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Borabenzene Derivatives. 21.[1] 2,4-Pentadienylboranes as Key Intermediates of a Novel Route to Boracyclohexadienes and Boratabenzenes. Structure of $[Li(TMPDA)](C_5H_5BNMe_2)$

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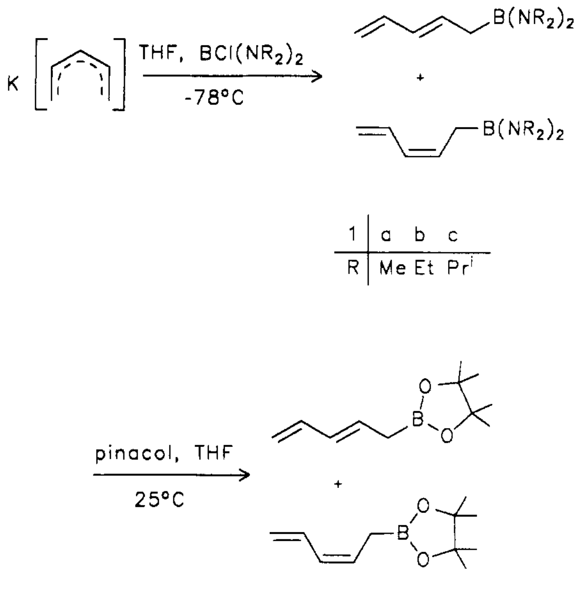
Summary: Under metalation conditions the 2,4-pentadienylboranes 2,4-$C_5H_7B(NR_2)_2$ *(R = Me, Et) and 2,4-*$C_5H_7B(O_2C_2Me_4)$ *undergo an electrocyclic ring closure to form borabenzene derivatives. This novel reaction provides a far more efficient access to borabenzene chemistry than previous methods. The dimethylamino derivative* $[Li\{Me_2N(CH_2)_3NMe_2\}](C_5H_5BNMe_2)$ *is the first boratabenzene salt to be structurally characterized.*

Borabenzene and boratabenzene derivatives[2] are accessible via the cobaltocene route[3] and via the tin route.[4] Both routes are difficult and laborious, and as a consequence, borabenzene chemistry has remained rather limited. We present here the first account of a new approach to this chemistry.

Bis(dialkylamino)-2,4-pentadienylboranes **1** can readily be made from potassium pentadienide[5] and chlorobis(dialkylamino)boranes.[6] They are obtained as mixtures of *E* and *Z* isomers of varying composition depending on the reaction conditions.[7] By addition of pinacol ($HOCMe_2CMe_2OH$) in THF they are smoothly converted to the dioxaborolane **2** (bp 80 °C/10 mbar) in near-quantitative yield.[8]

Scheme I



2

Metalation of organoboranes is not a straightforward matter.[9] The 2,4-pentadienylboranes **1b,c** react with KCH_2SiMe_3 in cyclohexane[10] to give the insoluble boryl-substituted pentadienides **3b,c** (of unspecified stereochemistry), which we characterized as trimethylsilyl derivatives **4b,c**.[11] Attempted metalation of the boranes **1a–c** by lithium amides $LiNR'_2$ (**5a–c**) in THF in the presence of tetramethylethylenediamine (TMEDA) results (i) in substitution of *B*-dialkylamino groups, (ii) in a nonproductive deborylation via primary attack at the boron center, and (iii) in ring closure which is thought to proceed via primary metalation at the BCH_2 group,

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[1] Part 20: Herberich, G. E.; Klein, W.; Spaniol, T. P. *Organometallics* **1993**, *12*, 2660.

[2] Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199.

[3] Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 805. Herberich, G. E.; Greiss, G.; *Chem. Ber.* **1972**, *105*, 3413. Herberich, G. E.; Becker, H. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 184.

[4] Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804.

[5] (a) Metalation of 1,3-pentadiene with Lochmann–Schlosser base: Bahl, J. J.; Bates, R. B.; Gordon, B., III. *J. Org. Chem.* **1979**, *44*, 2290. (b) Reaction of 1,3-pentadiene with potassium in THF/NEt_3: Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036. We used potassium (1.00 mol, in small pieces) under THF (800 mL)/NEt_3 (210 mL, 1.5 mol), added dropwise 1,3-pentadiene (220 mL, 2.20 mol, in 220 mL of THF, −10 °C, 1.5 h), and kept stirring at −10 to 0 °C for 3–4 h and then under reflux for 1–2 h to assure complete (!) consumption of the potassium.

