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1,3-Thiaborolide: A New Heteroaromatic Surrogate for Cyclopentadienide

Arthur J. Ashe, III,* Xinggao Fang, and Jeff W. Kampf

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

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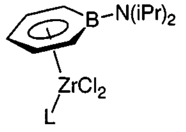
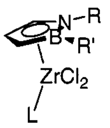
*Summary: The heteroaromatic anion lithium N,N-diisopropyl-3-amino-1,3-thiaborolide (**5**) has been prepared by a multistep synthesis and has been converted to Cp*Ru complex **7** and Cp*ZrCl$_2$ complex **8**. On activation by excess methylaluminoxane (MAO), a solution of **8** is an active catalyst toward the polymerization of ethylene.*



1a, L = $C_5H_5BN(iPr)_2$
1b, L = C_5Me_5



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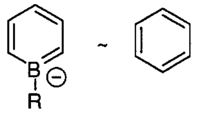

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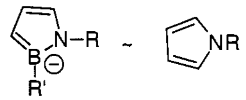

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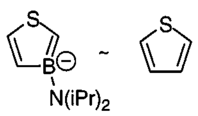

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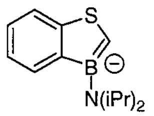

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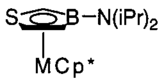
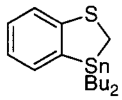


7, M = Ru
8, M = $ZrCl_2$



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Derivatives of the group 4 metallocenes are the most important class of homogeneous catalysts for the polymerization of olefins.[1] Recently it has been reported that several group 4 metal complexes such as **1**[2] and **2**,[3] which employ anionic boron heterocyclic ligands in place of Cp, have high polymerization activities.[4] These ligands include boratabenzenes **3**[5] and 1,2-azaborolides **4**,[6] which are derived from the neutral aromatic rings benzene and pyrrole, respectively, by the formal replacement of CH by BH^-. Since 1,3-thiaborolide **5** is similarily derived from thiophene, an exploration of the coordination chemistry of **5** is an attractive goal. The only prior work on **5** involves the recent synthesis of benzo-1,3-thiaborolide **6**.[7] We now wish to report on the first synthesis of a monocyclic thiaborolide **5** and on its conversion to metal complexes **7** and **8**.

Since the synthesis of **6** involved the use of benzothiastannolene **9** as a key synthon, we initially sought to prepare the corresponding monocyclic thiastannolene **12** as outlined in Scheme 1.[8] Chloromethyl trimethylsilylethynyl sulfide **10** is available in quantity using a procedure of Brandsma.[9] Desilylation of **10** with Bu_4NF in methanol affords the labile chloromethyl ethynyl sulfide **11**. Using an adaption of a ring closure developed by Jousseaume and co-workers,[10] **11** was treated with $LiSnHBu_2$ at low temperature followed by gentle warming, which affords **12** in reasonable yield. The reaction apparently takes place via nucleophilic displacement of chloride by tin followed by intramolecular hydrostannation of the ethynyl group.

We were disappointed that the reaction of **12** with BCl_3 afforded only intractable products. However, reaction of **12** with 2 equiv of BuLi gave the equally useful **13**. This dilithio reagent can be detected by NMR spectroscopy or by direct trapping with Me_2SiCl_2 to afford **14**. It seems likely that **13** may find general use in the preparation of sulfur heterocycles.[11] The reaction of **13** with i-Pr_2NBCl_2[12] gave the desired thiaborolene **15** in 33% yield. The ^1H and ^{13}C NMR spectra of **15** are consistent with its assigned structure and show that the isopropyl CH groups are nonequivalent due to slow rotation about the B−N bond.[13,14]

The reaction of **15** with t-BuLi in ether gave a yellow solution of the lithium *N*,*N*-diisopropyl-3-amino-1,3-thiaborolide **5**. The ^1H, ^{11}B, and ^{13}C NMR spectra of **5**

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[1] For recent reviews, see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, Germany, 1995. (c) Coates, G. W.; Waymouth, R. M. In *Comprehensive Organometallic Chemistry II*, Vol. 12 (Volume Ed: Hegedus, L. S.); Pergamon: Oxford, U.K., 1995; p 1193. (d) Aulbach, M.; Küber, F. *Chem. Z.* **1994**, *28*, 197. (e) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

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[7] Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 2379.

