(1)-B(5)-B(10)	105.6(3)
C(1)-B(5)-B(4)	59.9(2)
B(10)-B(5)-B(4)	108.7(3)
C(1)-B(5)-B(6)	58.3(2)
B(10)-B(5)-B(6)	59.8(3)
B(4)-B(5)-B(6)	108.0(3)
C(1)-B(5)-B(9)	107.3(3)
B(10)-B(5)-B(9)	61.0(3)
B(4)-B(5)-B(9)	60.6(2)
B(6)-B(5)-B(9)	109.0(3)
C(1)-B(6)-B(10)	106.1(3)
C(1)-B(6)-B(2)	59.9(2)
B(10)-B(6)-B(2)	109.4(3)
C(1)-B(6)-B(5)	59.0(2)
B(10)-B(6)-B(5)	59.7(3)
B(2)-B(6)-B(5)	108.8(3)
C(1)-B(6)-B(11)	108.1(3)
B(10)-B(6)-B(11)	61.1(3)
B(2)-B(6)-B(11)	61.3(2)
B(5)-B(6)-B(11)	109.6(3)
B(8)-B(7)-B(2)	108.8(3)
B(8)-B(7)-B(3)	60.9(2)
B(2)-B(7)-B(3)	59.4(2)
B(8)-B(7)-B(11)	109.8(3)
B(2)-B(7)-B(11)	61.0(2)
B(3)-B(7)-B(11)	109.3(3)
B(8)-B(7)-B(12)	60.8(2)
B(2)-B(7)-B(12)	109.7(3)
B(3)-B(7)-B(12)	109.9(3)
B(11)-B(7)-B(12)	60.9(2)
B(8)-B(7)-Rh	69.02(18)
B(2)-B(7)-Rh	135.0(2)
B(3)-B(7)-Rh	84.50(19)
B(11)-B(7)-Rh	163.9(2)
B(12)-B(7)-Rh	107.3(2)
B(7)-B(8)-B(4)	109.1(3)
B(7)-B(8)-B(3)	60.8(2)
B(4)-B(8)-B(3)	60.1(2)
B(7)-B(8)-B(12)	61.3(2)
B(4)-B(8)-B(12)	109.2(3)
B(3)-B(8)-B(12)	110.2(3)
B(7)-B(8)-B(9)	110.0(3)
B(4)-B(8)-B(9)	60.3(2)
B(3)-B(8)-B(9)	109.3(3)
B(12)-B(8)-B(9)	60.7(2)

B (7) -B (8) -Rh	68.74 (19)
B (4) -B (8) -Rh	135.7 (2)
B (3) -B (8) -Rh	84.32 (19)
B (12) -B (8) -Rh	107.4 (2)
B (9) -B (8) -Rh	164.0 (3)
C (3) -B (9) -B (5)	123.4 (3)
C (3) -B (9) -B (4)	123.4 (4)
B (5) -B (9) -B (4)	59.0 (2)
C (3) -B (9) -B (8)	123.9 (3)
B (5) -B (9) -B (8)	105.2 (3)
B (4) -B (9) -B (8)	59.4 (2)
C (3) -B (9) -B (10)	122.7 (3)
B (5) -B (9) -B (10)	58.7 (3)
B (4) -B (9) -B (10)	105.7 (3)
B (8) -B (9) -B (10)	105.0 (3)
C (3) -B (9) -B (12)	121.2 (3)
B (5) -B (9) -B (12)	106.4 (3)
B (4) -B (9) -B (12)	107.6 (3)
B (8) -B (9) -B (12)	59.6 (2)
B (10) -B (9) -B (12)	59.1 (3)
C (4) -C (3) -B (9)	114.8 (3)
B (5) -B (10) -B (6)	60.5 (3)
B (5) -B (10) -B (12)	109.0 (3)
B (6) -B (10) -B (12)	108.7 (3)
B (5) -B (10) -B (9)	60.3 (2)
B (6) -B (10) -B (9)	109.0 (3)
B (12) -B (10) -B (9)	60.7 (2)
B (5) -B (10) -B (11)	109.5 (3)
B (6) -B (10) -B (11)	60.1 (2)
B (12) -B (10) -B (11)	61.0 (2)
B (9) -B (10) -B (11)	110.3 (3)
C (5) -B (11) -B (6)	121.0 (3)
C (5) -B (11) -B (7)	125.6 (4)
B (6) -B (11) -B (7)	104.7 (3)
C (5) -B (11) -B (10)	122.7 (3)
B (6) -B (11) -B (10)	58.8 (2)
B (7) -B (11) -B (10)	105.0 (3)
C (5) -B (11) -B (2)	121.8 (3)
B (6) -B (11) -B (2)	58.8 (2)
B (7) -B (11) -B (2)	58.9 (2)
B (10) -B (11) -B (2)	105.6 (3)
C (5) -B (11) -B (12)	124.2 (3)
B (6) -B (11) -B (12)	105.9 (3)
B (7) -B (11) -B (12)	59.7 (2)
B (10) -B (11) -B (12)	58.9 (2)
B (2) -B (11) -B (12)	107.0 (3)
C (6) -C (5) -B (11)	115.3 (3)
C (7) -B (12) -B (10)	121.1 (3)
C (7) -B (12) -B (8)	123.4 (3)
B (10) -B (12) -B (8)	105.9 (3)
C (7) -B (12) -B (7)	126.1 (4)
B (10) -B (12) -B (7)	105.7 (3)
B (8) -B (12) -B (7)	57.9 (2)
C (7) -B (12) -B (9)	118.6 (3)
B (10) -B (12) -B (9)	60.2 (3)
B (8) -B (12) -B (9)	59.7 (2)
B (7) -B (12) -B (9)	106.5 (3)

C (7) -B (12) -B (11)	123.1 (3)
B (10) -B (12) -B (11)	60.1 (2)
B (8) -B (12) -B (11)	106.3 (3)
B (7) -B (12) -B (11)	59.4 (2)
B (9) -B (12) -B (11)	109.0 (3)
C (8) -C (7) -B (12)	117.4 (3)
B (8) -B (7) -H (7)	119.9 (16)
B (2) -B (7) -H (7)	118.5 (16)
B (3) -B (7) -H (7)	115.6 (16)
B (11) -B (7) -H (7)	124.3 (17)
B (12) -B (7) -H (7)	125.4 (16)
Rh-B (7) -H (7)	51.6 (16)
B (7) -B (8) -H (8)	119.1 (15)
B (4) -B (8) -H (8)	122.1 (16)
B (3) -B (8) -H (8)	119.5 (14)
B (12) -B (8) -H (8)	120.8 (15)
B (9) -B (8) -H (8)	122.5 (14)
Rh-B (8) -H (8)	52.2 (15)

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