

I. General

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

THF, Et₂O, CH₂Cl₂, and toluene were purified by passing through a neutral alumina column under argon. Anhydrous pentane and benzene were used as received (Aldrich).

ZrCpCl₃ (Strem), [Rh(cod)Cl]₂ (Strem), and Cr(CO)₃(CH₃CN)₃ (Acros) were used as received. Heterocycle **1** was prepared according to our published procedure.¹ KH (Strem) was washed with pentane three times and then dried under vacuum prior to use. KO-*t*-Bu (Aldrich) was sublimed prior to use. All other chemicals and solvents were purchased (Aldrich, Strem, or Alfa Aesar) and used as received.

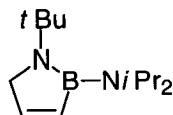
Silica gel (230-400 mesh) was heated under vacuum in a 200 °C sand bath for 12 hours. Flash chromatography was performed with this silica gel under an inert atmosphere.

¹¹B NMR spectra were recorded on a Varian Unity 300 or on a Varian Unity 500 spectrometer at ambient temperature. ³¹P NMR spectra were recorded on a Varian Mercury 300 spectrometer with complete proton decoupling at ambient temperature. All chemical shifts are externally referenced: ³¹P NMR to 85% H₃PO₄ (δ 0) and ¹¹B NMR to boron trifluoride diethyl etherate (δ 0).

(1) S.-Y. Liu, M. M.-C. Lo, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 174-176.

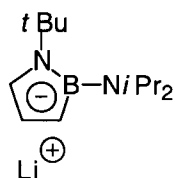
II. Synthesis of Lithium 1,2-Azaborolides (Table 1)

Because the yields that are reported in Table 1 are the average of two runs, the yields that are described below for a specific experiment may differ from the values presented in the table.



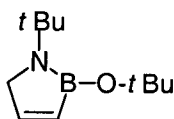
In a glove box, a vial was charged with a solution of **1** (324 mg, 2.05 mmol) in Et₂O (4.0 mL). This solution was cooled to -35 °C, and then a solution of LDA (generated from diisopropylamine (200 mg, 1.95 mmol in 7.0 mL of Et₂O) and *n*-BuLi (2.6 M solution in hexane; 750 μL, 2.0 mmol)) was added dropwise. The reaction mixture was allowed to stand at -35 °C, with occasional stirring, for 90 minutes, and then it was warmed to r.t. and stirred for 6 hours. The reaction mixture was filtered through an acrodisc, the precipitate (LiCl) was washed with pentane, and the combined filtrates were concentrated under vacuum to provide a pale-yellow oil (391 mg, 90% yield; 95% purity by NMR).

¹H NMR (500 MHz, C₆D₆): δ 6.73 (d, ³J_{HH} = 8.5 Hz, 1H), 6.42 (d, ³J_{HH} = 8.0 Hz, 1H), 3.71 (quintet, ³J_{HH} = 7.0 Hz, 2H), 3.65 (t, ³J_{HH} = 2.0 Hz, 2H), 1.33 (s, 9H), 1.23 (d, ³J_{HH} = 7.0 Hz, 12H). ¹³C NMR (125 MHz, C₆D₆): δ 143.9, 135.5 (br), 56.5, 52.0, 47.2, 32.3, 24.8. ¹¹B NMR (96 MHz, C₆D₆): δ 31.8. FTIR (thin film) 2969, 2929, 2871, 2825, 1591, 1571, 1470, 1446, 1430, 1377, 1364, 1300, 1229, 1156 cm⁻¹. HRMS (EI) calcd for C₁₃H₂₇BN₂ (M⁺) 222.2262, found 222.2273.



In a glove box, a vial was charged with a solution of **2** (Nu = NiPr₂) (79.2 mg, 0.356 mmol) in THF (0.2 mL). This solution was cooled to -35 °C, and then a solution of LiTMP (generated from 2,2,6,6-tetramethylpiperidine (156 mg, 1.11 mmol in 0.9 mL of THF) and *n*-BuLi (2.6 M solution in hexane; 410 μL, 1.1 mmol)) was added dropwise. The reaction mixture was allowed to stand at -35 °C, with occasional stirring, for 15 minutes, and then it was warmed to r.t. and stirred for 6 hours. The solvent was removed under vacuum (to dryness), and the crude reaction product was suspended in Et₂O, collected on a glass frit, and carefully washed with Et₂O. The product was dried under vacuum to give an off-white powder (53.3 mg, 66% yield; 95% purity by NMR).

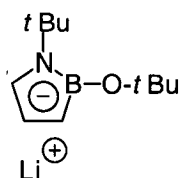
¹H NMR (500 MHz, THF-d₈): δ 5.84 (t, ³J_{HH} = 3.5 Hz, 1H), 5.73 (dd, ³J_{HH} = 5.5 Hz, 3 Hz, 1H), 3.76 (dd, ³J_{HH} = 5.0 Hz, 2.0 Hz, 1H), 3.22 (quintet, ³J_{HH} = 6.5 Hz, 2H), 1.51 (s, 9H), 1.09 (d, ³J_{HH} = 6.5 Hz, 12H). ¹³C NMR (125 MHz, THF-d₈): δ 110.1, 105.9, 85.0 (br), 53.9, 49.1, 33.2, 24.8. ¹¹B NMR (96 MHz, THF-d₈): δ 27.5. FTIR (thin film) 2966, 1615, 1434, 1400, 1363, 1319, 1228, 1156 cm⁻¹.



In a glove box, a vial was charged with a solution of **1** (324 mg, 2.05 mmol) in THF (2.5 mL). This solution was cooled to -35 °C, and then a solution of KO-*t*Bu (220 mg, 1.95 mmol in 7.5 mL of THF) was added dropwise. The reaction mixture was allowed to stand at -35 °C, with occasional stirring, for 90 minutes, and then it was warmed to r.t. and stirred for 4 hours. The reaction mixture was filtered through an acrodisc, the precipitate (KCl) was washed with pentane, and the combined filtrates were

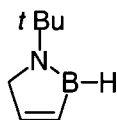
concentrated under vacuum. The remaining KCl was removed through extraction of the residue with pentane. The pentane layers were filtered and then concentrated, providing a pale-yellow oil (339 mg, 89% yield; 95% purity by NMR).

^1H NMR (500 MHz, C_6D_6): δ 6.86 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 6.11 (d, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 3.43 (s, 2H), 1.36 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 149.3, 130.2 (br), 72.8, 52.9, 51.9, 31.4, 30.8. ^{11}B NMR (96 MHz, C_6D_6): δ 30.6. FTIR (thin film) 3053, 2973, 1571, 1447, 1406, 1364, 1309, 1257, 1239, 1196, 1135 cm^{-1} .



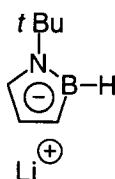
In a glove box, a vial was charged with a solution of **2** (Nu = O-*t*Bu) (88.0 mg, 0.451 mmol) in THF (0.4 mL). This solution was cooled to -35 $^{\circ}\text{C}$, and then a solution of LiTMP (generated from 2,2,6,6-tetramethylpiperidine (261 mg, 1.85 mmol in 1.7 mL of THF) and *n*-BuLi (2.6 M solution in hexane; 690 μL , 1.8 mmol)) was added dropwise. The reaction mixture was allowed to stand at -35 $^{\circ}\text{C}$, with occasional stirring, for 30 minutes, and then it was warmed to r.t. and stirred for 6 hours. The solvent was removed under vacuum (to dryness), and the residue was suspended in pentane/ Et_2O ($\sim 15/1$). The off-white powder was collected on a glass frit, carefully washed with pentane/ Et_2O ($\sim 15/1$), and then dried under vacuum (48 mg, 53% yield; 95% purity by NMR).

^1H NMR (500 MHz, THF-d_8): δ 5.58-5.55 (m, 2H), 3.08 (dd, $^3J_{\text{HH}} = 4.8$ Hz, 2.5 Hz, 1H), 1.38 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, THF-d_8): δ 110.0, 100.7, 71.0, 66.2 (br), 52.7, 32.1, 31.2. ^{11}B NMR (96 MHz, THF-d_8): δ 27.3. FTIR (thin film) 2972, 1602, 1572, 1471, 1398, 1387, 1361, 1237, 1196 cm^{-1} .



In a glove box, a vial was charged with a solution of **1** (514 mg, 3.26 mmol) in Et₂O (13.0 mL). This solution was cooled to -35 °C, and then a solution of LiEt₃BH (1.0 M in THF; 3.3 mL, 3.3 mmol) was added dropwise. The reaction mixture was allowed to stand at -35 °C, with occasional stirring, for 90 minutes, and then it was warmed to r.t. and stirred for 6 hours. The reaction mixture was filtered through an acrodisc, the precipitate (LiCl) was washed with pentane, and the combined filtrates were concentrated to ~10 mL under vacuum. Distillation under reduced pressure (bp = 58-62 °C at 48 mm) afforded the product as a colorless liquid (247 mg, 62% yield; 90% purity by NMR).