[6] Preparation of **1a**: A solution of $BCl(NMe_2)_2$ (135 mL, 0.83 mol) in THF (150 mL) is added dropwise to potassium pentadienide[4] (prepared from potassium (1 mol) and piperylene (2.2 mol)) in THF (800 mL) at −78 °C. The mixture is warmed to room temperature, and stirring is continued for 2 h. Filtration and distillative workup gives **1a** in 74% yield (103.5 g); bp 75 °C/9 mbar.

[7] NMR data for (*E*)-**1a**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.30 (ddd, *J* = 16.78, 10.38, 10.07 Hz, 1H, 4-H), 5.98 (ddm, *J* = 14.95, 10.38 Hz, 1H, 3-H), 5.77 (dt, *J* = 14.95, 7.63 Hz, 1H, 2-H), 4.99 (dm, *J* = 16.8 Hz, 1H, 5-H-*trans*), 4.84 (dm, *J* = 10.07 Hz, 1H, 5-H-*cis*), 2.66 (s, 12H, Me), 1.74 (d, *J* = 7.63 Hz, 2H, 1-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 134.7, 129.8 (CH), 112.5 ($CH_2{=}$), 39.4 (Me), 21 (br, CH_2B); ^{11}B NMR (32.08 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ external) δ 33; NMR data for (*Z*)-**1a**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.76 (ddd, *J* = 16.78, 11.0, 10.08 Hz, 1H, 4-H), 5.92 ("t" m, *J* = 11.0 Hz, 1H, 3-H), 5.51 (dt, *J* = 11.0, 7.1 Hz, 1H, 2-H), 5.13 (dd, *J* = 16.78, 2.13 Hz, 1H, 5-H-*trans*), 5.02 (dm, *J* = 10.08 Hz, 1H, 5-H-*cis*), 2.66 (s, 12H, Me), 1.84 (d, *J* = 7.1 Hz, 2H, 1-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.8, 131.8, 127.1 (CH), 115.2 ($CH_2{=}$), 40.3 (Me), 17.5 (br, CH_2B); ^{11}B NMR (32.08 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ external) δ 33.

[8] NMR data for (*E*)-**2**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.30 (d "t", *J* = 16.80, 10.0 Hz, 1H, 4-H), 6.04 (ddm, *J* = 15.1, 10.0 Hz, 1H, 3-H), 5.76 (dtm, *J* = 15.1, 7.5, 1H, 2-H), 5.03 (dm, *J* = 16.8 Hz, 1H, 5-H-*trans*), 4.89 (dm, *J* = 10.0 Hz, 1H, 5-H-*cis*), 1.75 (d, *J* = 7.5 Hz, 2H, 1-H), 1.24 (s, 12H, Me). NMR data for (*Z*)-**2**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.63 (dddd, *J* = 17.0, 11.0, 10.1, 1.1 Hz, 1H, 4-H), 6.01 (ddm, *J* = 11.0, 9.5 Hz, 1H, 3-H), 5.58 (dt, *J* = 9.5, 8.0 Hz, 1H, 2-H), 5.15 (dm, *J* = 17.0 Hz, 1H, 5-H-*trans*), 5.06 (dm, *J* = 10.0 Hz, 1H, 5-H-*cis*), 1.84 (d, *J* = 8.0 Hz, 2H, 1-H), 1.24 (s, 12H, Me); ^{13}C NMR (for *E* and *Z*) (126 MHz, $CDCl_3$) δ = 137.5, 132.2, 131.7, 130.5, 129.1, 127.6 (CH), 116.3, 113.8 ($CH_2{=}$), 83.4 (*C*Me_2), 24.8 (Me), 16.5, 12.0 (br, CH_2B); ^{11}B NMR (32.08 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ external) δ 33.

[9] (a) Pelter, A.; Singaram, B.; Williams, L.; Wilson, J. W. *Tetrahedron Lett.* **1983**, *24*, 623. (b) Paetzold, P.; Boeke, B. *Chem. Ber.* **1976**, *109*, 1011. (c) Matteson, D. S.; Moody, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 3196.

[10] (a) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453. (b) Zaidlewicz, M. *J. Organomet. Chem.* **1985**, *293*, 139.

