1,2-Benzothiaborolide: A New Heteroaromatic Analogue of Indenyl

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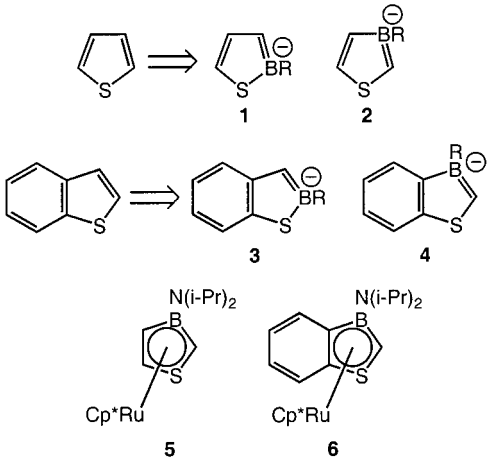
Received July 28, 2000

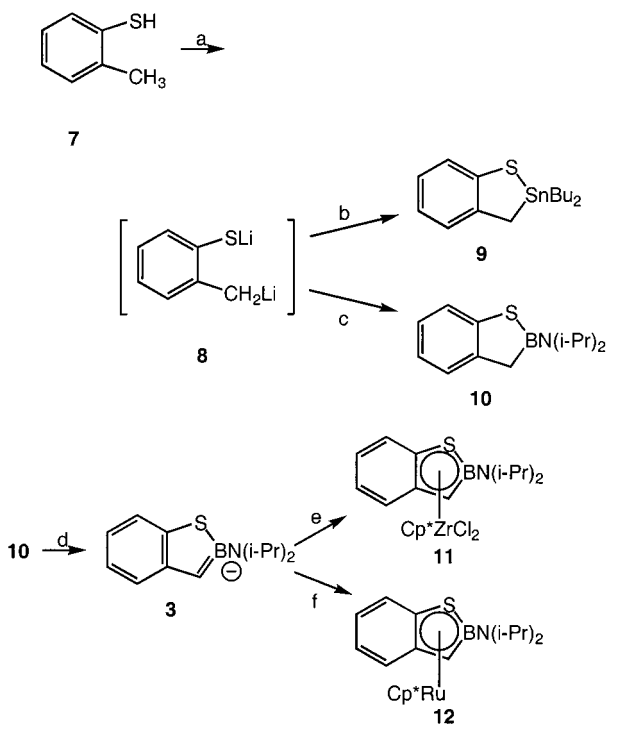
*Summary: The reaction of 2-methylbenzenethiol with 2 equiv of BuLi followed by (i-Pr)$_2$NBCl$_2$ affords 2,3-dihydro-2-(diisopropylamino)-1,2-benzothiaborole (**10**), which can be deprotonated by t-BuLi to form lithium 2-(diisopropylamino)-1,2-benzothiaborolide (**3**). The benzothiaborolide was converted to the Cp*ZrCl$_2$ complex **11** and the Cp*Ru complex **12**, in which the thiaborolide ring is η^5-coordinated to Ru.*

The replacement of CH by the isoelectronic BH$^-$ group converts a neutral aromatic species to an anion. In this manner thiophene is converted to 1,2-thiaborolide (**1**) or 1,3-thiaborolide (**2**), which are heterocyclic Cp derivatives. Similarly, benzothiophene becomes 1,2-benzothiaborolide (**3**) or 1,3-benzothiaborolide (**4**), which are heterocyclic analogues of indenyl. We recently reported on the syntheses of **2**[1] and **4**[2] and showed that their 1,3-thiaborolide rings could serve as η^5 ligands toward Ru in complexes **5** and **6**. We now wish to report on the first synthesis of 1,2-benzothiaborolide **3** and on its conversion to Zr(IV) and Ru(II) complexes **11** and **12**, respectively.



The key step in the synthesis of **3** involves the double deprotonation of 2-methylbenzenethiol (**7**) by BuLi to form **8** (Scheme 1). A variety of analogous 1,4-dilithio compounds have been prepared by dilithiation,[3−7] but to the best of our knowledge this reaction has never been reported for **7**. **8** is a useful precursor for five-membered-ring sulfur heterocycles. Reaction of **8** with Bu_2SnCl_2 gives 2,2-dibutyl-2,3-dihydro-1,2-benzothiastannole (**9**) in 63% yield.[8b] Since similar organotin compounds undergo facile exchange reactions with main-group-element halides,[9−11] **9** may be useful for the syntheses of other sulfur heterocycles.

Scheme 1[a]



[a] Legend: (a) BuLi; (b) Bu_2SnCl_2; (c) $Cl_2BN(i\text{-}Pr)_2$; (d) t-BuLi; (e) Cp*$ZrCl_3$; (f) $[Cp^*RuCl]_4$.