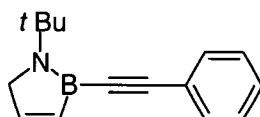
¹H NMR (500 MHz, C₆D₆): δ 6.93 (d, ³J_{HH} = 7.0 Hz, 1H), 6.45 (s, 1H), 5.16 (q, ¹J_{BH} = 129 Hz, 1H), 3.46 (s, 2H), 1.16 (s, 9H). ¹³C NMR (125 MHz, C₆D₆): δ 149.7, 135.2 (br), 56.5, 52.4, 31.7. ¹¹B NMR (160 MHz, C₆D₆): δ 36.4 (d, ¹J_{BH} = 129 Hz). FTIR (thin film) 2973, 2556, 1550, 1434, 1394, 1364, 1340, 1247, 1220, 1146 cm⁻¹.



In a glove box, a vial was charged with a solution of **2** (Nu = H) (176 mg, 1.43 mmol) in Et₂O (1.5 mL). This solution was cooled to -35 °C, and then a solution of LiTMP (generated from 2,2,6,6-tetramethylpiperidine (222 mg, 1.57 mmol in 5.0 mL of Et₂O) and *n*-BuLi (2.6 M solution in hexane; 600 μL, 1.6 mmol)) was added dropwise. The reaction mixture was allowed to stand at -35 °C, with occasional stirring, for 60 minutes, and then it was warmed to r.t. and stirred for 22 hours. Pentane (~1.0 mL) was added, and the reaction product was collected on a glass frit, carefully washed with Et₂O, and dried under vacuum to give a white powder (106 mg, 57% yield; 95% purity

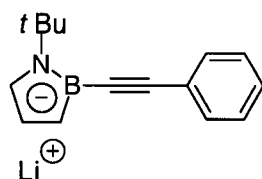
by NMR).

^1H NMR (500 MHz, THF- d_8): δ 6.08 (s, 1H), 5.82 (s, 1H), 4.66-3.63 (broad, 1H), 4.14 (d, $^3J_{\text{HH}} = 2.5$ Hz, 1H), 1.39 (s, 9H). ^{13}C NMR (125 MHz, THF- d_8): δ 112.2, 109.8, 87.0 (br), 52.4, 33.4. ^{11}B NMR (96 MHz, THF- d_8): δ 19.7. FTIR (thin film) 3042, 2975, 2563, 1602, 1462, 1414, 1366, 1284, 1233, 1163 cm^{-1} .



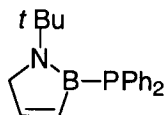
In a glove box, a vial was charged with a solution of **1** (282 mg, 1.79 mmol) in Et₂O (3.0 mL). This solution was cooled to -35 $^{\circ}\text{C}$, and then a solution of lithium phenylacetylide (generated from phenyl acetylene (219 mg, 2.10 mmol in 3.0 mL of THF) and *n*-BuLi (2.6 M solution in hexane; 690 μL , 1.8 mmol)) was added dropwise. The reaction mixture was allowed to stand at -35 $^{\circ}\text{C}$, with occasional stirring, for 3 hours, and then it was warmed to r.t. and stirred for 4 hours. The reaction mixture was filtered through an acrodisc, the precipitate (LiCl) was washed with pentane, and the combined filtrates were concentrated under vacuum. The remaining LiCl was removed through extraction of the residue with pentane. The pentane layers were filtered and then concentrated under vacuum. Repetition of the extraction procedure provided a pale-yellow oil (331 mg, 83% yield; 95% purity by NMR).

^1H NMR (500 MHz, C_6D_6): δ 7.53-7.50 (m, 2H), 6.98-6.95 (m, 3H), 6.82 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 6.54 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 3.51 (t, $^3J_{\text{HH}} = 2.0$ Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 149.0, 136.7 (br), 132.3, 128.9, 128.8, 125.0, 95.2 (br), 78.2, 58.0, 54.0, 31.6. ^{11}B NMR (96 MHz, C_6D_6): δ 31.5. FTIR (thin film) 3032, 2972, 2907, 2177, 1597, 1557, 1490, 1434, 1397, 1337, 1295, 1237, 1126 cm^{-1} . HRMS (EI) calcd for $\text{C}_{15}\text{H}_{18}\text{BN}$ (M^+) 223.1527, found 223.1529.



In a glove box, a vial was charged with a solution of **2** (Nu = CCPh) (172 mg, 0.770 mmol) in Et₂O (1.0 mL). This solution was cooled to –35 °C, and then a solution of LiTMP (generated from 2,2,6,6-tetramethylpiperidine (120 mg, 0.848 mmol in 3.0 mL of Et₂O) and *n*-BuLi (2.6 M solution in hexane; 326 μL, 0.85 mmol)) was added dropwise. The reaction mixture was allowed to stand at –35 °C, with occasional stirring, for 90 minutes, and then it was warmed to r.t. and stirred for 23 hours. The reaction mixture was concentrated to half of its original volume, and then pentane was slowly layered on top of the reaction mixture. The reaction vessel was stored at –35 °C, which resulted in crystallization of a yellow-orange solid, which is the desired compound as an Et₂O solvate (1/2 Et₂O; Mw= 266; 143 mg, 70% yield; 95% purity by NMR).

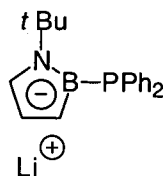
¹H NMR (500 MHz, THF-d₈): δ 7.25 (d, ³J_{HH} = 8.0 Hz, 2H), 7.16 (t, ³J_{HH} = 7.5 Hz, 2H), 7.03 (t, ³J_{HH} = 7.0 Hz, 1H), 6.16 (s, 1H), 5.75 (t, ³J_{HH} = 3.0 Hz, 1H), 4.62 (d, ³J_{HH} = 2.5 Hz, 1H), 3.38 (q, ³J_{HH} = 7.0 Hz, 2H), 1.59 (s, 9H), 1.12 (t, ³J_{HH} = 7.0 Hz, 3H). ¹³C NMR (125 MHz, THF-d₈): δ 130.8, 129.2, 128.7, 125.7, 112.8, 109.9, 105.7 (br), 104.3, 94.6 (br), 66.5, 53.9, 33.3, 15.8. ¹¹B NMR (96 MHz, THF-d₈): δ 17.1. FTIR (thin film) 3053, 2968, 2147, 1595, 1488, 1363, 1335, 1228, 1026, 756, 691 cm⁻¹.



In a glove box, a vial was charged with a solution of **1** (95 mg, 0.60 mmol) in Et₂O (1.0 mL). This solution was cooled to –35 °C, and then a solution of KPh₂ (generated from HPh₂ (107 mg, 0.573 mmol in 0.5 mL of Et₂O) and KH (29 mg, 0.72 mmol in 1.5 mL of THF)) was added dropwise. The reaction mixture was allowed to stand at –35 °C, with occasional stirring, for one hour, and then it was warmed to r.t. and stirred for

5 hours. The reaction mixture was filtered through an acrodisc, the precipitate (KCl) was washed with pentane, and the combined filtrates were concentrated under vacuum. The remaining KCl was removed through extraction of the residue with pentane. The pentane layers were filtered and then concentrated under vacuum, providing a pale-yellow oil (159 mg, 90% yield; 95% purity by NMR).

^1H NMR (500 MHz, C_6D_6): δ 7.58-7.54 (m, 4H), 7.12-7.08 (m, 4H), 7.06-7.03 (m, 2H), 6.70 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 6.11 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H), 3.60-3.59 (m, 2H), 1.25 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 147.6 (d, $J_{\text{PC}} = 4.6$ Hz), 140.2 (d, $J_{\text{PC}} = 10.3$ Hz), 137.4 (br), 135.5 (d, $J_{\text{PC}} = 17.1$ Hz), 129.0 (d, $J_{\text{PC}} = 6.9$ Hz), 127.9, 60.5 (d, $J_{\text{PC}} = 5.1$ Hz), 55.1 (d, $J_{\text{PC}} = 1.8$ Hz), 32.0 (d, $J_{\text{PC}} = 8.0$ Hz). ^{11}B NMR (96 MHz, C_6D_6): δ 43.8. ^{31}P NMR (121 MHz, C_6D_6): δ -53.6. FTIR (thin film) 3051, 2972, 2907, 1583, 1555, 1477, 1432, 1383, 1363, 1333, 1268, 1240, 1094 cm^{-1} . HRMS (EI) calcd for $\text{C}_{19}\text{H}_{23}\text{BNP}$ (M^+) 307.1656, found 307.1670.



In a glove box, a vial was charged with a solution of **2** ($\text{Nu} = \text{PPh}_2$) (38.9 mg, 0.126 mmol) in Et_2O (0.1 mL). This solution was cooled to -35°C , and then a solution of LiTMP (generated from 2,2,6,6-tetramethylpiperidine (25.0 mg, 0.177 mmol in 1.0 mL of Et_2O) and $n\text{-BuLi}$ (2.6 M solution in hexane; 63 μL , 0.17 mmol)) was added dropwise. The reaction mixture was allowed to stand at -35°C , with occasional stirring, for 15 minutes, and then it was warmed to r.t. and stirred for 21 hours. Pentane (~ 0.4 mL) was added, and the reaction product was collected on a glass frit, carefully washed with pentane/ Et_2O (10/1), and dried under vacuum to give a white powder (28.6 mg, 73% yield; 95% purity by NMR).