[11] NMR data for **4b**: ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (dd, *J* = 17.70, 10.30 Hz, 1H, 4-H), 5.98 (ddm, *J* = 15.42, 10.30 Hz, 1H, 3-H), 5.71 (d, *J* = 17.85, 1H, 5-H), 5.61 (dt, *J* = 15.87, 8.4 Hz, 1H, 2-H), 2.99 (q, *J* = 7.01 Hz, 8H, Me*C*H_2), 1.54 (d, *J* = 8.55 Hz, 2H, 1-H), 1.01 (t, *J* = 7.01 Hz, 12H, *Me*CH_2), 0.01 (s, 9H, $SiMe_3$); ^{13}C NMR (68 MHz, $CDCl_3$, −50 °C, $CDCl_3$) δ 142.6 (d), 132.1 (d), 131.1 (d), 130.1 (d, CHB), 40.7 (t, Me*C*H_2), 23.4 (t, CH_2Si), 14.7 (q, *Me*CH_2), −2.1 (q, $SiMe_3$); ^{11}B NMR (32.08 MHz, $CDCl_3$, $BF_3{\cdot}Et_2O$ external) δ 34.

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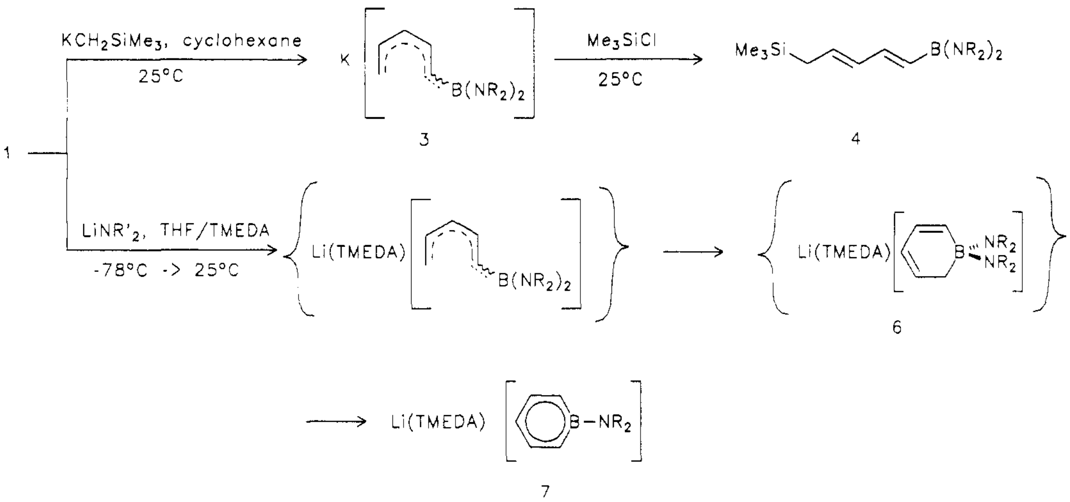
Scheme II



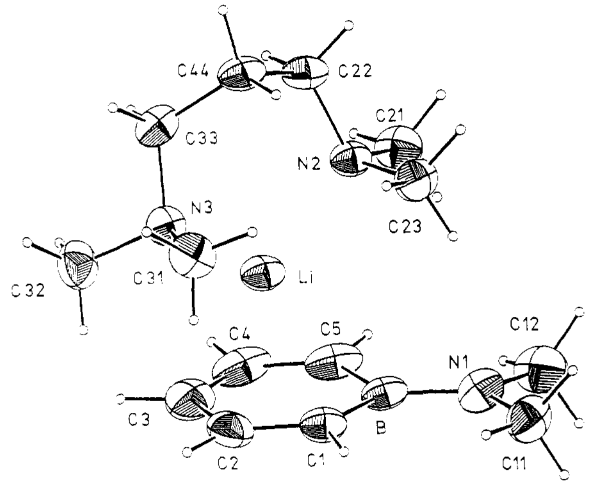
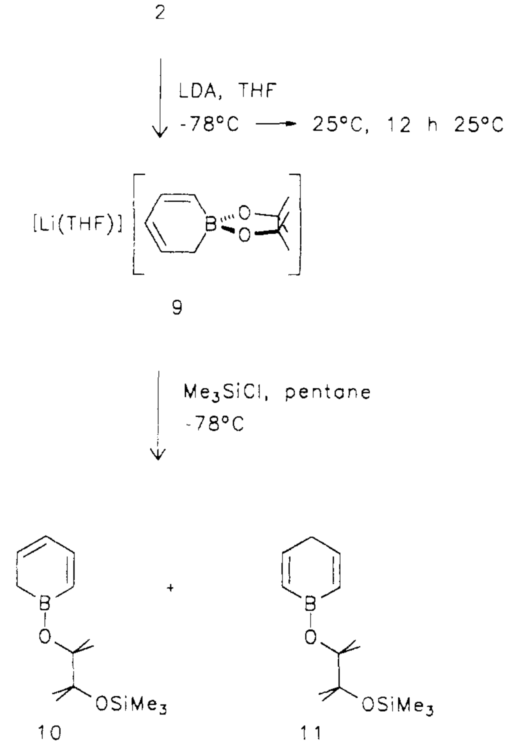


