1,2-Thiaborolide: A New Heteroaromatic π-Ligand Containing Boron and Sulfur

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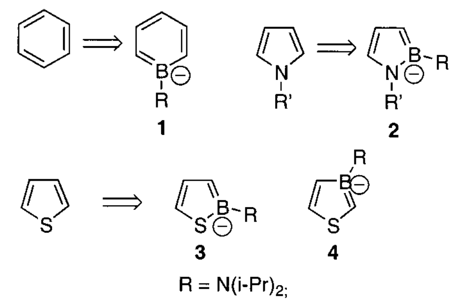
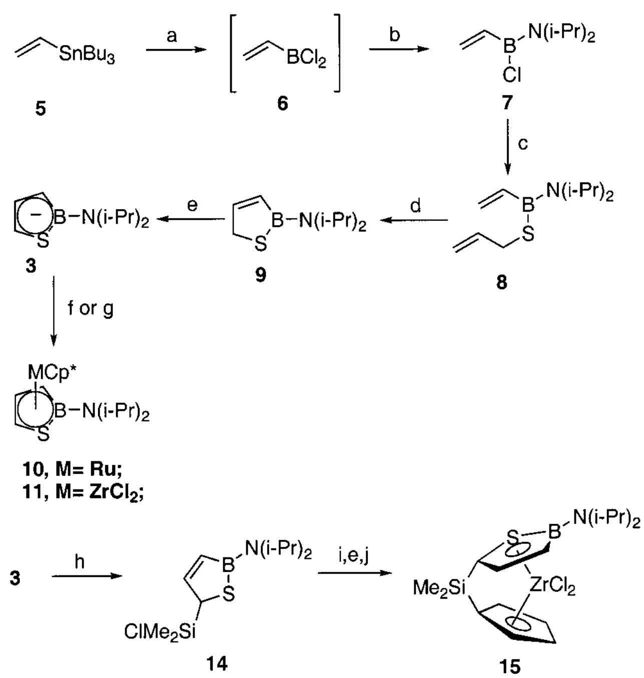
*Summary: The heteroaromatic anion lithium 2-(diisopropylamino)-1,2-thiaborolide (**3**) has been prepared by a synthesis using the Grubbs ring-closing metathesis. **3** has been converted to the Cp*Ru complex **10**, the Cp*$ZrCl_2$ complex **11**, and the Me_2Si-bridged Cp$ZrCl_2$ complex **15**.*

Cyclopentadienyl derivatives of the group 4 metals are important homogeneous catalysts for the polymerization of olefins[1,2] and for organic synthesis.[3,4] The substitution of anionic 6-π-electron heterocyclic ligands for cyclopentadienyl in these complexes has led to a new generation of catalysts.[5−8] For example, certain boratabenzene (**1**)[5] and 1,2-azaborolide (**2**)[6] complexes of zirconium have high activity for the polymerization of olefins. Ligands **1**[9,10] and **2**[11,12] are derived from benzene and pyrrole, respectively, by the replacement of CH by the isoelectronic BH^- group. Thiaborolides **3** and **4** are similarly derived from thiophene. It was recently reported that 1,3-thiaborolides[8,13] and 1,2-benzothiaborolide[14] could be used to prepare Cp-like transition-metal complexes. We now wish to report the first synthesis of the parent 1,2-thiaborolide ring system and on its conversion to transition-metal π-complexes.



Our synthesis of **3** involves an extension of the ring-closing metathesis (RCM)[15,16] route recently used to prepare **2**.[17] The appropriate (allylthio)vinylborane (**8**) needed for RCM was prepared in three steps for tributylvinyltin (**5**), as illustrated in Scheme 1.[18a] The reac-

Scheme 1. Synthesis[a]



[a] Key: (a) BCl_3; (b) 2HN(i-Pr)$_2$; (c) C_3H_5SH, then NEt_3; (d) $(Cy_3P)_2(PhCH)RuCl_2$; (e) LDA; (f) [Cp*RuCl]$_4$; (g) Cp*$ZrCl_3$; (h) Me_2SiCl_2; (i) CpLi; (j) $ZrCl_4$.

