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1,3-Benzothiaborolide: A New Heteroaromatic Anion

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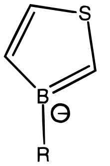
*Summary: Lithium N,N-diisopropyl-3-amino-1,3-benzothiaborolide (**5**) was prepared by a multistep synthesis starting from thioanisole. The thiaborolide **5** was converted to a Cp*Ru η^5-adduct, which was characterized by X-ray diffraction.*

1,3-Thiaborolide (**1**) is a potentially aromatic anion which is related to thiophene (**2**)[1] in the same manner that boratabenzene (**3**)[2,3,4] is related to benzene. Comparison of the coordination chemistry of **1** with that of **2** and **3** should be particularly interesting. Thiophene forms rather few stable π-coordinated transition-metal complexes,[5] while boratabenzene has a particularly rich transition-metal chemistry.[3] We report here on the synthesis of the first benzothiaborolide **5** and on structural data which show that the thiaborolide ring can serve as an η^5-ligand toward transition metals.



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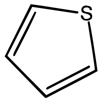

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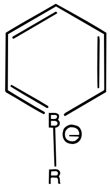

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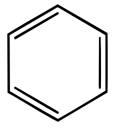

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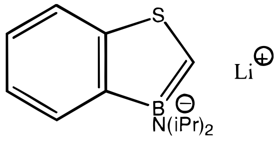

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The synthesis of **5** relies on the general synthesis of sulfur heterocycles developed by Cabiddu and co-workers.[6] Double deprotonation of thioanisole by butyllithium followed by reaction with dibutyltin dichloride affords the benzothiastannolene **7** in 47% yield, Scheme 1.[7] The reaction of **7** with excess BCl_3 at 25 °C followed by gentle warming to 50 °C gives the rather sensitive

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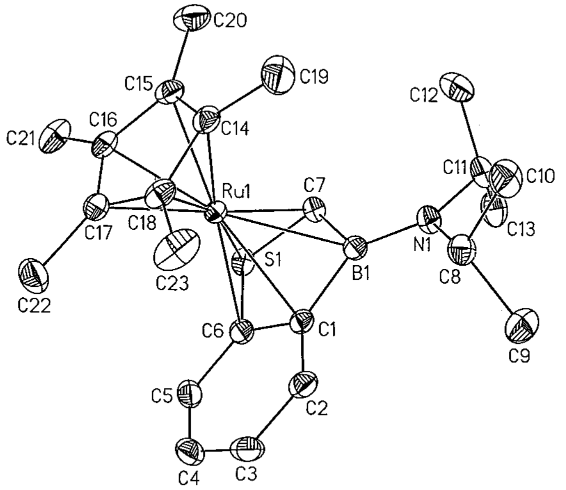

Figure 1. Solid-state structure of **10**. Selected distances (Å): RuB, 2.449(2); RuC(1), 2.326(2); Ru C(6), 2.243(2); RuS, 2.3566(5); RuC(7), 2.213(2); RuC(Cp*, average), 2.17(2); BC(1), 1.570(3); C(1)C(6), 1.439(3); C(6)S, 1.761(2); SC(7), 1.758(2); C(7)B, 1.523(4); BN, 1.443(3); C(1)C(2), 1.442(3); C(2)C(3), 1.370(3); C(3)C(4), 1.419(3); C(4)C(5), 1.354(3); C(5)C(6), 1.420(3).

benzothiaborolene chloride **8**. Immediate reaction of **8** with excess diisopropylamine gave *N*,*N*-diisopropyl-3-amino-1,3-benzothiaborolene **9** in 92% yield from **7**. The ^{1}H and ^{13}C NMR spectra of **9a** show that isopropyl CH groups are nonequivalent due to slow rotation about the B−N bond.[8]

The reaction of **9a** with tBuLi in ether gave a bright yellow solution of anion **5**, which on quenching with methyl iodide afforded the expected 2-methyl derivative **9b** in 92% yield. The ^{1}H, ^{11}B, and ^{13}C NMR spectra of **5** in THF-d_8 show that this carbanion is strongly stabilized by π-bonding to boron. The BCH group shows a ^{1}H NMR signal (δ 3.14) and a ^{13}C NMR signal (δ 60.9) far downfield from those of sp^3-hybridized organolithium compounds,[9] which indicates that the carbon is sp^2 hybridized. The ^{11}B NMR shift of **5** at δ 43.6 is upfield relative to **9a** (δ 47.1) due to the enhanced electron density at B.[10] Indeed, this chemical shift value is virtually identical to that reported by Pelter for the similarly substituted acyclic anion.[11] The ^{1}H and ^{13}C NMR spectra of **5** at ambient temperature show that the two isopropyl groups are identical due to rapid rotation about the B−N bond. As had previously been found for lithium aminoboratabenzenes, incorporation of the boron atom into the aromatic ring of **5** greatly diminishes its ability to form an external π-bond to nitrogen.[12]