Figure 1. Molecular structure of [Li(TMPDA)](C_5H_5-$BNMe_2$) (**8**) (ORTEP plot at the 30% probability level). Selected bond distances (Å): Li-C(1) = 2.472(4), Li-C(2) = 2.382(4), Li-C(3) = 2.403(3), Li-C(4) = 2.493(3), Li-C(5) = 2.621(4), Li-B = 2.676(4), Li-N(1) = 3.773(4), B-N(1) = 1.448(2), C-N(1) = 1.442(2), B-C(1) = 1.506(1), B-C(5) = 1.525(2), C(1)-C(2) = 1.393(2), C(2)-C(3) = 1.388(2), C(3)-C(4) = 1.379(3), C(4)-C(5) = 1.375(3), Li-N(2) = 2.136(3), Li-N(3) = 2.187(2). Selected angles (deg): C(1)-B-C(5) = 112.6(1), B-C(1)-C(2) = 120.95(9), C(1)-C(2)-C(3) = 122.8(1), C(2)-C(3)-C(4) = 119.2(1), C(3)-C(4)-C(5) = 123.6(1), C(4)-C(5)-B = 120.8(2), C(1)-B-N(1) = 123.62(8), C(5)-B-N(1) = 123.8(1), C(11)-N(1)-C(12) = 112.2(1), C(11)-N(1)-B = 123.6, C(12)-N(1)-B = 124.0(1).

subsequent electrocyclization to give the intermediate borate **6**, and finally formation of boratabenzene salts [Li(TMEDA)]($C_5H_5BNR_2$) (**7a**,**b**).

The reaction rate decreases strongly with increasing size of the groups R and R′, that is in the series **1a**/**5a**–**c** and **1b**/**5b**,**c**; no reaction is observed for **1c**/**5c** or for **1a**–**c** with lithium 2,2,6,6-tetramethylpiperidide as base. With R′ smaller than R an exchange of the amido group takes place; for instance the combination **1b**/**5a** produces **7a**.[12] For practical reasons the combination **1a**/**5b** is most useful:

Scheme III



from 1 mol of potassium 40 g of spectroscopically (NMR) pure **7a**[13] can be obtained in one run.[14]

We also prepared the tetramethylpropylenediamine (TMPDA) compound [Li(TMPDA)]($C_5H_5BNMe_2$) (**8**)

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[12] Similar observations were made for the metalation of 1-(dialkylamino)-2,5-dihydro-1*H*-boroles with lithium amides: Herberich, G. E.; Hostalek, M.; Laven, R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 317.

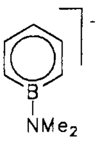
[13] NMR data for **7a**: ^1H NMR (500 MHz, [D_8]-THF) δ 7.04 (dd, *J* = 10.68, 6.71 Hz, 2H, 3-/5-H), 5.65 (dd, *J* = 10.70, 0.92 Hz, 2H, 2-/6-H), 5.50 (tt, *J* = 6.70, 0.91 Hz, 1H, 4-H), 2.69 (s, 6H, Me), 2.26 [s, 4H, CH_2 (TMEDA)], 2.11 [s, 12H, Me (TMEDA)]; ^{13}C NMR (68 MHz, [D_8]-THF, TMS) δ 134.4 (C-3,5), 110 (br, C-2,6), 99.7 (C-4), 58.7 [CH_2 (TMEDA)], 46.0 [Me (TMEDA)], 39.6 (Me); ^{11}B NMR (32.08 MHz, THF, 25 °C, BF_3·Et_2O external) δ 28.