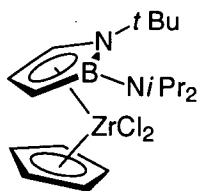
^1H NMR (500 MHz, THF-d_8): δ 7.45-7.42 (m, 4H), 7.07-7.03 (m, 4H), 7.01-6.98 (m, 2H), 6.39 (d, $^3J_{\text{HH}} = 3.0$ Hz, 1H), 5.90 (dd, $^3J_{\text{HH}} = 4.8$ Hz, 2.5 Hz, 1H), 4.31 (dd, $^3J_{\text{HH}} = 4.8$ Hz,

2.5 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, THF- d_8): δ 146.5 (d, $J_{\text{PC}} = 13.6$ Hz), 136.0 (d, $J_{\text{PC}} = 16.6$ Hz), 127.6 (d, $J_{\text{PC}} = 6.3$ Hz), 126.0, 114.4 (d, $J_{\text{PC}} = 5.6$ Hz), 110.9 (d, $J_{\text{PC}} = 4.6$ Hz), 100.1 (br), 54.9 (d, $J_{\text{PC}} = 1.8$ Hz), 33.7 (d, $J_{\text{PC}} = 9.6$ Hz). ^{11}B NMR (96 MHz, THF- d_8): δ 24.5. ^{31}P NMR (121 MHz, THF- d_8): δ -43.9. FTIR (thin film) 3049, 2969, 2903, 1581, 1476, 1431, 1361, 1298, 1235, 1164, 1094, 1025, 832, 740, 697 cm^{-1} .

III. Synthesis of 1,2-Azaborolylylzirconium Complexes (Table 2)

Because the yields that are reported in Table 2 are the average of two runs, the yields that are described below for a specific experiment may differ from the values presented in the table.

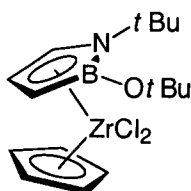
General procedure. In a glove box, a vial was charged with a suspension of ZrCpCl_3 in THF/ Et_2O (1/1). This mixture was cooled to $-35\text{ }^\circ\text{C}$, and then a solution of **3** in THF/ Et_2O (1/1) was added dropwise. The reaction mixture was allowed to stand at $-35\text{ }^\circ\text{C}$, with occasional stirring, for 45 minutes, and then it was warmed to r.t. and stirred for 5 hours. After workup, the product was crystallized from the indicated solvent mixture.



The general procedure was applied using ZrCpCl_3 (21.1 mg, 0.0800 mmol) in THF/ Et_2O (1/1; 0.3 mL) and **3** (Nu = NiPr_2) (18.3 mg, 0.0800 mmol) in THF/ Et_2O (1/1; 0.4 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with Et_2O , and the combined extracts were filtered through an acrodisc and then concentrated. The desired product was crystallized from pentane/ CH_2Cl_2 at $-35\text{ }^\circ\text{C}$ (orange crystals; 24 mg, 67% yield).

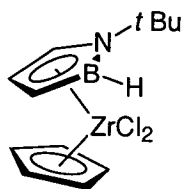
^1H NMR (500 MHz, CD_2Cl_2): δ 6.76 (t, $^3J_{\text{HH}} = 3.0\text{ Hz}$, 1H), 6.36 (s, 5H), 5.76 (dd, $^3J_{\text{HH}} = 5.3\text{ Hz}$, 3.0 Hz , 1H), 4.18 (dd, $^3J_{\text{HH}} = 5.0\text{ Hz}$, 3.0 Hz , 1H), 3.81 (quintet, $^3J_{\text{HH}} = 7.0\text{ Hz}$, 2H), 1.63 (s, 9H), 1.20 (d, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 6H), 1.15 (d, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 123.7, 114.7, 109.6, 84.8 (br), 58.9, 47.5, 32.4, 22.9, 22.7. ^{11}B NMR (160 MHz,

CD₂Cl₂): δ 31.2. FTIR (thin film) 3149, 2967, 2930, 2867, 1476, 1440, 1402, 1378, 1357, 1341, 1201, 1187, 1087, 812, 627 cm⁻¹. HRMS (EI) calcd for C₁₈H₃₁BCl₂N₂Zr (M⁺) 446.0999, found 446.0975.



The general procedure was applied using ZrCpCl₃ (25.7 mg, 0.0980 mmol) in THF/Et₂O (1/1; 0.3 mL) and **3** (Nu = OtBu) (19.7 mg, 0.0980 mmol) in THF/Et₂O (1/1; 0.7 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with Et₂O, and the combined extracts were filtered through an acrodisc and then concentrated. The desired product was crystallized from Et₂O at -35 °C (evaporation) (yellow crystals; 26.5 mg, 64% yield).

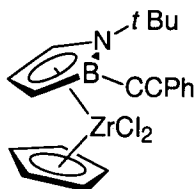
¹H NMR (500 MHz, CD₂Cl₂): δ 6.59 (t, ³J_{HH} = 3.5 Hz, 1H), 6.41 (s, 5H), 6.04 (dd, ³J_{HH} = 5.0 Hz, 3.5 Hz, 1H), 3.91 (dd, ³J_{HH} = 5.3 Hz, 2.5 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). ¹³C NMR (125 MHz, CD₂Cl₂): δ 119.6, 115.3, 112.7, 79.2 (br), 75.0, 59.1, 30.6, 30.0. ¹¹B NMR (160 MHz, CD₂Cl₂): δ 30.6. FTIR (thin film) 3141, 2974, 2931, 1444, 1411, 1394, 1365, 1241, 1192, 1132, 1018, 814, 635 cm⁻¹. HRMS (EI) calcd for C₁₆H₂₆BCl₂NOZr (M⁺) 419.0526, found 419.0520.



The general procedure was applied using ZrCpCl₃ (40.0 mg, 0.151 mmol) in THF/Et₂O (1/1; 0.3 mL) and **3** (Nu = H) (19.5 mg, 0.151 mmol) in THF/Et₂O (1/1; 0.7 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum.

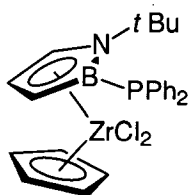
The crude mixture was extracted with Et₂O, and the combined extracts were filtered through an acrodisc and then concentrated. The desired product was crystallized from pentane/Et₂O at -35 °C (pale-yellow crystals; 40.2 mg, 76% yield).

¹H NMR (500 MHz, CD₂Cl₂): δ 7.00 (s, 1H), 6.47 (s, 5H), 6.36 (s, 1H), 5.2-4.2 (broad, 1H), 5.05 (s, 1H), 1.54 (s, 9H). ¹³C NMR (125 MHz, CD₂Cl₂): δ 124.3, 116.2, 115.8, 98.4 (br), 59.4, 31.7. ¹¹B NMR (160 MHz, CD₂Cl₂): δ 29.6 (d, ¹J_{BH} = 129 Hz). FTIR (thin film) 3109, 2973, 2583, 1457, 1370, 1303, 1208, 1172, 1022, 830 cm⁻¹. HRMS (EI) calcd for C₁₂H₁₈BCl₂NZr (M⁺) 346.9951, found 346.9938.



The general procedure was applied using ZrCpCl₃ (39.7 mg, 0.150 mmol) in THF/Et₂O (1/1; 0.5 mL) and **3** (Nu = CCPh) (40.2 mg, 0.150 mmol) in THF/Et₂O (1/1; 1.0 mL). At the conclusion of the reaction, the mixture was filtered through an acrodisc, the precipitate (LiCl) was washed with Et₂O, and the combined filtrates were concentrated under vacuum. The residue was extracted with Et₂O, and the combined extracts were filtered through an acrodisc and concentrated. The desired product was crystallized from pentane/CH₂Cl₂ at -35 °C (pale-yellow crystals; 28 mg, 75% yield).

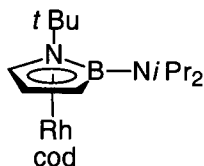
¹H NMR (500 MHz, CD₂Cl₂): δ 7.56-7.54 (m, 2H), 7.38-7.37 (m, 3H), 7.01 (t, ³J_{HH} = 3.0 Hz, 1H), 6.58 (s, 5H), 6.54 (dd, ³J_{HH} = 5.0 Hz, 3.0 Hz, 1H), 4.98 (dd, ³J_{HH} = 4.8 Hz, 2.0 Hz, 1H), 1.67 (s, 9H). ¹³C NMR (125 MHz, CD₂Cl₂): δ 132.0, 129.3, 129.0, 124.0, 122.7, 119.9, 117.3, 109.7, 100.8 (br), 92.0 (br), 60.6, 31.0. ¹¹B NMR (160 MHz, CD₂Cl₂): δ 25.1. FTIR (thin film) 2975, 2183, 1489, 1441, 1353, 1205, 1017, 817, 757 cm⁻¹. HRMS (EI) calcd for C₂₀H₂₂BCl₂NZr (M⁺) 447.0264, found 447.0249.