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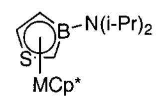
tion of **5** with BCl_3 at −78 °C afforded vinylboron dichloride[19] (**6**), which was not isolated. In situ addition of 2 equiv of $HN(^iPr)_2$ gave adduct **7**, which was isolated by distillation in 83% yield. Sequential treatment of **7** with allyl mercaptan followed by triethylamine gave **8** as a colorless liquid in 74% yield. Upon treatment of **8** with 1 mol % Grubbs catalyst ($(Cy_3P)_2(PhCH)RuCl_2$) in CH_2Cl_2 at 25 °C for 10 h, cyclization occurred smoothly to afford **9** in 95% yield.[18b]

Deprotonation of **9** with LDA in ether at −78 °C followed by warming and removal of the solvent gave the thiaborolide as a white solid in 82% yield.[18c] The ^1H, ^{11}B, and ^{13}C NMR spectra of **3** in THF-d_8 show that the 1,2-thiaborolide has a highly delocalized structure. The ^{13}C NMR signals for C(3) and C(5) at δ 80.6 and 84.0, respectively, are consistent with the carbanionic character of these atoms, while the signal for C(4) at δ 136.8 suggests little excess π-electron density at this position.[20] The ^{11}B NMR shift of **3** (δ 39.5) shows an upfield shift relative to **9** (δ 43.6) consistent with an increase in the electron density at boron upon deprotonation.[21] Apparently the negative charge in the π system is distributed largely to B(2), C(3), and C(5) as is expected from consideration of the classical resonance structure of **3**.

Like its 1,3 isomer,[8] 1,2-thiaborolide readily forms transition-metal complexes. The reaction of **3** with $[Cp^*RuCl]_4$ gave amber crystals of **10** in 49% yield,[18d] while a similar reaction with Cp^*ZrCl_3 afforded yellow crystals of **11** in 36% yield.[18e] The crystal structure of **10**,[22] illustrated in Figure 1, shows that it is a diheteroruthenocene in which the thiaborolide ring is η^5-bound to Ru in the same manner as in the corresponding 1,3-thiaborolide complex **12**. Although a partial disorder



12, M= Ru;
13, M= $ZrCl_2$;

between S(1) and C(1) limits the accuracy of the bond distances, the structural data show that the 1,2-thiaborolide ring of **10** is a π-coordinated aromatic ring.