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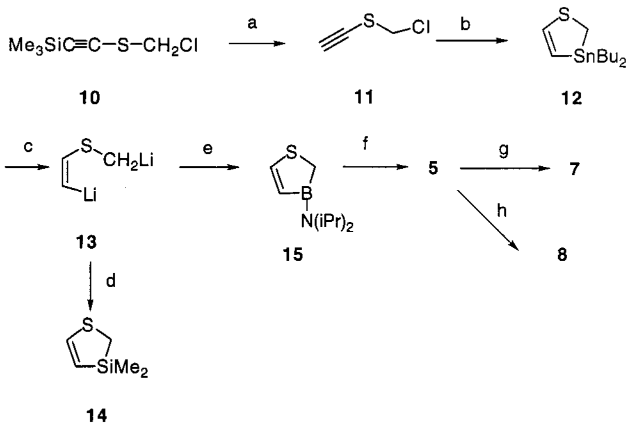
Scheme 1



Key: **a**, Bu_4NF, MeOH; **b**, Bu_2SnH_2, LDA, -78 °C; **c**, BuLi; **d**, Me_2SiCl_2; **e**, $(iPr)_2NBCl_2$; **f**, *t*-BuLi; **g**, $[Cp^*RuCl]_4$; **h**, Cp^*ZrCl_3.

in THF-d$_8$ show that this carbanion is strongly stabilized by π-bonding to boron in the same manner as found for **6**. The BCH group shows a ^{1}H NMR signal (δ 2.89) and a ^{13}C NMR signal (δ 59.8) downfield from those of sp^{3}-hydridized organolithium compounds, which indicates that C(2) is sp^{2} hybridized.[15] The ^{11}B NMR shift of **5** (δ 35.1) shows an upfield shift relative to **15** (δ 43.9) consistent with enhanced electron density at boron.[16] 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 **6**[7] and lithium aminoboratabenzenes,[14,17] the strong C–B π-bonding of the aromatic ring diminishes the ability of boron to π-bond to the exocyclic nitrogen. Interestingly the ^{1}H NMR signals (δ 6.19, 6.95) and the ^{13}C NMR signal (δ 126.8, 132.2) for the CH groups at C(4) and C(5), respectively, are in the normal aromatic/olefinic region. Apparently little negative charge is transferred to these atoms,[18,19] which is as expected from consideration of the classical resonance structures of **5**.

As we had anticipated, **5** readily forms transition metal complexes. The reaction of **5** with $[Cp^*RuCl]_4$ gives **7** as bright amber crystals in 37% yield. Similar reaction of **5** with Cp^*ZrCl_3 affords the yellow **8** in 35% yield. The crystal structure of **7**,[20] illustrated in Figure 1, shows that it is a diheteroruthenocene. The thiaborolide ring is η^5-bound to Ru in the same manner found for the corresponding complex of **6**.[7] Although a partial disorder between S(1) and C(2) limits the accuracy of the bond distances, the structural data clearly