The general procedure was applied using ZrCpCl_3 (19.2 mg, 0.0730 mmol) in THF/ Et_2O (1/1; 0.3 mL) and **3** (Nu = PPh_2) (22.9 mg, 0.0730 mmol) in THF/ Et_2O (1/1; 0.5 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with CH_2Cl_2 , and the combined extracts were filtered through an acrodisc and then concentrated. The desired product was crystallized from pentane/ CH_2Cl_2 at $-35\text{ }^\circ\text{C}$ (yellow crystals; 27 mg, 69% yield).

^1H NMR (500 MHz, THF-d_8): δ 7.51-7.21 (m, 11H), 6.21 (dd, $^3J_{\text{HH}} = 4.3\text{ Hz}$, 2.5 Hz , 1H), 6.14 (d, $^3J_{\text{HH}} = 1.0\text{ Hz}$, 5H), 5.00 (t, $^3J_{\text{HH}} = 4.0\text{ Hz}$, 1H), 1.59 (s, 9H). ^{13}C NMR (125 MHz, THF-d_8): δ 142.3 (d, $J_{\text{PC}} = 17.1\text{ Hz}$), 139.3 (d, $J_{\text{PC}} = 12.0\text{ Hz}$), 137.7 (d, $J_{\text{PC}} = 17.8\text{ Hz}$), 135.4 (d, $J_{\text{PC}} = 17.8\text{ Hz}$), 133.9 (d, $J_{\text{PC}} = 2.9\text{ Hz}$), 129.2 (d, $J_{\text{PC}} = 6.3\text{ Hz}$), 128.9, 128.4 (d, $J_{\text{PC}} = 6.9\text{ Hz}$), 127.8, 116.7, 110.7 (d, $J_{\text{PC}} = 1.8\text{ Hz}$), 105.7 (br), 62.5 (d, $J_{\text{PC}} = 1.8\text{ Hz}$), 32.3 (d, $J_{\text{PC}} = 8.0\text{ Hz}$). ^{11}B NMR (160 MHz, THF-d_8): δ 37.2. ^{31}P NMR (202 MHz, THF-d_8): δ -57.4. FTIR (thin film) 3108, 2975, 1646, 1583, 1478, 1434, 1401, 1372, 1318, 1204, 1019, 817 cm^{-1} . HRMS (EI) calcd for $\text{C}_{24}\text{H}_{27}\text{BCl}_2\text{NPZr}$ (M^+) 531.0393, found 531.0372.

IV. Synthesis of 1,2-Azaborolyrhodium Complex 4 (eq 1)



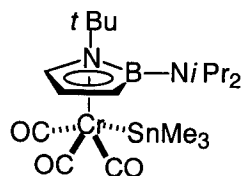
In a glove box, a vial was charged with a solution of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (25.1 mg, 0.0510 mmol) in THF (0.1 mL). This solution was cooled to $-35\text{ }^\circ\text{C}$, and then a solution of **3** ($\text{Nu} = \text{NiPr}_2$) (23.2 mg, 0.102 mmol) in THF (0.5 mL) was added dropwise. The reaction mixture was allowed to stand at $-35\text{ }^\circ\text{C}$, with occasional stirring, for 30 minutes, and then it was warmed to r.t. and stirred for 5 hours. At the conclusion of the reaction, the mixture was concentrated under vacuum. The residue was extracted with pentane, and the combined extracts were filtered through an acrodisc and then concentrated. The product was crystallized from a concentrated pentane solution at $-35\text{ }^\circ\text{C}$ (evaporation) (orange crystals; 29.5 mg, 67% yield).

^1H NMR (500 MHz, C_6D_6): δ 5.43-5.42 (m, 1H), 5.05 (s, 1H), 4.42-4.28 (broad, 2H), 4.28-4.25 (m, 2H), 4.13 (dd, $^3J_{\text{HH}} = 5.3\text{ Hz}$, 2.0 Hz , 1H), 3.54 (quintet, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 2H), 2.30-2.18 (broad, 4H), 2.14-2.00 (broad, 4H), 1.30 (s, 9H), 1.20 (d, $^3J_{\text{HH}} = 2.5\text{ Hz}$, 6H), 1.19 (d, $^3J_{\text{HH}} = 2.5\text{ Hz}$, 6H). ^{13}C NMR (125 MHz, C_6D_6): δ 89.2 (d, $J_{\text{RhC}} = 5.1\text{ Hz}$), 86.6 (d, $J_{\text{RhC}} = 4.6\text{ Hz}$), 77.5 (br), 68.3, 68.2, 54.2, 47.8, 33.5, 33.2, 33.0, 24.9, 23.8. ^{11}B NMR (160 MHz, C_6D_6): δ 21.8. FTIR (thin film) 2966, 2926, 2869, 2823, 1471, 1429, 1360, 1323, 1206, 1185, 1155 cm^{-1} . HRMS (EI) calcd for $\text{C}_{21}\text{H}_{38}\text{BN}_2\text{Rh}$ (M^+) 432.2178, found 432.2166.

V. Synthesis of 1,2-Azaborolychromium Complexes (Table 3)

Because the yields that are reported in Table 3 are the average of two runs, the yields that are described below for a specific experiment may differ from the values presented in the table.

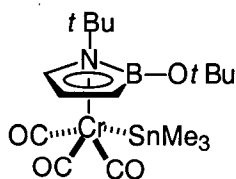
General procedure. In a glove box, a vial was charged with a solution of $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ in THF. This solution was cooled to $-35\text{ }^\circ\text{C}$, and then a solution of **3** in THF was added dropwise. The reaction mixture was allowed to stand at $-35\text{ }^\circ\text{C}$, with occasional stirring, for 40 minutes, and then a solution of Me_3SnCl in THF was added dropwise. The reaction mixture was warmed to r.t. and stirred for 4 hours. After workup, the product was purified by column chromatography (Et_2O as the eluant) or by crystallization.



The general procedure was applied using $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (22.1 mg, 0.0850 mmol) in THF (0.1 mL), **3** (Nu = NiPr_2) (19.5 mg, 0.0850 mmol) in THF (0.4 mL), and Me_3SnCl (17.0 mg, 0.0850 mmol) in THF (0.5 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with pentane, and the combined extracts were filtered through an acrodisc and then concentrated. The desired product was crystallized from a concentrated pentane solution at $-35\text{ }^\circ\text{C}$ (yellow needles; 20.2 mg, 46% yield).

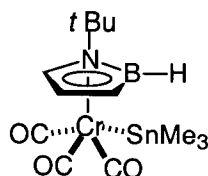
^1H NMR (500 MHz, C_6D_6): δ 5.28 (s, 1H), 4.39 (dd, $^3J_{\text{HH}} = 5.8\text{ Hz}$, 1.0 Hz, 1H), 3.51 (quintet, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 2H), 2.63 (d, $^3J_{\text{HH}} = 4.5\text{ Hz}$, 1H), 1.39 (d, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 6H), 1.06 (d, $^3J_{\text{HH}} = 7.0\text{ Hz}$, 6H), 1.01 (s, 9H), 0.62 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 89.7, 85.7,

66.0 (br), 56.3, 47.5, 31.8, 22.9, 22.3, -3.3. ^{11}B NMR (96 MHz, C_6D_6): δ 21.5. FTIR (thin film) 1958, 1894, 1819 cm^{-1} . HRMS (EI) calcd for $\text{C}_{19}\text{H}_{35}\text{BCrN}_2\text{O}_3\text{Sn}$ (M^+) 522.1162, found 522.1165.



The general procedure was applied using $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (23.3 mg, 0.0900 mmol) in THF (0.1 mL), **3** (Nu = OtBu) (18.1 mg, 0.0900 mmol) in THF (0.3 mL), and Me_3SnCl (17.9 mg, 0.0900 mmol) in THF (0.5 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with pentane, and the combined extracts were filtered through an acrodisc and then concentrated. The crude material was purified by flash chromatography (Et_2O), which furnished the desired product as a yellow solid (23.8 mg, 54% yield).

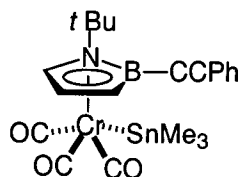
^1H NMR (500 MHz, C_6D_6): δ 5.07 (s, 1H), 4.24 (d, $^3J_{\text{HH}} = 4.5$ Hz, 1H), 2.44 (d, $^3J_{\text{HH}} = 5.0$ Hz, 1H), 1.34 (s, 9H), 1.04 (s, 9H), 0.60 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 88.5, 82.6, 75.0, 61.3 (br), 56.4, 30.5, 29.6, -3.1. ^{11}B NMR (160 MHz, C_6D_6): δ 20.1. FTIR (thin film) 1965, 1900, 1830 cm^{-1} . HRMS (EI) calcd for $\text{C}_{17}\text{H}_{30}\text{BCrNO}_4\text{Sn}$ (M^+) 495.0689, found 495.0668.