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(18) Experimental procedures and characterization of new compounds are as follows. (a) *[(Diisopropylamino)vinylboryl]allyl sulfide (**8**).* Tributylvinyltin (56.0 g, 176 mmol) in 50 mL of pentane was added dropwise to a solution of BCl_3 (18.8 g, 160 mmol) in 160 mL of pentane at −78 °C. The mixture was stirred at −78 °C until it solidified and was then warmed to 25 °C for 30 min. After this mixture was cooled to −15 °C, diisopropylamine (35.5 g, 352 mmol) was added via a syringe. After it was stirred at 25 °C for 4 h, the mixture was filtered and the volatiles were removed under vacuum. Distillation gave 23.0 g (83%) of **7** (bp 34 °C at 0.005 Torr), which was dissolved in 120 mL of CH_2Cl_2. Allyl mercaptan (9.84 g, 133 mmol) was added to this solution of **7**, which had been cooled to −78 °C. The mixture was shaken until almost all the solid dissolved. The temperature was raised to 25 °C for 10 min with stirring and recooled to −78 °C. NEt_3 (13.4 g, 133 mmol) was added, and the mixture was warmed with stirring to 25 °C for 10 h. After filtration and removal of the solvent, the product was obtained by vacuum distillation as a clear colorless liquid (20.8 g, 74%), bp = 58−60 °C at 0.05 Torr. ^1H NMR (C_6D_6, 400 MHz): δ 6.18 (dd, 1H, J = 20.0, 14.8 Hz, vinyl), 5.87 (m, 1H, vinyl), 5.57 (dd(br), 1H, J = 6.3, 3.3 Hz, vinyl), 5.33 (dd, 1H, J = 20.0, 3.9 Hz, vinyl), 5.12 (dm, 1H, J = 16.8 Hz, vinyl), 4.93 (dm, 1H, J = 8.5 Hz, vinyl), 3.66 (br, 1H, NCH), 3.65 (br, 1H, NCH), 3.27 (d, 2H, J = 6.6 Hz, SCH_2), 1.20 (d, 3H, J = 5.5 Hz, CH_3), 1.01 (d, 3H, J = 6.3 Hz, CH_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 138.2 (br, BC), 137.6, 125.2, 115.3 (vinyl), 49.1 (br, NC), 48.1 (br, NC), 33.0 (SC), 23.2 (br, CH_3), 22.3 (br, CH_3). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 40.8. HRMS (EI, m/z): calcd for $C_{11}H_{22}{}^{11}BNS$ (M^+), 211.1566; found, 211.1563. Anal. Calcd for $C_{11}H_{22}BNS$: C, 62.57; H, 10.50; N, 6.63. Found: C, 62.31; H, 10.26; N, 6.57. (b) *2,5-Dihydro-2-(diisopropylamino)-1,2-thiaborole (**9**).* A solution of **8** (27.5 g, 130 mmol) in 200 mL of CH_2Cl_2 was added to a solution of bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (1.07 g, 1.0 mol %) in 20 mL of CH_2Cl_2 at 25 °C. Bubbles formed immediately. The mixture was stirred at 25 °C for 10 h to make sure the reaction was complete. The solvent was removed under reduced pressure, and the product was obtained by vacuum distillation as a clear colorless liquid (22.5 g, 95%), bp 52−53 °C at 0.05 Torr. ^1H NMR (C_6D_6, 400 MHz): δ 6.83 (d(br), 1H, J = 7.7 Hz, vinyl), 6.35 (d, 1H, J = 7.7 Hz, BCH=), 3.62 (septet, 1H, J = 6.6 Hz, NCH), 3.38 (m, 2H, SCH_2), 3.37 (septet, 1H, J = 6.6 Hz, NCH), 1.10 (t, 6H, J = 6.6 Hz, CH_3). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 154.0 (vinyl), 132.7 (br, BC), 52.1 (br, NC), 47.3 (br, NC), 39.2 (SCH_2), 24.1 (br, CH_3), 21.9 (br, CH_3). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 43.6. HRMS (EI, m/z): calcd for $C_9H_{18}{}^{11}BNS$ (M^+), 183.1253; found, 183.1252. Anal. Calcd for $C_9H_{18}BNS$: C, 59.03; H, 9.91; N, 7.65. Found: C, 59.31; H, 9.83; N, 7.60. (c) *Lithium 2-(Diisopropylamino)-1,2-thiaborolide (**3**).