The reaction of **5** with [Cp*RuCl]$_4$ gives adduct **10** as bright red crystals in 64% yield. The X-ray structure, illustrated in Figure 1, shows that **10** is essentially a diheteroruthenocene.[13] While the thiaborolide is η-bound to Ru, the noncoordinated portion of the benzo ring shows a diene-like C−C bond alternation.[14] The Ru atom is closer to the Cp* ring (Ru−ring = 1.793 Å) than to the thiaborolide ring (Ru−ring = 1.867 Å). Relative to the thiaborolide ring, the Ru atom is slip-distorted away from B and C(1) toward S so that the Ru−C(7) and Ru−C(6) distances average 0.1 Å less than the Ru−C(1) distance. The Ru−S distance is nearly 0.1 Å shorter than the Ru−B distance. Similar slip distortions away from boron are common features of π-coordinated boron heterocycles.[3] It is also interesting to note that the Ru−S bond of **10** is essentially the same length as that reported for the bis(tetrafluoroborate) of bis(tetramethylthiophene)ruthenium.[15]

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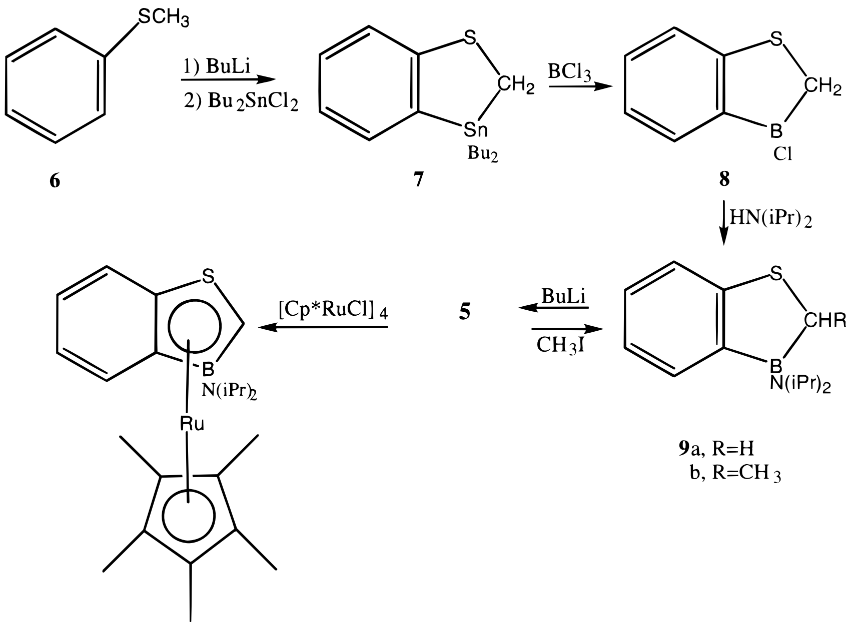
(7) Experimental procedures and characterization of new compounds are as follows. (a) 3,3-Dibutyl-1,3-benzothiastannolene (**7**): BuLi (36.8 mL, 2 M in hexane, 92 mmol) was added to a solution of thioanisole (4.68 mL, 40 mmol) and TMEDA (13.9 mL) in 100 mL of hexane at −78 °C with stirring. After warming to 25 °C, the mixtue was allowed to stir for 26 h. After cooling to −78 °C, a solution of Bu_2SnCl_2 (12.8 g, 42.0 mmol) in 20 mL of pentane was added, after which the solution was allowed to warm to 25 °C and stirred for 12 h. After quenching with aqueous NH_4Cl at 0 °C, the organic layer was separated and the aqueous layer was extracted with hexane. The combined organic fractions were washed with a saturated NaCl solution and then dried over anhydrous $MgSO_4$. After the solvent was removed, the yellow residue was purified by flash column chromatography (hexane) to give 6.76 g (47%) of **7** as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, $J = 7.3$ Hz, Bu), 1.32 (m, 1.64, Bu), 2.23 (s, J^{119}SnCH $= 33.6$ Hz, SCH_2), 7.03 (dt, $J = 7.1$, 1.1 Hz, ArH), 7.24 (dt, $J = 7.1$, 1.5 Hz, ArH), 7.31 (dd, $J = 7.4$, 0.4 Hz, ArH), 7.47 (ddd, $J = 7.1$, 1.4, 0.5 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 5.7, 13.6, 13.8, 27.3, 29.0, 123.3, 123.4, 129.0, 136.0, 137.7, 152.5. HRMS (EI, *m*/*z*): calcd for $C_{15}H_{24}S^{120}Sn$, 356.0621; found 356.0612. Anal. Calcd for $C_{15}H_{24}SSn$: C, 50.56; H, 6.74. Found C, 50.86; H, 6.73. (b) *N*, *N*-Diisopropyl-3-amino-1,3-benzothiaborolene (**9a**): A heptane solution of BCl_3 (1.0 M, 1.03 mL, 1.03 mmol) was added to a solution of **7** (0.33 g, 0.93 mmol) in 3 mL of pentane at −78 °C, after which the mixture was allowed to warm to 25 °C with stirring for 40 min. The solvent was removed in vacuo, and the residue was heated to 50 °C. On cooling, the residue was washed twice with 5 mL of pentane to remove the Bu_2SnCl_2, leaving **8** as a white powder. **8** was suspended in 8 mL of CH_2Cl_2 and cooled to −78 °C, and diisopropylamine (0.39 mL, 3.0 mmol) was added. The resulting mixture was warmed to 25 °C and stirred for 30 min. Removal of solvent left a residue, which was extracted with pentane (2 × 8 mL). After filtration, the extracts were concentrated by partial removal of solvent and cooled to −78 °C to give **9a** (0.2 g, 92%) as a white solid, mp, 50−52 °C. ^{1}H NMR (300 MHZ, THF-d_8): δ 