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(8) Experimental procedures and characterization of new compounds are as follows: (a) 3,3-Dibutyl-2,3-dihydro-1,3-thiastannole (**12**): An aqueous solution of 75% (w/w) Bu_4NF (20 mL, 49.3 mmol) was added dropwise to a solution of chloromethyl trimethylsilylethynyl sulfide (8.0 g, 44.9 mmol) in 10 mL of methanol at 0 °C. The resulting mixture was allowed to stir at 0 °C for 2 h. Ice cold H_2O was added, and the mixture was extracted with pentane. The extracts were washed with cold H_2O and dried over anhydrous Na_2SO_4. Removal of solvent afforded 5.5 g of a mixture of 60% (31.4 mmol, 70% yield) of chloromethyl ethynyl sulfide (**11**) and hexamethyldisiloxane, which was not further purified. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.08 (s, 1H), 4.76 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.8, 86.4, 95.5. MS (EI, *m/z*): 106 (M^+ for $C_3H_3{}^{37}ClS$). This mixture was added to a solution of Bu_2SnHLi prepared from Bu_2SnH_2 (10.0 g, 42.6 mmol) and LDA (47.3 mmol) in 40 mL of THF and 20 mL of hexane at −78 °C. The reaction mixture was kept at −78 °C for 12 h. After warming to 0 °C 20 mL of H_2O was added to quench the reaction. Solvent was removed on a rotary evaporator, and the residue was added to H_2O and extracted with hexane. The extracts were washed with H_2O and dried over anhydrous Na_2SO_4. Distillation gave 3.73 g (39%) of **12** as a colorless oil, bp 100–120 °C/0.03 Torr. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, $J = 7.3$ Hz, 6H, Bu), 1.15 (m, 4H, Bu), 1.31 (m, 4H, Bu), 1.56 (m, 4H, Bu), 1.94 (s, $^{2}J^{119}{}_{SnH} = 31.6$ Hz, CH_2S), 6.66 (d, $J = 9.8$ Hz, $^{2}J_{SnH} = 132$ Hz, SnCH), 7.39 (d, $J = 9.8$ Hz, $^{3}J_{SnH} = 147$ Hz, CHS). ^{13}C NMR (125 MHz, $CDCl_3$): δ 3.5, 13.3, 13.9, 27.1, 29.0, 120.2, 146.0. MS (EI, *m/e*) (intensity): 306 (M^+ for $C_{11}H_{22}S^{120}Sn$, 10), 249 ($M^+ - Bu$, 100). Anal. Calcd for $C_{11}H_{22}SSn$: C, 43.28; H, 7.21. Found: C, 43.18; H, 7.34. (b) *N*,*N*-Diisopropyl-3-amino-2,3-dihydro-1,3-thiaborole (**15**): BuLi (2.5 M in hexane, 6.47 mL, 16.18 mmol) was added dropwise to a solution of **12** (2.35 g, 7.70 mmol) in THF (15 mL) at −78 °C. The solution was stirred at −78 °C for 1 h followed by 40 min at 25 °C. NMR spectroscopy showed the presence of **13**. ^{1}H NMR (200 MHz, THF-d_8): δ −0.16 (d, $J = 3.6$ Hz, 2H, SCH_2Li), 6.31 (d, $J = 14.3$ Hz, 1H, CHLi), 7.32 (dt, $J = 14.3, 3.0$ Hz, 1H, SCH). After recooling the solution of **13** to −78 °C it was added dropwise to a solution of i-Pr_2NBCl_2 (1.40 g, 7.70 mmol) in 10 mL of THF at −78 °C. The reaction mixture was allowed to warm slowly to 25 °C and then allowed to stand at −10 °C for 12 h. The solvent was removed in vacuo, and the residue was extracted with pentane. Distillation gave **15** (0.46 g, 33%) as a colorless liquid, bp 30–60 °C/0.03 Torr. ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.16 (d, $J = 6.7$ Hz, 6H, 2(Me)), 1.24 (d, $J = 7.0$ Hz, 6H, 2 Me′), 2.50 (s, 2H, SCH_2), 3.48 (hept, $J = 6.7$ Hz, 1H, NCH), 3.61 (hept, $J = 7.0$ Hz, 1H, NCH′), 6.15 (d, $J = 8.0$ Hz, 1H, BCH), 7.64 (d, $J = 7.8$, 1H, SCH). ^{1}H NMR spectrum showed Bu_4Sn as an impurity, which did not interfere with subsequent reactions. ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2 (Me), 24.5 (Me′), 46.5 (NCH), 51.3 (NCH′), 125.3 (br, BCH), 157.7 (SCH). ^{11}B NMR (115 MHz, $CDCl_3$): δ 43.9. MS (EI, *m/z*): 183(M^+ for $C_9H_{18}11BNS$). (c) 2,3-Dihydro-3,3-dimethyl-1,3-thiasilole (**14**): In the same manner as above except Me_2SiCl_2 was substituted for i-Pr_2NBCl_2 the reaction gave **14** (83%) as light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 6H, $SiMe_2$), 1.91 (s, 2H, SCH_2), 5.76 (d, $J = 9.9$ Hz, 1H, CHSi), 7.01 (d, $J = 9.6$ Hz, 1H, CHS). ^{13}C NMR (75 MHz, $CDCl_3$): δ −0.7 ($SiMe_2$), 12.6 ($SiCH_2$), 119.0 (SiCH), 146.7 (SCH). MS (EI, *m/z*): 130 (M^+ for $C_5H_{10}SSi$). Satisfactory combusion analogues could not be obtained. However the ^{1}H NMR spectrum indicates good purity. (d) Lithium *N*,*N*-diisopropyl-3-amino-1,3-thiaborolide (**5**): t-BuLi (1.7 M in hexane, 0.37 mL, 0.63 mmol) was added to a solution of **15** (0.10 g, 0.55 mmol) in 5 mL of ether at −78 °C. After the solution was allowed to warm to 0 °C for 1 h, the solvent was removed, giving **5** as a yellow solid. ^{1}H NMR (500 MHz, THF-d_8): δ 1.06 (d, $J = 6.9$ Hz, 12H, Me), 2.89 (m, SCHB), 3.58 (hept, $J = 6.9$ Hz, 2H, NCH) 6.19 (dd, $J = 7.0, 1.0$ Hz, 1H, BCH), 6.95 (dd, $J = 7.0, 2.7$ Hz, 1H, SCH). ^{1}H NMR spectrum showed Bu_4Sn as an impurity which did not interfere with subsequent reactions. ^{13}C NMR (100 MHz, THF-d_8): δ 23.5 (Me), 47.8 (NCH), 59.8 (br, BCHS), 126.8 (br, BCH), 132.2 (SCH). ^{11}B NMR (115 MHz, THF-d_8): δ 35.1. (e) (η-*N*,*N*-Diisopropyl-3-amino-1,3-thiaborolyl) (η-pentamethylcyclopentadienyl) ruthenium(II) (**7**): A solution of **5** (prepared from 0.10 g of **15**) in ether (5 mL) was added slowly to a suspension of $(Cp^*RuCl)_4$ (0.17 g, 0.55 mmol) in 5 mL of ether at −78 °C. The mixture was allowed to warm to 25 °C and stirred for 12 h. After removal of solvent, the residue was extracted with pentane. The extracts were filtered, and the product was purified by flash column chromotography on alumina (pentane, eluant) to give **7** (0.09 g, 39%) as a red solid, mp 82–4 °C. ^{1}H NMR (360 MHz, $CDCl_3$): δ 1.13 (d, $J = 6.7$ Hz, 12H, 2CH-$(Me)_2$), 1.93 (s, 15H, CpMe), 2.58 (s, 1H, BCHS), 3.33 (hept, $J = 6.7$ Hz, 2H, NCH), 3.57 (d, $J = 4.5$ Hz, 1H, BCH), 4.84 (d, $J = 4.4$ Hz, 1H, SCH). ^{13}C NMR (100 MHz, THF-d_8): δ 12.5 (CpMe), 23.41 (i-PrMe), 23.48 (i-PrMe′), 47.98 (NCH), 47.95 (BCHS), 68.7 (BCH), 81.3 (SCH), 88.3 (Cp). ^{11}B NMR (115 MHz, $CDCl_3$): δ 20.6. HRMS(EI): calcd for $C_{19}H_{32}11BNSRu$ 419.1392; found 419.1395. Anal. Calcd for $C_{19}H_{32}$-BNSRu: C, 54.54; H, 7.66; N, 3.35. Found: C, 54.75; H, 7.90; N, 3.38. (f) (η^5-*N*,*N*-Diisopropyl-3-amino-1,3-thiaborolyl) (η^5-pentamethylcyclopentadienyl) zirconium dichloride (**8**): A solution of **5** (prepared from 0.27 g **12**) in Et_2O (10 mL) was slowly added to a suspension of Cp^*ZrCl_3 (0.50 g, 1.49 mmol) in Et_2O (10 mL) at −78 °C. The mixture was slowly warmed and stirred 15 h at room temperature to give a yellow suspension. Solvent was removed in vacuo, and the residue was extracted with pentane and filtered. The pentane solution was concentrated and cooled to −78 °C to give product (0.25 g, 35%) as a yellow solid, containing a small amount of Bu_4Sn. ^{1}H NMR (500 MHz, C_6D_6): δ 1.082 (d, 3H, $J = 6.6$ Hz), 1.086 (d, 3H, $J = 7.1$ Hz), 1.13 (d, 3H, $J = 6.6$ Hz), 1.30 (d, 23H, $J = 6.8$ Hz), 1.89 (s, 15H), 2.65 (s, 1H, BCHS), 3.28 (p, 1H, $J = 6.6$ Hz), 3.46 (p, 1H, $J = 6.6$ Hz), 6.83 (d, 1H, $J = 7.3$ Hz, SCH), 7.05 (d, 1H, $J = 7.3$ Hz, BCH). ^{13}C NMR (100 MHz, C_6D_6): δ 12.8 ($C_5\mathit{Me}_5$), 22.3, 23.0, 24.7, 25.2, 46.8 (NCH), 50.5 (NCH′), 62.2 (br, BCH), 123.7 (C_5Me_5), 142.9 (br, BCH), 147.9 (SCH). HRMS (EI): calcd for $C_{19}H_{32}{}^{11}BNSCl_2Zr$ 477.0773; found 477.0763.