* A solution of **9** (3.50 g, 19.1 mmol) in 15 mL of ether was added to a solution of LDA (2.04 g, 19.1 mmol) in 10 mL of ether at −78 °C. A white solid formed immediately. The mixture was stirred at −78 °C for 2 h and at 25 °C for 3 h. After removal of the volatiles and washing with 3 × 30 mL of pentane, the residue was dried under vacuum and the product was isolated as a white solid (2.96 g, 82%). ^1H NMR (THF-d_8, 400 MHz): δ 6.78 (t, 1H, J = 5.1 Hz, H_4), 4.69 (dd, 1H, J = 4.4, 1.8 Hz, H_3), 3.93 (dd, 1H, J = 5.5, 1.5 Hz, H_5), 3.45 (septet, 2H, J = 6.6 Hz, NCH), 1.16 (d, 6H, J = 6.6 Hz, CH_3). ^{13}C NMR (THF-d_8, 100.6 MHz): δ 136.8 (C_4), 84.0 (C_3), 80.6 (br, C_5), 49.1 (NC), 22.9 (CH_3). ^{11}B NMR (THF-d_8, 115.5 MHz): δ 39.5. (d) *[2-(Diisopropylamino)-1,2-thiaborolyl][pentamethylcyclopentadienyl]ruthenium(II) (**10**).* A solution of **3** (0.42 g, 2.22 mmol) in 10 mL of THF was added dropwise to a suspension of $[Cp^*RuCl]_4$ (603 mg, 2.22 mmol) in 10 mL of THF at −78 °C. The mixture was stirred at −78 °C for 1 h and at 25 °C for 4 h. The solvent was removed under reduced pressure, and the residue was extracted with 3 × 30 mL of pentane. After filtration, the solution was concentrated and the crystallization was performed at −30 °C. The product was obtained as amber crystals (0.45 g, 49%), mp 84 °C. ^1H NMR (C_6D_6, 400 MHz): δ 4.83 (dd, 1H, J = 4.8, 2.6 Hz, H_4), 4.08 (dd, 1H, J = 2.6, 1.1 Hz, H_5), 3.30 (d, 1H, J = 4.8 Hz, H_3), 3.18 (sept, 2H, J = 6.6 Hz, NCH), 1.87 (s, 15H, Cp*Me), 1.18 (d, 6H, J = 6.6 Hz, Me), 1.17 (d, 6H, J = 6.6 Hz, Me). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 87.2, 85.6 (Cp*C), 60.7, 48.7 (NCH), 22.8, 22.2 (Me), 12.0 (Cp*Me). BCH was not observed. ^{11}B NMR (C_6D_6, 115.5 MHz): δ 21.3. HRMS (EI, m/z): calcd for $C_{19}H_{32}{}^{11}BNRuS$ (M^+), 419.1392; found, 419.1405. Anal. Calcd for $C_{19}H_{32}BNRuS$: C, 54.54; H, 7.71; N, 3.35. Found: C, 54.23; H, 7.91; N, 3.31. (e) *[2-(Diisopropylamino)-1,2-thiaborolyl][pentamethylcyclopentadienyl]zirconium(IV) dichloride (**11**).* A solution of **3** (0.50 g, 2.64 mmol) in 10 mL of THF was added dropwise to a suspension of Cp^*ZrCl_3 (0.88 g, 2.64 mmol) in 10 mL of ether at −78 °C. The mixture was stirred at −78 °C for 2 h and at 25 °C for 3 h. The volatiles were removed under reduced pressure. The residue was extracted with 3 × 30 mL of pentane. After filtration the solution was concentrated and stored at −30 °C. The product was obtained as yellow crystals (0.45 g, 36%), mp 182 °C dec. ^1H NMR (C_6D_6, 360 MHz): δ 7.05 (dd, 1H, J = 7.0, 3.8 Hz, H_4), 5.13 (dd, 1H, J = 7.0, 1.4 Hz, H_3), 4.48 (dd, 1H, J = 3.8, 1.4 Hz, H_5), 3.63 (septet, 1H, J = 6.8 Hz, NCH), 3.22 (septet, 1H, J = 6.8 Hz, NCH), 1.85 (s, 15H, Cp*Me), 1.25 (d, 3H, J = 6.8 Hz, Me), 1.17 (d, 3H, J = 6.8 Hz, Me), 1.14 (d, 3H, J = 6.8 Hz, Me), 1.06 (d, 3H, J = 6.8 Hz, Me). ^{13}C NMR (C_6D_6, 100.6 MHz): δ 152.5 (C_4), 123.4 (Cp*), 104.5 (br, C_3), 84.9 (C_5), 49.6 (NCH_2), 48.7 (NCH_2), 23.4 (Me), 23.2 (Me), 22.9 (Me), 22.2 (Me), 12.3 (Cp*Me). ^{11}B NMR (C_6D_6, 115.5 MHz): δ 37.9. HRMS (EI, m/z): calcd for $C_{19}H_{32}{}^{11}B^{35}Cl_2NS^{90}Zr$ (M^+), 477.0773; found, 477.0781. (f, g) Experimental procedures for **14** and **15** are given in the Supporting Information.