Quenching **8** with (i-Pr)$_2$NBCl$_2$ [12] affords **10** in 79% yield.[8a] The substantial π-bond character of the exocyclic B−N bond of **10** makes rotation about this bond slow on the NMR time scale.[13] At 25 °C ^{1}H and ^{13}C NMR spectra show that the isopropyl CH groups are nonequivalent. The reaction of **10** with t-BuLi in ether gives a bright yellow solution of **3**, which could be isolated as a pale yellow solid.[8c] In contrast to **10** the ^{1}H and ^{13}C NMR spectra of **3** in THF-d_8 at 25 °C show that the two

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10.1021/om000650b CCC: $19.00
Publication on Web 10/12/2000

isopropyl groups are identical, due to rapid rotation about the B−N bond. As has previously been demonstrated for lithium 1-aminoboratabenzenes[14] and 3-amino-1,3-thiaborolides **2**[1] and **4**,[2] the incorporation of boron into a carbanionic aromatic ring greatly diminishes its ability to form an external π-bond to nitrogen. The chemical shift values of the BCH group in the ^{1}H, ^{11}B, and ^{13}C NMR spectra of **3** are consistent with strong stabilization of the carbanion by π-bonding to boron. The BCH group shows a ^{1}H NMR signal (δ 3.86) and a ^{13}C NMR signal (δ 72) which are far downfield from those expected for sp^3-hybridized organolithium compounds and indicate sp^2 hybridization at this carbon.[15] Similarly, the ^{11}B NMR shift of **3** at δ 41 is shifted upfield from that of **10** (δ 45.6), due to the transfer of electron density to boron in the aromatic anion.[16]

The reaction of **3** with Cp*$ZrCl_3$ gives complex **11** as a bright yellow solid in 49% yield.[8d] Analogous treatment of **3** with $[Cp^*RuCl]_4$ affords red crystals of **12** in 48% yield.[8e] The X-ray structure of **12**, illustrated in Figure 1, shows that the compound has the expected diheteroruthenocene structure.[17] In this respect it closely resembles the structure of the isomeric complex **6**. Relative to the 1,2-thiaborolide ring of **12** the Ru atom is slip-distorted away from B toward C(1) and C(6). Similar slip distortions away from boron are common

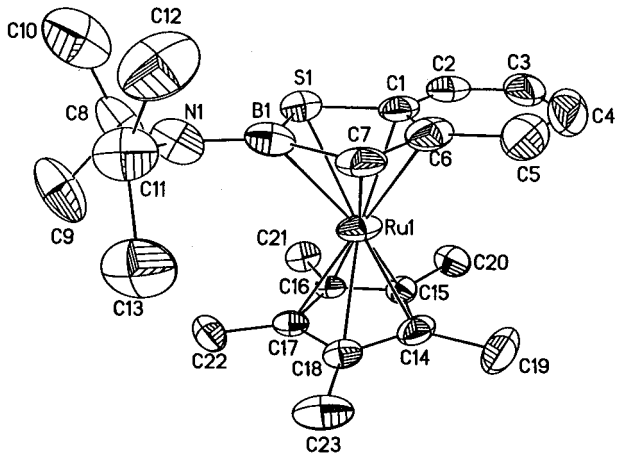

Figure 1. Solid-state structure of **12**. Selected distances (Å): Ru−S = 2.4395(12); Ru−B = 2.445(5); Ru−C(7) = 2.311(4); Ru−C(6) = 2.217(4); Ru−C(1) = 2.213(4); S−B = 1.894(5); B−C(7) = 1.604(7); C(7)−C(6) = 1.467(7); C(6)−C(1) = 1.436(7); C(1)−S = 1.744(5); B−N = 1.423(7).