The general procedure was applied using $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (33.1 mg, 0.128 mmol) in THF (0.1 mL), **3** (Nu = H) (16.5 mg, 0.128 mmol) in THF (0.4 mL), and Me_3SnCl (25.5 mg, 0.128 mmol) in THF (0.5 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with pentane, and the

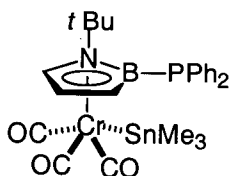
combined extracts were filtered through an acrodisc and then concentrated. The crude material was purified by flash chromatography (Et₂O), which furnished the desired product as a yellow oil that solidified upon standing at -35 °C (49.4 mg, 92% yield).

¹H NMR (500 MHz, C₆D₆): δ 5.29 (s, 1H), 4.00 (d, ³J_{HH} = 4.5 Hz, 1H), 3.8-2.8 (broad, 1H), 3.44 (d, ³J_{HH} = 5.0 Hz, 1H), 0.76 (s, 9H), 0.70 (s, 9H). ¹³C NMR (125 MHz, C₆D₆): δ 90.0, 89.1, 82.8 (br), 56.6, 31.1, -2.0. ¹¹B NMR (96 MHz, C₆D₆): δ 9.5. FTIR (thin film) 1968, 1899, 1868 cm⁻¹. HRMS (EI) calcd for C₁₃H₂₂BCrNO₃Sn (M⁺) 423.0114, found 423.0121.



The general procedure was applied using Cr(CO)₃(CH₃CN)₃ (17.8 mg, 0.0680 mmol) in THF (0.1 mL), **3** (Nu = CCPh) (18.3 mg, 0.0680 mmol) in THF (0.2 mL), and Me₃SnCl (13.7 mg, 0.0680 mmol) in THF (0.3 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with pentane, and the combined extracts were filtered through an acrodisc and then concentrated. The crude material was purified by flash chromatography (Et₂O), which furnished the desired product as a yellow solid (32 mg, 90% yield).

¹H NMR (500 MHz, C₆D₆): δ 7.55-7.53 (m, 2H), 6.99-6.97 (m, 3H), 5.22 (s, 1H), 4.01 (d, ³J_{HH} = 4.5 Hz, 1H), 3.52 (d, ³J_{HH} = 3.5 Hz, 1H), 1.16 (s, 9H), 0.72 (s, 9H). ¹³C NMR (125 MHz, C₆D₆): δ 132.1, 129.12, 129.05, 124.4, 109.6, 90.7 (br), 88.5, 88.0, 81.2 (br), 58.6, 31.0, -2.3. ¹¹B NMR (96 MHz, C₆D₆): δ 9.5. FTIR (thin film) 1965, 1894, 1871 cm⁻¹.



The general procedure was applied using $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ (16.5 mg, 0.0640 mmol) in THF (0.1 mL), **3** (Nu = PPh_2) (20.0 mg, 0.0640 mmol) in THF (0.3 mL), and Me_3SnCl (12.7 mg, 0.0640 mmol) in THF (0.3 mL). At the conclusion of the reaction, the mixture was concentrated under vacuum. The crude mixture was extracted with pentane/ Et_2O mixture (~6/1), and the combined extracts were filtered through an acrodisc and then concentrated. The desired product was crystallized from pentane/ CH_2Cl_2 at $-35\text{ }^\circ\text{C}$ (yellow solid; 25.5 mg, 66% yield; 95% purity; slowly decomposes in solution).

^1H NMR (500 MHz, C_6D_6): δ 7.90 (t, $^3J_{\text{HH}} = 7.5\text{ Hz}$, 2H), 7.75 (t, $^3J_{\text{HH}} = 6.5\text{ Hz}$, 2H), 7.21-7.03 (m, 6H), 5.37 (s, 1H), 4.34 (d, $^3J_{\text{HH}} = 5.3\text{ Hz}$, 1H), 3.07 (d, $^3J_{\text{HH}} = 4.5\text{ Hz}$, 1H), 0.96 (s, 9H), 0.48 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6): δ 140.1 (d, $J_{\text{PC}} = 13.1\text{ Hz}$), 138.0 (d, $J_{\text{PC}} = 9.8\text{ Hz}$), 137.8 (d, $J_{\text{PC}} = 18.3\text{ Hz}$), 134.1 (d, $J_{\text{PC}} = 18.4\text{ Hz}$), 129.13 (d, $J_{\text{PC}} = 6.9\text{ Hz}$), 129.12, 128.9 (d, $J_{\text{PC}} = 6.9\text{ Hz}$), 128.0, 92.9 (d, $J_{\text{PC}} = 2.3\text{ Hz}$), 91.0, 84.2 (br), 60.0 (d, $J_{\text{PC}} = 1.6\text{ Hz}$), 31.6 (d, $J_{\text{PC}} = 8.0\text{ Hz}$), -2.9. ^{11}B NMR (160 MHz, C_6D_6): δ 18.9. ^{31}P NMR (202 MHz, C_6D_6): δ -61.6. FTIR (thin film) 1966, 1905, 1865 cm^{-1} . HRMS (EI) calcd for $\text{C}_{25}\text{H}_{31}\text{BCrNO}_3\text{PSn}$ (M^+) 607.0556, found 607.0547.

VI. X-ray Crystal Structure of 1,2-Azaborolyrhodium Complex 4 (Figure 1)

An orange solution of **4** in pentane was prepared. Crystals suitable for X-ray structural analysis were obtained by evaporation from pentane at $-35\text{ }^{\circ}\text{C}$. A clear, pale-orange block of dimensions $0.27 \times 0.2 \times 0.12\text{ mm}^3$ was mounted under STP and transferred to a Bruker AXS/CCD three-circle diffractometer (χ fixed at 54.78°) equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20\sigma(I)$ from 45×10 -s frames of 0.30° ω scan data with monochromated Mo K_{α} radiation ($\lambda = 0.71073\text{ \AA}$). The cell thus determined was monoclinic.

A hemisphere of data was then collected using ω scans of 0.30° and 10-s frames. The raw data frames were integrated using the Bruker program SAINT+ for NT version 6.01. Actual integration was performed with constant spot sizes of 1.6° in the detector plane and 0.6° in ω . The data that were collected (8215 total reflections, 3026 unique, $R_{\text{int}} = 0.0190$) had the following Miller index ranges: -11 to 10 in h , -14 to 9 in k , and -13 to 17 in l . The data were corrected for Lorentz and polarization effects. SADABS absorption correction was applied with $\mu = 0.81\text{ mm}^{-1}$.

All aspects of the solution and refinement were handled by SHELXTL NT version 5.10. The structure was solved by direct methods in the monoclinic space group $P2(1)/c$, $a = 10.4114(6)\text{ \AA}$; $b = 13.3264(8)\text{ \AA}$; $c = 15.7688(9)\text{ \AA}$; $\alpha = 90^{\circ}$; $\beta = 105.8360(10)^{\circ}$; $\gamma = 90^{\circ}$, and refined using standard difference Fourier techniques. Final, full-matrix least-squares refinement (3026 data for 234 parameters) on F^2 yielded residual of R_1 and wR_2^2 of 0.0203 and 0.0495 for data $I > 2\sigma(I)$, and 0.0235 and 0.0507, respectively, for all

$$\begin{aligned} (2) \quad R_1 &= \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \\ wR_2 &= [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2} \\ w &= 1 / [\sigma^2(F_o)^2 + (0.0237 * P)^2 + 1.4596 * P] \end{aligned}$$

data. During the final refinement, all non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically on a riding model. No secondary extinction coefficient was used in the refinement. Residual electron density amounted to a maximum of 0.226 e/Å³ and a minimum of -0.187 e/Å³.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-178106. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Tables 1-6 provide the full crystallographic data for the X-ray structure.

$$\text{where } P = [\text{Max}(F_o^2, 0) + 2 * F_c^2]/3$$

Table 1. Crystal data and structure refinement for complex 4.