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(22) Crystal data for **10**: $C_{19}H_{32}BNRuS$, orthorhombic, *Pbca*, a = 11.906(3) Å, b = 14.607(3) Å, c = 22.907(5) Å, v = 3983.5(15) Å^3, Z = 8, D_c = 1.395 g cm^{-3}, T = 158(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD. Final R indices ($I > 2\sigma(I)$): R1 = 0.0348, wR2 = 0.1040. R indices (all data): R1 = 0.0409, wR2 = 0.1080.

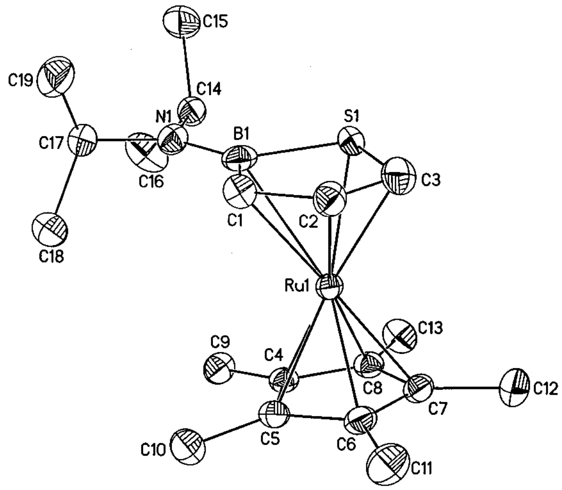
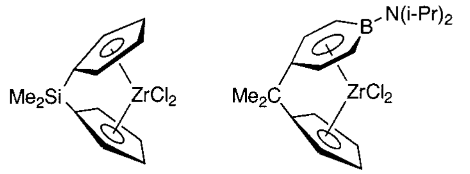


Figure 1. Solid-state structure of **10** (ORTEP). Selected bond distances (Å): Ru−B, 2.463(4); Ru−S, 2.43(2); Ru−C(1), 2.29(1); Ru−C(2), 2.14(3); Ru−C(3), 2.141(4); Ru−C(Cp*), 2.175(4); N−B, 1.416(4); B−C(1), 1.53(2); B−S, 1.83(2); C(1)−C(2), 1.43(1); C(2)−C(3), 1.40(1).

It was of major interest to examine polymerization activities of catalysts derived from zirconium thiaborolide complexes. On activation by excess methylaluminoxane, complex **11** was active toward the polymerization of ethylene. Under identical conditions the relative activities of **11** and **13** were found to be 6.0 × 10^4 and 7.5 × 10^4 (mol of polymer)/((mol of Zr) atm), respectively.[23] Clearly thiaborolides can serve as replacement ligands for Cp in metallocene-based polymerization catalysts. However, the bulky pentamethylcyclopentadienyl ligands of **11** and **13** are likely to limit access of olefin to the Zr atoms and hence limit the activity of the catalysts. Further work has been directed toward the preparation of more open thiaborolide complexes.

Silylation of **3** with dichlorodimethylsilane afforded **14** in 93% yield.[18f] Sequential reaction of **14** with CpLi followed by LDA and $ZrCl_4$ gave red crystals of **15** in 23% yield.[18g] Although the catalytic activity of **15** has not been evaluated yet, the X-ray structure,[24] illustrated in Figure 2, shows the expected dimethylsilyl-bridged structure, which resembles that of the corresponding bis-Cp complex $[Me_2Si(C_5H_4)_2]ZrCl_2$ (**16**).[25] In **16** the



16 **17**

angle between the Cp planes is 57°, while the corresponding angles between the ring planes of **15** is 63°. While **15** and **16** have similar pseudotetrahedral ligand

(23) For conditions of polymerization see ref 5d.