(8) Experimental procedures and characterization of new compounds are as follows. (a) 2-(Diisopropylamino)-2,3-dihydro-1,2-benzothiaborole (**10**): a solution of BuLi in hexane (41.0 mL, 102.5 mmol) was added dropwise to a solution of **7** (6.22 g, 50.1 mmol) in 175 mL of ether at 0 °C, affording a yellow solution which was stirred for 15 min at 0 °C followed by 24 h at 25 °C. This mixture was added dropwise via a cannula to a solution of $(i\text{-Pr})_2NBCl_2$ (9.61 g, 52.8 mmol) in 250 mL of ether at −78 °C. After the addition was complete, the mixture was warmed to 25 °C and stirred for 15 h. Volatiles were removed in vacuo, and the residue was extracted twice with pentane. The combined extracts were filtered and distilled, yielding 9.26 g (79%) of product (bp 85−90 °C/0.03 Torr), which formed a waxy solid on cooling. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.32 (d, J = 7.6 Hz, 1H, Ar H), 7.21 (d, J = 7.2 Hz, 1H, Ar H); 7.07 (t, J = 7.5 Hz, 1H, Ar H); 7.00 (t, J = 7.4 Hz, 1H, Ar H); 3.63 (m, 1H, CHN); 3.50 (m, 1H, CHN′); 2.75 (s, 2H, CH_2B); 1.27 (d, J = 6.8 Hz, 6H, Me); 1.22 (d, J = 6.8 Hz, 6H, Me′). ^{13}C NMR (90.5 MHz, $CDCl_3$): δ 127.1, 126.5, 125.0, 124.1 (Ar); 47.7 (CHN); 47.4 (CHN′), 29.0 (br, CH_2B); 22.5 (Me). ^{11}B NMR (115.5 MHz, C_6D_6): δ 45.6. HRMS(EI): calcd for $C_{13}H_{20}{}^{11}BNS$, 233.1409; found, 233.1412. A satisfactory combustion analysis was not obtained. However, the ^{1}H NMR spectrum indicates good purity. (b) 2,2-Dibutyl-2,3-dihydro-1,2-benzothiastannole (**9**): a suspension of **8** in 25 mL of ether, which had been prepared from **7** (0.7 g, 5.60 mmol) and BuLi (11.75 mmol), was added dropwise to a solution of Bu_2SnCl_2 (1.70 g, 5.60 mmol) in 25 mL of ether at −78 °C. The reaction mixture was slowly warmed with stirring to 25 °C for 15 h. Volatiles were removed in vacuo, and the residue was extracted with pentane. The extracts were filtered, the solvent was removed in vacuo, and 1.25 g (63%) of product was isolated by distillation (bp 120 °C/0.03 Torr) as a colorless oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.40 (dd, J = 7.7, 1.1 Hz, 1H, Ar H); 7.25 (m, 1H, Ar H); 6.95 (tt, J = 7.7, 0.8 Hz, 1H, Ar H); 6.90 (dt, J = 7.3, 1.4 Hz, 1H, Ar H); 2.71 (s, 2H, CH_2Sn); 1.65 (m, 4H, Bu); 1.30 (m, 8H, Bu), 0.9 (t, J = 7.3 Hz, 6H, Bu). ^{13}C NMR (90.5 MHz, $CDCl_3$): δ 141.8, 139.8, 130.9, 130.1, 126.0, 123.3 (Ar); 28.5 (CH_2Sn); 26.9, 22.1, 15.8, 13.6 (Bu). HRMS (EI): calcd for $C_{15}H_{24}S^{120}Sn$, 356.0621; found, 356.0620. Anal. Calcd for $C_{15}H_{24}SSn$: C, 50.73; H, 6.81. Found: C, 51.36; H, 7.18. (c) Lithium 2-(diisopropylamino)-1,2-benzothiaborolide (**3**): a solution of t-BuLi (3.0 mL, 5.10 mmol) in hexane was added slowly to a solution of **10** (1.14 g, 4.89 mmol) in 10 mL of ether at −78 °C, giving a bright yellow solution. After it was stirred for 5 min at −78 °C, the solution was warmed to 25 °C and stirred for 90 min. Volatiles were removed in vacuo, and the residue was washed with pentane, giving (0.86 g) of a yellow powder, which was dried under vacuum. ^{1}H NMR (360 MHz, THF-d_8): δ 6.90 (d, J = 7.2 Hz, 1H, Ar H); 6.47 (dd, J = 7.7, 1.2 Hz, 1H, Ar H); 6.41 (dt, J = 7.3, 1.2 Hz, 1H, Ar H); 5.81 (dt, J = 7.0, 1.9 Hz, 1H, Ar H), 3.86 (s, 1H, CHB); 3.50 (sept, J = 6.7 Hz, 2H, NCH); 1.20 (d, J = 6.7 Hz, 12H, Me). ^{13}C NMR (90.5 MHz, THF-d_8): δ 124.0, 122.2, 114.3, 107.6 (Ar); 66.4 (br, CHB); 49.0 (CHN); 23.4 (Me). ^{11}B NMR (115.5 MHz, THF-d_8): δ 41.0. The ^{1}H NMR spectrum showed Et_2O as an impurity, which did not affect subsequent reactions. (d) (2-(Diisopropylamino)-1,2-thiaborolide)(pentamethylcyclopentadienyl)-zirconium(IV) dichloride (**11**): toluene (20 mL) was added to a sample of **3**, prepared from 1.82 g (7.81 mmol) of **10**, and Cp*$ZrCl_3$ (1.93 g, 5.80 mmol) at −78 °C. The mixture was warmed slowly to 25 °C over 15 h with stirring. The solvent was then removed in vacuo, and the residue was extracted with CH_2Cl_2. The extracts were filtered through Celite, and the solvent was removed in vacuo, leaving a residue which was washed 3 times with 50 mL of pentane. Removal of solvent left 1.47 g (48%) of a bright yellow powder, mp 197 °C dec. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.66 (d, J = 7.0 Hz, 1H, Ar H); 7.20 (t, J = 7.3 Hz, 1H, Ar H); 7.19 (d, J = 7.2 Hz, 1H, Ar H); 7.04 (t, J = 7.3 Hz, 1H, Ar H); 3.85 (s, 1H, BCH); 3.53 (m, 1H, NCH); 3.48 (m, 1H, NCH′); 1.88 (s, 15H, CpMe); 1.21−1.17 (m, 12H, Me). ^{13}C NMR (90.5 MHz, $CDCl_3$): δ 132.6, 128.5, 125.8, 125.0 (Ar); 124.1 (Cp); 79 (br, CHB); 49.8 (CHN); 47.3 (CHN′); 23.2 (Me); 22.8 (Me′); 22.6 (Me?); 21.6 (Me‴); 12.5 (CpMe). ^{11}B NMR (115.5 MHz, $CDCl_3$): δ 38.9. HRMS: calcd for $C_{23}H_{34}{}^{11}B^{35}Cl_2NSZr$, 527.0929; found, 527.0921. Anal. Calcd for $C_{23}H_{34}BCl_2NSZr$: C, 51.68; H, 7.35; N, 2.62. Found: C, 51.17; H, 6.73; N, 3.18. (e) (2-(Diisopropylamino)-1,2-benzothiaborolide)(pentamethylcyclopentadienyl)ruthenium(II) (**12**): an ether solution of **3**, prepared from 0.47 g (2.02 mmol) of **10**, was added to a suspension of $[Cp^*RuCl]_4$ (0.55 g, 2.02 mmol) in 10 mL of ether at −78 °C. The reaction mixture was slowly warmed to 25° with stirring for 15 h. Volatiles were removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through Celite and concentrated. When the temperature was lowered to −30 °c, 0.47 g (49%) of **12** was obtained as dark red crystals, mp 145−146 °C. ^{1}H NMR (360 MHz, C_6D_6): δ 7.10 (d, J = 8 Hz, 1H, Ar H); 7.00 (d, J = 8 Hz, 1H, Ar H); 6.77 (m, 2H, Ar H); 3.80 (s, 1H, BCH); 3.18 (sept, J = 6.7 Hz, 2H, NCH); 1.59 (s, 15H, CpMe); 1.20 (d, J = 6.7 Hz, 6H, Me); 1.16 (d, J = 6.7, 6H, Me). ^{13}C NMR (90.5 MHz, C_6D_6): δ 132.3, 129.6, 124.5, 120.4 (Ar); 82.4 (Cp); 49.0 (CHN); 23.3 (Me); 22.6 (Me′); 11.2 (CpMe) (CHB not observed). ^{11}B NMR ($CDCl_3$, 115.5 MHz): δ 21.6. HRMS (EI): calcd for $C_{23}H_{34}{}^{11}BN^{102}RuS$, 469.1549; found, 469.1556. Anal. Calcd for $C_{23}H_{34}NRuS$: C, 58.97; H, 7.26; N, 2.99. Found: C, 59.00, H, 7.52; N, 2.78.