[14] A solution of **1a** (103.5 g, 0.623 mol) in THF (500 mL) is added dropwise to $LiNEt_2$ (73.9 g, 0.93 mol) in THF/TMEDA (139 mL, 0.93 mol) at −78 °C. The mixture is warmed to room temperature within 3–4 h, and stirring is continued for 12 h at 25 °C. After removal of all volatiles *in vacuo*, hexane (400 mL) is added to precipitate a white powder consisting of $LiNEt_2$ and **7a**, which is filtered off. The solution is cooled to −30 °C, and pure **7a** crystallizes within 12 h. A second crop of pure **7a** may be isolated by extracting the mixture of $LiNEt_2$ and **7a** with pentane to give a total yield of 40.1 g (0.165 mol, 26.5%); mp 82 °C.

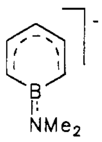
and obtained the first X-ray structure of a boratabenzene salt (Figure 1).[15]

The structure of **8** is that of a contact ion pair consisting of a Li(TMPDA) cation and a 1-(dialkylamino)boratabenzene anion. C–C bond lengths in the ring indicate delocalization. The distance B–C is longer than in borabenzene–pyridine (1.474 Å, average),[16] and the distance B–N is not much longer than in aminoboranes (1.41 Å).[17] We conclude that the resonance formula **B** for the 1-aminoboratabenzene ion predominates over formula **A**; in other words, the exocyclic amino group strongly perturbs the aromatic borabenzene system.

Metalation of **2** produces the labile spiroborate **9** as a white precipitate in good yield (ca. 70%).[18] It conforms to expectation that the analogous intermediate **6** in Scheme II is less stable and did not yield to direct observation. The spiroborate **9** tends to undergo ring-opening reactions, especially when attacked by electrophiles. With Me_3SiCl in hexane a 1:1 mixture of a bora-2,4- (**10**) and a bora-2,5-cyclohexadiene (**11**) forms. Both isomers are amenable to further modification, *i.e.* deprotonation to form the corresponding boratabenzene ion and substitution at boron. We are presently working on further variations of this synthetic theme.



A



B

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables of crystal data, crystallographic procedures, atomic positional and thermal displacement parameters, and bond lengths and bond angles for **7a** (9 pages). Ordering information is given on any current masthead page.

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[15] Crystal data for **8**: $C_{14}H_{29}N_3BLi$, $M = 257.16$, 3439 reflections (3° < θ < 28°) collected at 243 K on an Enraf-Nonius CAD4 diffractometer, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.585(8)$ Å, $b = 11.907(2)$ Å, $c = 17.033(3)$ Å, $\beta = 100.89(3)°$, $V = 1710(2)$ Å^3, $Z = 4$, $D_c = 0.999$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.7107$ Å, $\mu = 0.54$ cm^{-1}, final $R = 0.052$ ($R_w = 0.059$) for 2231 independent reflections ($I > 2\sigma(I)$) and 288 parameters.

[16] Boese, R.; Finke, N.; Henckelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. R.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644.

[17] A B–N distance of 1.41 Å is typical for aminoboranes: Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123. Cf. also B–N = 1.56 Å in $[Li(OEt_2)]_2[Ph(Me_2N)B{=}B(NMe_2)Ph]$: Moezzi, A.; Bartlett, R. A.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1082.

[18] NMR data for **9**: ^1H NMR (500 MHz, [D$_6$]-acetone) δ 6.13 (dd, J = 12.20, 5.00 Hz, 1H, 2-H), 5.92 (d, J = 12.20 Hz, 1H, 1-H), 5.85 (dt, 9.5, 4.60 Hz, 1H, 4-H), 5.62 (ddm, J = 9.5, 5.0 Hz, 1H, 3-H), 3.63 (m, 4H, THF), 1.79 (m, 4H, THF), 1.19 (dd, J = 4.60, 2.14 Hz, 2H, 5-H), 1.09 (s, 6H, Me), 1.06 (s, 6H, Me); ^{13}C NMR (126 MHz, [D$_6$]-acetone) δ 149.0 (br, CHB), 134.5, 131.4, 125.4 (CH), 78.3 (CMe_2), 26.3, 26.1 (Me), signal for CH_2B not found; ^{11}B NMR (32 MHz, [D$_6$]-acetone, 25 °C, $BF_3{\cdot}OEt_2$ external) δ 5.7.