(24) Crystal data for **15**: $C_{16}H_{26}BCl_2NSSiZr$, monoclinic, $P2_1/n$, $a = 12.421(3)$ Å, $b = 11.317(3)$ Å, $c = 15.408(4)$ Å, $\beta = 107.082(4)°$, $V = 2070.2(8)$ Å^3, $Z = 4$, $D_c = 1.493$ g cm^{-3}, $T = 158(2)$ K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD. Final R indices ($I > 2\sigma(I)$): R1 = 0.0195, wR2 = 0.0470. R indices (all data): R1 = 0.0227, wR2 = 0.0482.

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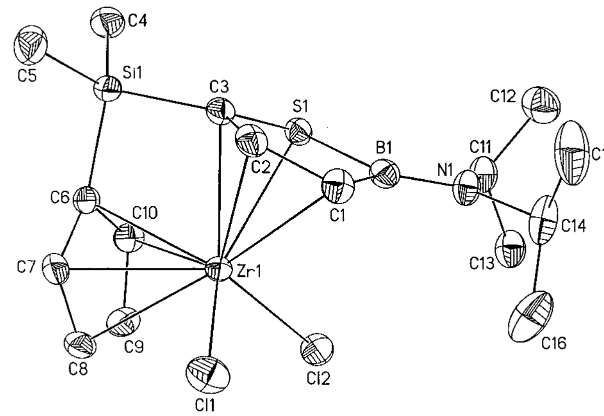

Figure 2. Solid-state structure of **15** (ORTEP). Selected distances (Å): B(1)−N(1), 1.395(2); B(1)−C(1), 1.523(2); B(1)−S(1), 1.8897(19); S(1)−C(3), 1.7843(16); C(1)−C(2), 1.404(2); C(2)−C(3), 1.402(2); C−C(Cp), 1.39−1.42; Zr(1)−C(3), 2.4471(15); Zr(1)−C(2), 2.5018(16); Zr(1)−C(1), 2.6359(16); Zr(1)−S(1), 2.7032; Zr(1)−B(1), 2.952(2).

arrangements about Zr, the major difference is in the unsymmetrical bonding of Zr to the thiaborolide ring of **16**. The Zr atom is slip-distorted away from B so that the B−Zr distance (2.952(2) Å) is too long for effective bonding, which leaves it η^4-coordinated to the C_3S unit. These structural features are strongly reminiscent of those of the Zr complexes of aminoboratabenzenes, which show a similar slippage to η^5-coordination.[5a,d] In both cases the slippage away from boron is probably due to the high electron demand of Zr(IV), which prefers coordination to the more electron rich ring atoms.

The intra-ring C−C bonds (1.40 Å) and C−B bond (1.52 Å) of the thiaborolide ring of **15** are typical of those found for transition-metal complexes of boratabenzenes, e.g. **17**. On the other hand, the B−S bond (1.89 Å) is about 0.02−0.06 Å longer than the corresponding bonds found in **10** and other complexes of B−S heterocycles.[26] Apparently the preferential coordination of Zr(IV) to carbon and sulfur leaves the boron electronically isolated from the adjacent atoms. Compensating for this deficiency, the boron atom is strongly π-bonded to the sp^2-hybridized nitrogen, as is shown by the short B−N distance (1.395 (21) Å).

In summary, the 1,2-thiaborolide ring system is easily prepared by an RCM procedure. 1,2-Thiaborolides can serve as replacement ligands for cyclopentadienyl in complexes of early and late transition metals.

Acknowledgment. This work was supported by the National Science Foundation. We are grateful to the Dow Chemical Co. for running the polymerization experiment.

Supporting Information Available: Tables of crystallographic data for **10** and **15**, ^{1}H NMR spectra of **11**, **14**, and **15**, and text giving experimental procedures for the preparation and characterization of **14** and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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