1.31 (d, $J = 6.7$ Hz, CH_3), 2.70 (s, BCH_2), 3.58 (br, NCH), 4.50 (br, NCH′), 6.96 (t, $J = 7.0$ Hz, ArH), 7.18 (t, $J = 7.3$ Hz, ArH), 7.23 (d, $J = 7.7$ Hz, ArH), 7.72 (d, $J = 7.1$ Hz, ArH). ^{13}C NMR (90 MHz, THF-d_8): δ 22.5 (CH_3), 24.1 (CH_3'), 47.7 (br, NCH), 50.6 (br NCH′), 123.1, 124.0, 131.3, 134.4 (ArC). ^{11}B NMR (115.5 MHz, THF-d_8): δ 47.1. HRMS (EI, *m*/*z*): calcd for $C_{13}H_{20}{}^{11}BNS$, 233.1410; found, 233.1411. Anal. Calcd for $C_{13}H_{20}BNS$: C, 66.95; H, 8.58; N, 6.01. Found: C, 66.61; H, 8.42; N, 5.85. (c) Lithium *N*,*N*-diisopropyl-3-amino-1,3-benzothiaborolide (**5**): *tert*-butyllithium was added to a solution of **9a** in THF-d_8 producing a solution of **5**. ^{1}H NMR (360 MHz, THF-d_8): δ 1.26 (d, $J = 6.8$ Hz, CH_3), 3.14 (s, BCH), 3.86 (sept, $J = 6.8$ Hz, NCH), 6.74 (dd, $J = 5.9$, 2.2 Hz, ArH), 7.37 (dd, $J = 5.6$, 3.4 Hz, ArH), 7.81 (dd, $J = 6.0$, 3.1 Hz). ^{13}C NMR (90 MHz, THF-d_8): δ 24.35 (CH_3), 24.38 (CH_3'), 48.1 (NCH), 60.9 (BCH), 119.0 (Ar), 120.8 (Ar), 123.9 (Ar), 145.2 (BC(Ar)), 152.1 (SC(Ar)). ^{11}B NMR (115.5 MHz, THF-d_8): δ 43.6. ^{7}Li NMR (140 MHz, THF-d8): δ 3.14. (d) *N*,*N*-Diisopropyl-3-amino-2-methyl-1,3-benzothiaborolene (**9b**): t-BuLi (1.7 N in pentane, 0.83 mL, 1.42 mmol) was added to a solution of **9a** (0.30 g, 1.29 mmol) in 5 mL of ether at −78 °C. The resulting bright yellow solution was allowed to warm to 25 °C and stand at this temperature for 1 h. After cooling to −78 °C, methyl iodide (0.16 mL, 2.58 mmol) was added. The mixture was allowed to warm to 25 °C for 12 h. After filtration and removal of solvent, **9b** (0.29 g, 92%) was isolated as an oil. ^{1}H NMR (300 MHz, C_6D_6): δ 0.99 (br d, $J = 6.6$ Hz, $NCH(CH_3)_2$), 1.04 (d, $J = 7.0$ Hz, $NCHCH_3'$), 1.10 (d, $J = 6.9$ Hz, NCH CH_3''), 1.43 (d, $J = 7.2$ Hz, $SCHCH_3$), 3.35 (br, SCH), 3.87 (br, $N(CH)_2$), 6.98 (t, $J = 7.4$ Hz, ArH), 7.07 (t, $J = 7.4$ Hz, ArH), 7.35 (d, $J = 7.7$ Hz, ArH), 7.74 (d, $J = 7.0$ Hz, ArH). HRMS (EI, *m*/*z*): calcd for $C_{14}H_{22}{}^{11}BNS$, 247.1566; found 247.1560. (e) (η^5-*N*,*N*-diisopropyl-3-amino-1,3-benzothiaborolyl)(η^5-pentamethylcyclopentadienyl)ruthenium(II) (**10**): A solution of **5**, prepared from 0.2 g of **9a** in 8 mL of ether, was added to a suspension of $(Cp^*RuCl)_4$ (0.27 g, 0.86 mmol) in 6 mL of ether at −78 °C. The mixture was allowed to warm to 25 °C and stirred for 12 h. The solvent was removed, and the residue was extracted with 2 × 8 mL of pentane. The pentane solution was concentrated and cooled to −78 °C, affording **10** (0.26 g, 64%) as red crystals, mp 146−8 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 1.17 (d, $J = 6.6$ Hz, $NCH(CH_3)_2$), 1.29 (d, $J = 6.6$ Hz, NCH $(CH_3)_2'$), 1.61 (s, C_5Me_5), 2.79 (s, BCH), 3.73 (sept, $J = 6.6$ Hz, $N(CH)_2$), 6.78−6.90 (m, 2ArH), 7.02 (dd, $J = 8.7$, 0.9 Hz, ArH), 7.54 (dd, $J = 8.5$, 0.8 Hz, ArH). ^{13}C NMR (100 MHz, THF-d_8, $T = 25$ °C): δ 11.2 ($CpMe_5$), 23.6 ($NCH(CH_3)_2$), 24.2 (NCH $(CH_3)_2'$), 47.6 (NCH), 49.9 (BCH), 84.1 (C(Cp)), 90.5 (CS(Ar)), 103.6 (CB(Ar)), 122.3 (ArH), 124.2 (ArH), 126.5 (ArH), 136.6 (ArH). At −95 °C, the δ 47.6 peak separates to two peaks at δ 50.162 and 44.491 with T_c at −40 °C. ^{11}B NMR (115.5 MHz, C_6D_6): δ 20.8. HRMS (EI, *m*/*z*): calcd for $C_{23}H_{35}{}^{11}BN^{102}RuS$ 469.1548; found, 469.1548. Anal. Calcd for $C_{23}H_{34}BNRuS$: C, 58.97; H, 7.26; N, 2.99. Found C, 59.20; H, 7.31; N, 2.96.