Identification code	1196syls	
Empirical formula	C ₂₁ H ₃₈ B N ₂ Rh	
Formula weight	432.25	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.4114(6) Å	$\alpha = 90^\circ$.
	b = 13.3264(8) Å	$\beta = 105.8360(10)^\circ$.
	c = 15.7688(9) Å	$\gamma = 90^\circ$.
Volume	2104.8(2) Å ³	
Z	4	
Density (calculated)	1.364 Mg/m ³	
Absorption coefficient	0.817 mm ⁻¹	
F(000)	912	
Crystal size	0.27 x 0.20 x 0.12 mm ³	
Theta range for data collection	2.54 to 23.29°	
Index ranges	-11 ≤ h ≤ 10, -14 ≤ k ≤ 9, -13 ≤ l ≤ 17	
Reflections collected	8215	
Independent reflections	3026 [R(int) = 0.0190]	
Completeness to theta = 23.29°	99.6 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3026 / 0 / 234	
Goodness-of-fit on F ²	1.028	
Final R indices [I > 2σ(I)]	R1 = 0.0203, wR2 = 0.0495	
R indices (all data)	R1 = 0.0235, wR2 = 0.0507	
Extinction coefficient	0.0000(2)	
Largest diff. peak and hole	0.226 and -0.187 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1196sylS. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Rh(1)	8595(1)	6225(1)	2269(1)	24(1)
N(1)	7013(2)	5770(1)	899(1)	23(1)
N(2)	6012(2)	7638(1)	641(1)	26(1)
B(1)	6454(2)	6746(2)	1135(2)	23(1)
C(3)	6398(2)	6544(2)	2085(2)	28(1)
C(4)	6677(2)	5527(2)	2285(2)	30(1)
C(5)	7182(2)	5110(2)	1628(1)	27(1)
C(6)	7400(2)	5416(2)	98(2)	27(1)
C(7)	6165(2)	5422(2)	-699(2)	35(1)
C(8)	8556(2)	6056(2)	-31(2)	33(1)
C(9)	7903(3)	4333(2)	204(2)	39(1)
C(10)	6167(2)	7906(2)	-232(2)	31(1)
C(11)	7105(3)	8793(2)	-201(2)	47(1)
C(12)	4820(2)	8076(2)	-912(2)	42(1)
C(13)	5352(2)	8444(2)	1020(2)	32(1)
C(14)	4039(2)	8104(2)	1182(2)	43(1)
C(15)	6281(3)	8963(2)	1825(2)	42(1)
C(16)	9700(2)	7574(2)	2322(2)	36(1)
C(17)	9489(2)	7401(2)	3147(2)	34(1)
C(18)	10574(3)	7033(2)	3938(2)	43(1)
C(19)	10592(3)	5898(2)	4022(2)	45(1)
C(20)	10094(2)	5364(2)	3148(2)	37(1)
C(21)	10513(2)	5575(2)	2395(2)	36(1)
C(22)	11580(2)	6348(2)	2376(2)	44(1)
C(23)	11002(3)	7386(2)	2098(2)	48(1)

Table 3. Bond lengths [Å] and angles [°] for 1196sylS.

Rh(1)-C(20)	2.120(2)
Rh(1)-C(16)	2.124(2)
Rh(1)-C(17)	2.131(2)
Rh(1)-C(21)	2.135(2)
Rh(1)-C(5)	2.141(2)
Rh(1)-C(4)	2.209(2)
Rh(1)-C(3)	2.266(2)
Rh(1)-N(1)	2.4084(17)
Rh(1)-B(1)	2.544(2)
N(1)-C(5)	1.419(3)
N(1)-C(6)	1.504(3)
N(1)-B(1)	1.513(3)
N(2)-B(1)	1.427(3)
N(2)-C(10)	1.473(3)
N(2)-C(13)	1.486(3)
B(1)-C(3)	1.538(3)
C(3)-C(4)	1.403(3)
C(4)-C(5)	1.400(3)
C(6)-C(9)	1.530(3)
C(6)-C(7)	1.533(3)
C(6)-C(8)	1.533(3)
C(10)-C(11)	1.525(3)
C(10)-C(12)	1.532(3)
C(13)-C(14)	1.527(3)
C(13)-C(15)	1.534(3)
C(16)-C(17)	1.397(4)
C(16)-C(23)	1.512(4)
C(17)-C(18)	1.518(3)
C(18)-C(19)	1.518(4)
C(19)-C(20)	1.511(4)
C(20)-C(21)	1.401(4)
C(21)-C(22)	1.522(4)
C(22)-C(23)	1.524(4)

C(20)-Rh(1)-C(16)	97.92(10)
C(20)-Rh(1)-C(17)	81.93(9)
C(16)-Rh(1)-C(17)	38.33(10)
C(20)-Rh(1)-C(21)	38.46(10)
C(16)-Rh(1)-C(21)	81.76(10)
C(17)-Rh(1)-C(21)	90.37(9)
C(20)-Rh(1)-C(5)	102.83(9)
C(16)-Rh(1)-C(5)	154.33(9)
C(17)-Rh(1)-C(5)	160.02(9)
C(21)-Rh(1)-C(5)	105.50(9)
C(20)-Rh(1)-C(4)	105.74(9)
C(16)-Rh(1)-C(4)	146.86(9)
C(17)-Rh(1)-C(4)	122.52(9)
C(21)-Rh(1)-C(4)	130.82(10)
C(5)-Rh(1)-C(4)	37.51(9)
C(20)-Rh(1)-C(3)	136.25(9)
C(16)-Rh(1)-C(3)	111.31(9)
C(17)-Rh(1)-C(3)	101.04(9)
C(21)-Rh(1)-C(3)	166.81(9)
C(5)-Rh(1)-C(3)	61.98(9)
C(4)-Rh(1)-C(3)	36.51(9)
C(20)-Rh(1)-N(1)	130.70(8)
C(16)-Rh(1)-N(1)	118.60(8)
C(17)-Rh(1)-N(1)	146.96(8)
C(21)-Rh(1)-N(1)	112.02(8)
C(5)-Rh(1)-N(1)	35.75(7)
C(4)-Rh(1)-N(1)	60.39(7)
C(3)-Rh(1)-N(1)	60.87(7)
C(20)-Rh(1)-B(1)	162.77(9)
C(16)-Rh(1)-B(1)	99.08(9)
C(17)-Rh(1)-B(1)	113.51(9)
C(21)-Rh(1)-B(1)	142.57(9)
C(5)-Rh(1)-B(1)	60.03(8)
C(4)-Rh(1)-B(1)	60.12(8)
C(3)-Rh(1)-B(1)	36.73(8)
N(1)-Rh(1)-B(1)	35.43(7)

C(5)-N(1)-C(6)	118.88(18)
C(5)-N(1)-B(1)	107.77(17)
C(6)-N(1)-B(1)	133.34(18)
C(5)-N(1)-Rh(1)	61.78(11)
C(6)-N(1)-Rh(1)	123.93(13)
B(1)-N(1)-Rh(1)	77.18(11)
B(1)-N(2)-C(10)	127.67(18)
B(1)-N(2)-C(13)	119.91(18)
C(10)-N(2)-C(13)	112.38(18)
N(2)-B(1)-N(1)	132.1(2)
N(2)-B(1)-C(3)	125.8(2)
N(1)-B(1)-C(3)	102.01(19)
N(2)-B(1)-Rh(1)	134.57(16)
N(1)-B(1)-Rh(1)	67.39(11)
C(3)-B(1)-Rh(1)	61.78(12)
C(4)-C(3)-B(1)	109.2(2)
C(4)-C(3)-Rh(1)	69.53(13)
B(1)-C(3)-Rh(1)	81.48(13)
C(5)-C(4)-C(3)	108.3(2)
C(5)-C(4)-Rh(1)	68.58(12)
C(3)-C(4)-Rh(1)	73.96(13)
C(4)-C(5)-N(1)	111.4(2)
C(4)-C(5)-Rh(1)	73.91(13)
N(1)-C(5)-Rh(1)	82.47(12)
N(1)-C(6)-C(9)	111.49(19)
N(1)-C(6)-C(7)	109.24(17)
C(9)-C(6)-C(7)	106.3(2)
N(1)-C(6)-C(8)	109.66(18)
C(9)-C(6)-C(8)	106.37(19)
C(7)-C(6)-C(8)	113.76(19)
N(2)-C(10)-C(11)	113.0(2)
N(2)-C(10)-C(12)	112.13(19)
C(11)-C(10)-C(12)	111.4(2)
N(2)-C(13)-C(14)	112.7(2)
N(2)-C(13)-C(15)	113.72(19)
C(14)-C(13)-C(15)	112.7(2)

C(17)-C(16)-C(23)	124.7(2)
C(17)-C(16)-Rh(1)	71.09(14)
C(23)-C(16)-Rh(1)	111.16(17)
C(16)-C(17)-C(18)	123.2(2)
C(16)-C(17)-Rh(1)	70.58(13)
C(18)-C(17)-Rh(1)	113.00(16)
C(17)-C(18)-C(19)	112.6(2)
C(20)-C(19)-C(18)	113.3(2)
C(21)-C(20)-C(19)	124.8(2)
C(21)-C(20)-Rh(1)	71.38(14)
C(19)-C(20)-Rh(1)	110.54(16)
C(20)-C(21)-C(22)	123.4(2)
C(20)-C(21)-Rh(1)	70.17(13)
C(22)-C(21)-Rh(1)	113.15(17)
C(21)-C(22)-C(23)	112.8(2)
C(16)-C(23)-C(22)	113.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1196sylS. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	23(1)	22(1)	25(1)	-1(1)	1(1)	0(1)
N(1)	21(1)	24(1)	22(1)	-1(1)	4(1)	-2(1)
N(2)	26(1)	28(1)	23(1)	-1(1)	7(1)	3(1)
B(1)	16(1)	28(1)	26(1)	-4(1)	5(1)	-2(1)
C(3)	23(1)	35(1)	28(1)	-1(1)	8(1)	0(1)
C(4)	28(1)	37(1)	26(1)	5(1)	7(1)	-9(1)
C(5)	26(1)	23(1)	28(1)	3(1)	1(1)	-5(1)
C(6)	25(1)	30(1)	26(1)	-5(1)	9(1)	0(1)
C(7)	32(1)	45(2)	26(1)	-8(1)	6(1)	-6(1)
C(8)	25(1)	37(1)	39(1)	0(1)	13(1)	0(1)
C(9)	44(2)	33(1)	43(2)	-8(1)	16(1)	1(1)
C(10)	31(1)	32(1)	29(1)	6(1)	7(1)	5(1)
C(11)	42(2)	45(2)	55(2)	15(1)	15(1)	-1(1)
C(12)	36(1)	57(2)	30(1)	6(1)	6(1)	11(1)
C(13)	32(1)	29(1)	32(1)	-3(1)	3(1)	7(1)
C(14)	32(1)	49(2)	49(2)	-10(1)	12(1)	10(1)
C(15)	47(2)	35(2)	41(2)	-10(1)	4(1)	6(1)
C(16)	32(1)	23(1)	47(2)	0(1)	0(1)	-5(1)
C(17)	33(1)	23(1)	39(2)	-10(1)	-3(1)	0(1)
C(18)	42(2)	40(2)	37(2)	-12(1)	-7(1)	5(1)
C(19)	46(2)	44(2)	34(2)	2(1)	-9(1)	8(1)
C(20)	34(1)	25(1)	42(2)	2(1)	-5(1)	7(1)
C(21)	25(1)	35(1)	42(2)	-10(1)	-2(1)	8(1)
C(22)	27(1)	53(2)	48(2)	-12(1)	5(1)	0(1)
C(23)	35(2)	49(2)	58(2)	-3(1)	10(1)	-14(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 1196sylS.