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(17) Crystal data for **12**: $C_{23}H_{34}BNRuS$, monoclinic, $P2_1/n$, a = 10.9118(14) Å, b = 8.9030(11) Å, c = 23.727(3) Å, β = 98.502(2)°, V = 2279.7(5) Å^3, Z = 4, D_c = 1.365 g cm^{-3}, T = 158(2) K, λ(Mo Kα) = 0.710 73 Å. Data were collected on a Siemens SMART CCD instrument. Final R indices ($I > 2\sigma(I)$): R1 = 0.0498, wR2 = 0.1215. R indices (all data): R1 = 0.0593, wR2 = 0.1265. The GOF on F^2 was 1.147.

features of transition metal π-coordinated boron heterocycles.[18] For example, **6** shows an analogous slip distortion away from B toward S, so that the Ru−S distance (2.36 Å) is shorter than in **12** (Ru−S = 2.44 Å). However, the Ru−B distances (2.45 Å) are essentially the same in both complexes. The intra-ring bond distances of the 1,2-thiaborolide unit are consistent with those of a π-coordinated aromatic ring.[19]

Although benzothiophene and benzothiaborolides **3** and **4** are isoelectronic, there are marked differences in their coordination chemistry. Benzothiophene forms π-coordinated transition-metal complexes to its benzocyclic ring,[20,21] while **3** and **4** form π-coordinated transition-metal complexes to their heterocyclic rings. In summary, the 1,2-thiaborolide ring of **3** forms η^5 complexes with both early and late transition metals.

Acknowledgment. We thank the National Science Foundation for generous financial support of this work.

Supporting Information Available: Tables of crystallographic data for **12** and ^{1}H NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000650B

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