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show that the thiaborolide ring of **7** is a π-coordinted aromatic ring.

On activation by excess methylaluminoxane, the thiaborolide zirconium complex **8** was active toward the polymerization of ethylene.[21] Under identical conditions the relative activities of **8** and **1a** were found to be 7.5 $\times$ 10^4 and 20.4 $\times$ 10^4 (g polymer)/(mol Zr·atm), respectively. Since **1b** had previously been found to be half as active as **1a**, the identically substituted Cp*(L)$ZrCl_2$ complexes of boratabenzene (**1b**) and thiaborolide (**8**) have very similar polymerization activities.[22] Our preliminary results show that 1,3-thiaborolide can serve as replacement ligand for Cp in metallocene-based polymerization catalysts. In a broader context the use of thiaborolide and similar anionic boron heterocycles as ligands provides a new tool for the construction of important organometallic compounds.

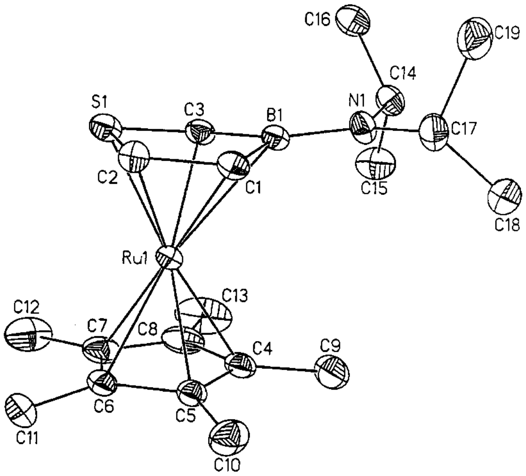

Figure 1. Solid-state structure of **7**. Selected distances (Å): RuB, 2.507(3); RuC(1), 2.240(2); RuC(2), 2.185(11); RuS(average), 2.34(4); RuC(3), 2.240(2); RuC (Cp*, average), 2.18(2); BC(1), 1.546(4); BC(3), 1.547(4); BN, 1.423(1).

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

Supporting Information Available: Tables of crystallographic data for **7** and ^1H NMR spectra of **5**, **8**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Crystal data for **7**: $C_{19}H_{32}NBRuS$, triclinic, $P\bar{1}$, $a = 7.9652(2)$ Å, $b = 14.8240(4)$ Å, $c = 17.0019(5)$ Å, $\alpha = 90.034(1)°$, $\beta = 97.509(1)°$, $\gamma = 90.371(1)°$, $V = 1990.26(9)$ Å^3, $D_c = 1.396$ g cm^{-3}, $T = 158(2)$ K, λ (Mo Kα) = 0.710 73 Å. Data were collected on a Siemans SMART CCD. Final R indices [$I > 2\sigma I$]: R1 = 0.0345, wR2 = 0.0769, R indices (all data): R1 = 0.0509, wR2 = 0.0849, GOF on $F^2 = 1.058$.

(21) For conditions of polymerization see: Ashe, A. J., III; Al-Ahmad, S.; Fang, X.; Kampf, J. W. *Organometallics* **1998**, *17*, 3883.

(22) For comparison the activity of Cp_2ZrCl_2 was 84% of that of **1a**. However, the polymerization conditions were different. See ref 2a.