	x	y	z	U(eq)
H(3)	6036	7021	2452	34
H(4)	6496	5156	2792	36
H(5)	7408	4383	1605	33
H(7A)	5702	6066	-726	52
H(7B)	5562	4878	-638	52
H(7C)	6440	5325	-1240	52
H(8A)	9360	5924	451	49
H(8B)	8321	6768	-30	49
H(8C)	8726	5885	-595	49
H(9A)	7192	3891	283	59
H(9B)	8678	4284	721	59
H(9C)	8163	4129	-323	59
H(10)	6588	7315	-440	37
H(11A)	7959	8660	235	70
H(11B)	6704	9401	-34	70
H(11C)	7255	8887	-783	70
H(12A)	4394	8677	-753	62
H(12B)	4243	7493	-920	62
H(12C)	4961	8166	-1496	62
H(13)	5104	8973	554	39
H(14A)	4215	7571	1627	64
H(14B)	3443	7850	631	64
H(14C)	3615	8674	1392	64
H(15A)	7086	9197	1677	63
H(15B)	6531	8487	2316	63
H(15C)	5819	9537	1996	63
H(16)	9169	8145	1990	43
H(17)	8834	7871	3298	41
H(18A)	10433	7332	4480	52
H(18B)	11452	7263	3884	52

H(19A)	11517	5677	4308	54
H(19B)	10031	5700	4410	54
H(20)	9844	4647	3200	44
H(21)	10501	4982	2004	43
H(22A)	12083	6121	1961	53
H(22B)	12216	6393	2969	53
H(23A)	11660	7900	2392	57
H(23B)	10855	7461	1453	57

Table 6. Torsion angles [°] for 1196sylS.

C(20)-Rh(1)-N(1)-C(5)	46.11(17)
C(16)-Rh(1)-N(1)-C(5)	178.63(14)
C(17)-Rh(1)-N(1)-C(5)	-144.54(17)
C(21)-Rh(1)-N(1)-C(5)	86.09(14)
C(4)-Rh(1)-N(1)-C(5)	-39.45(14)
C(3)-Rh(1)-N(1)-C(5)	-81.58(14)
B(1)-Rh(1)-N(1)-C(5)	-118.52(17)
C(20)-Rh(1)-N(1)-C(6)	-61.32(19)
C(16)-Rh(1)-N(1)-C(6)	71.19(18)
C(17)-Rh(1)-N(1)-C(6)	108.0(2)
C(21)-Rh(1)-N(1)-C(6)	-21.35(18)
C(5)-Rh(1)-N(1)-C(6)	-107.4(2)
C(4)-Rh(1)-N(1)-C(6)	-146.89(18)
C(3)-Rh(1)-N(1)-C(6)	170.98(18)
B(1)-Rh(1)-N(1)-C(6)	134.0(2)
C(20)-Rh(1)-N(1)-B(1)	164.63(14)
C(16)-Rh(1)-N(1)-B(1)	-62.85(14)
C(17)-Rh(1)-N(1)-B(1)	-26.0(2)
C(21)-Rh(1)-N(1)-B(1)	-155.40(13)
C(5)-Rh(1)-N(1)-B(1)	118.52(17)
C(4)-Rh(1)-N(1)-B(1)	79.06(13)
C(3)-Rh(1)-N(1)-B(1)	36.93(12)
C(10)-N(2)-B(1)-N(1)	-9.8(4)
C(13)-N(2)-B(1)-N(1)	172.7(2)
C(10)-N(2)-B(1)-C(3)	173.4(2)
C(13)-N(2)-B(1)-C(3)	-4.1(3)
C(10)-N(2)-B(1)-Rh(1)	89.5(3)
C(13)-N(2)-B(1)-Rh(1)	-87.9(3)
C(5)-N(1)-B(1)-N(2)	-175.2(2)
C(6)-N(1)-B(1)-N(2)	5.5(4)
Rh(1)-N(1)-B(1)-N(2)	130.4(2)
C(5)-N(1)-B(1)-C(3)	2.1(2)
C(6)-N(1)-B(1)-C(3)	-177.2(2)
Rh(1)-N(1)-B(1)-C(3)	-52.25(13)

C(5)-N(1)-B(1)-Rh(1)	54.39(13)
C(6)-N(1)-B(1)-Rh(1)	-124.9(2)
C(20)-Rh(1)-B(1)-N(2)	-170.3(3)
C(16)-Rh(1)-B(1)-N(2)	0.2(2)
C(17)-Rh(1)-B(1)-N(2)	37.3(2)
C(21)-Rh(1)-B(1)-N(2)	-88.1(3)
C(5)-Rh(1)-B(1)-N(2)	-163.9(3)
C(4)-Rh(1)-B(1)-N(2)	152.6(3)
C(3)-Rh(1)-B(1)-N(2)	113.8(3)
N(1)-Rh(1)-B(1)-N(2)	-127.5(3)
C(20)-Rh(1)-B(1)-N(1)	-42.7(4)
C(16)-Rh(1)-B(1)-N(1)	127.70(13)
C(17)-Rh(1)-B(1)-N(1)	164.88(12)
C(21)-Rh(1)-B(1)-N(1)	39.4(2)
C(5)-Rh(1)-B(1)-N(1)	-36.34(12)
C(4)-Rh(1)-B(1)-N(1)	-79.90(13)
C(3)-Rh(1)-B(1)-N(1)	-118.64(18)
C(20)-Rh(1)-B(1)-C(3)	75.9(3)
C(16)-Rh(1)-B(1)-C(3)	-113.65(14)
C(17)-Rh(1)-B(1)-C(3)	-76.48(15)
C(21)-Rh(1)-B(1)-C(3)	158.07(15)
C(5)-Rh(1)-B(1)-C(3)	82.30(15)
C(4)-Rh(1)-B(1)-C(3)	38.74(14)
N(1)-Rh(1)-B(1)-C(3)	118.64(18)
N(2)-B(1)-C(3)-C(4)	168.7(2)
N(1)-B(1)-C(3)-C(4)	-8.8(2)
Rh(1)-B(1)-C(3)-C(4)	-64.76(15)
N(2)-B(1)-C(3)-Rh(1)	-126.5(2)
N(1)-B(1)-C(3)-Rh(1)	55.93(14)
C(20)-Rh(1)-C(3)-C(4)	-41.24(19)
C(16)-Rh(1)-C(3)-C(4)	-169.65(14)
C(17)-Rh(1)-C(3)-C(4)	-131.07(14)
C(21)-Rh(1)-C(3)-C(4)	18.4(5)
C(5)-Rh(1)-C(3)-C(4)	37.69(13)
N(1)-Rh(1)-C(3)-C(4)	78.59(14)
B(1)-Rh(1)-C(3)-C(4)	114.21(19)