Scheme 1



10

The C−S bonds (average 1.76 Å) and the C-B bonds (average 1.55 Å) of **10** are typical of those found for transition-metal complexes of thiophenes,[16] boratabenzenes,[12,13,17] and other heterocycles containing both boron and sulfur.[18,19] The exocyclic B−N bond (1.443 Å) is longer than those of the aminoboratabenzene complexes (1.39−1.41 Å).[12,17] Weaker B−N π bonding is independently shown by the low rotation barrier about the B−N bond. At 25 °C, the ^{13}C NMR spectrum shows a single peak (δ 47.6) for the i-Pr methine groups. On cooling, this peak separates (δ 50.2, 44.5) with a coalescence at −40 °C, indicating that the barrier to interconversion of the methine groups is $\Delta G^{\ddagger} = 10.2 \pm 0.5$ kcal/mol. The nonequivalent isopropyl methine groups of the crystallographic conformation can become equivalent only by rotations about both the B−N and C−N[20] bonds. On this basis, the maximum value for rotation about the B−N π-bond of **10** is 10 kcal/mol, which is lower than that found for coordinated boratabenzenes ($\Delta G^{\ddagger} = 18-15$ kcal/mol).[12,17] The weaker exocyclic boron π-bonding is consistent with a stronger endocyclic π-bonding.[12]

In summary, the structural data for **10** show that the thiaborolide ring is a π-coordinated aromatic ring.

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Supporting Information Available: Tables of crystallographic data of **10** (6 pages). Ordering information is given on any current masthead page.

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[13] Crystal data for **10**: $C_{23}H_{34}BNRuS$, orthorhombic, *Pbca*, $a = 14.9948(2)$ Å, $b = 15.1975(3)$ Å, $c = 19.4546(3)$ Å, $V = 4433.38(13)$ Å^3, $D_c = 1.404$ g cm^{-3}, $T = 158(2)$ °K, λ (Mo Kα) = 0.71073 Å. Data were collected on a Siemens SMART CCD. Final R indices [$I > 2\sigma I$]: $R_1 = 0.0347$, w$R_2 = 0.0637$. R indices (all data): $R_1 = 0.0508$, w$R_2 = 0.0701$. GOF on $F^2 = 1.083$.

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