C(20)-Rh(1)-C(3)-B(1)	-155.45(14)
C(16)-Rh(1)-C(3)-B(1)	76.14(15)
C(17)-Rh(1)-C(3)-B(1)	114.72(14)
C(21)-Rh(1)-C(3)-B(1)	-95.8(4)
C(5)-Rh(1)-C(3)-B(1)	-76.52(14)
C(4)-Rh(1)-C(3)-B(1)	-114.21(19)
N(1)-Rh(1)-C(3)-B(1)	-35.63(12)
B(1)-C(3)-C(4)-C(5)	12.4(3)
Rh(1)-C(3)-C(4)-C(5)	-60.32(15)
B(1)-C(3)-C(4)-Rh(1)	72.72(15)
C(20)-Rh(1)-C(4)-C(5)	-90.68(15)
C(16)-Rh(1)-C(4)-C(5)	135.42(18)
C(17)-Rh(1)-C(4)-C(5)	178.93(13)
C(21)-Rh(1)-C(4)-C(5)	-56.95(17)
C(3)-Rh(1)-C(4)-C(5)	117.59(19)
N(1)-Rh(1)-C(4)-C(5)	37.57(12)
B(1)-Rh(1)-C(4)-C(5)	78.60(14)
C(20)-Rh(1)-C(4)-C(3)	151.73(14)
C(16)-Rh(1)-C(4)-C(3)	17.8(2)
C(17)-Rh(1)-C(4)-C(3)	61.35(16)
C(21)-Rh(1)-C(4)-C(3)	-174.54(14)
C(5)-Rh(1)-C(4)-C(3)	-117.59(19)
N(1)-Rh(1)-C(4)-C(3)	-80.02(14)
B(1)-Rh(1)-C(4)-C(3)	-38.98(13)
C(3)-C(4)-C(5)-N(1)	-11.2(3)
Rh(1)-C(4)-C(5)-N(1)	-74.97(15)
C(3)-C(4)-C(5)-Rh(1)	63.76(16)
C(6)-N(1)-C(5)-C(4)	-175.30(18)
B(1)-N(1)-C(5)-C(4)	5.3(2)
Rh(1)-N(1)-C(5)-C(4)	69.40(16)
C(6)-N(1)-C(5)-Rh(1)	115.31(16)
B(1)-N(1)-C(5)-Rh(1)	-64.12(14)
C(20)-Rh(1)-C(5)-C(4)	99.21(15)
C(16)-Rh(1)-C(5)-C(4)	-117.7(2)
C(17)-Rh(1)-C(5)-C(4)	-2.6(3)
C(21)-Rh(1)-C(5)-C(4)	138.83(14)

C(3)-Rh(1)-C(5)-C(4)	-36.68(13)
N(1)-Rh(1)-C(5)-C(4)	-114.87(19)
B(1)-Rh(1)-C(5)-C(4)	-78.85(14)
C(20)-Rh(1)-C(5)-N(1)	-145.92(13)
C(16)-Rh(1)-C(5)-N(1)	-2.8(3)
C(17)-Rh(1)-C(5)-N(1)	112.2(3)
C(21)-Rh(1)-C(5)-N(1)	-106.30(13)
C(4)-Rh(1)-C(5)-N(1)	114.87(19)
C(3)-Rh(1)-C(5)-N(1)	78.19(13)
B(1)-Rh(1)-C(5)-N(1)	36.02(11)
C(5)-N(1)-C(6)-C(9)	1.6(3)
B(1)-N(1)-C(6)-C(9)	-179.2(2)
Rh(1)-N(1)-C(6)-C(9)	75.3(2)
C(5)-N(1)-C(6)-C(7)	118.7(2)
B(1)-N(1)-C(6)-C(7)	-62.0(3)
Rh(1)-N(1)-C(6)-C(7)	-167.51(15)
C(5)-N(1)-C(6)-C(8)	-116.0(2)
B(1)-N(1)-C(6)-C(8)	63.3(3)
Rh(1)-N(1)-C(6)-C(8)	-42.2(2)
B(1)-N(2)-C(10)-C(11)	-112.6(3)
C(13)-N(2)-C(10)-C(11)	65.0(2)
B(1)-N(2)-C(10)-C(12)	120.5(2)
C(13)-N(2)-C(10)-C(12)	-61.9(3)
B(1)-N(2)-C(13)-C(14)	-63.2(3)
C(10)-N(2)-C(13)-C(14)	119.0(2)
B(1)-N(2)-C(13)-C(15)	66.7(3)
C(10)-N(2)-C(13)-C(15)	-111.1(2)
C(20)-Rh(1)-C(16)-C(17)	-66.15(16)
C(21)-Rh(1)-C(16)-C(17)	-101.16(15)
C(5)-Rh(1)-C(16)-C(17)	150.0(2)
C(4)-Rh(1)-C(16)-C(17)	69.4(2)
C(3)-Rh(1)-C(16)-C(17)	80.68(15)
N(1)-Rh(1)-C(16)-C(17)	148.20(13)
B(1)-Rh(1)-C(16)-C(17)	116.70(14)
C(20)-Rh(1)-C(16)-C(23)	54.7(2)
C(17)-Rh(1)-C(16)-C(23)	120.9(3)

C(21)-Rh(1)-C(16)-C(23)	19.71(19)
C(5)-Rh(1)-C(16)-C(23)	-89.1(3)
C(4)-Rh(1)-C(16)-C(23)	-169.72(17)
C(3)-Rh(1)-C(16)-C(23)	-158.44(17)
N(1)-Rh(1)-C(16)-C(23)	-90.93(19)
B(1)-Rh(1)-C(16)-C(23)	-122.42(19)
C(23)-C(16)-C(17)-C(18)	2.2(4)
Rh(1)-C(16)-C(17)-C(18)	105.3(2)
C(23)-C(16)-C(17)-Rh(1)	-103.1(2)
C(20)-Rh(1)-C(17)-C(16)	113.80(16)
C(21)-Rh(1)-C(17)-C(16)	76.16(15)
C(5)-Rh(1)-C(17)-C(16)	-140.7(2)
C(4)-Rh(1)-C(17)-C(16)	-142.64(14)
C(3)-Rh(1)-C(17)-C(16)	-110.50(15)
N(1)-Rh(1)-C(17)-C(16)	-58.1(2)
B(1)-Rh(1)-C(17)-C(16)	-74.16(16)
C(20)-Rh(1)-C(17)-C(18)	-4.94(19)
C(16)-Rh(1)-C(17)-C(18)	-118.7(3)
C(21)-Rh(1)-C(17)-C(18)	-42.6(2)
C(5)-Rh(1)-C(17)-C(18)	100.5(3)
C(4)-Rh(1)-C(17)-C(18)	98.6(2)
C(3)-Rh(1)-C(17)-C(18)	130.76(19)
N(1)-Rh(1)-C(17)-C(18)	-176.80(15)
B(1)-Rh(1)-C(17)-C(18)	167.09(17)
C(16)-C(17)-C(18)-C(19)	-92.5(3)
Rh(1)-C(17)-C(18)-C(19)	-11.4(3)
C(17)-C(18)-C(19)-C(20)	29.0(3)
C(18)-C(19)-C(20)-C(21)	48.5(4)
C(18)-C(19)-C(20)-Rh(1)	-32.6(3)
C(16)-Rh(1)-C(20)-C(21)	-65.94(16)
C(17)-Rh(1)-C(20)-C(21)	-100.89(16)
C(5)-Rh(1)-C(20)-C(21)	98.85(15)
C(4)-Rh(1)-C(20)-C(21)	137.50(15)
C(3)-Rh(1)-C(20)-C(21)	161.55(14)
N(1)-Rh(1)-C(20)-C(21)	73.27(17)
B(1)-Rh(1)-C(20)-C(21)	104.5(3)

C(16)-Rh(1)-C(20)-C(19)	55.2(2)
C(17)-Rh(1)-C(20)-C(19)	20.2(2)
C(21)-Rh(1)-C(20)-C(19)	121.1(3)
C(5)-Rh(1)-C(20)-C(19)	-140.06(19)
C(4)-Rh(1)-C(20)-C(19)	-101.4(2)
C(3)-Rh(1)-C(20)-C(19)	-77.4(2)
N(1)-Rh(1)-C(20)-C(19)	-165.64(16)
B(1)-Rh(1)-C(20)-C(19)	-134.4(3)
C(19)-C(20)-C(21)-C(22)	2.7(4)
Rh(1)-C(20)-C(21)-C(22)	105.2(2)
C(19)-C(20)-C(21)-Rh(1)	-102.5(2)
C(16)-Rh(1)-C(21)-C(20)	113.96(16)
C(17)-Rh(1)-C(21)-C(20)	76.48(15)
C(5)-Rh(1)-C(21)-C(20)	-91.23(15)
C(4)-Rh(1)-C(21)-C(20)	-59.24(18)
C(3)-Rh(1)-C(21)-C(20)	-73.6(4)
N(1)-Rh(1)-C(21)-C(20)	-128.45(14)
B(1)-Rh(1)-C(21)-C(20)	-151.85(15)
C(20)-Rh(1)-C(21)-C(22)	-118.8(2)
C(16)-Rh(1)-C(21)-C(22)	-4.86(19)
C(17)-Rh(1)-C(21)-C(22)	-42.34(19)
C(5)-Rh(1)-C(21)-C(22)	149.95(18)
C(4)-Rh(1)-C(21)-C(22)	-178.06(16)
C(3)-Rh(1)-C(21)-C(22)	167.6(3)
N(1)-Rh(1)-C(21)-C(22)	112.73(18)
B(1)-Rh(1)-C(21)-C(22)	89.3(2)
C(20)-C(21)-C(22)-C(23)	-91.7(3)
Rh(1)-C(21)-C(22)-C(23)	-10.9(3)
C(17)-C(16)-C(23)-C(22)	49.6(3)
Rh(1)-C(16)-C(23)-C(22)	-31.5(3)
C(21)-C(22)-C(23)-C(16)	27.8(3)

Symmetry transformations used to generate equivalent atoms: