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Communications

Borabenzene Derivatives. 33. 3,5-Dimethylborabenzene 1,3,4,5-Tetramethylimidazol-2-ylidene: The First Carbene Adduct of a Borabenzene[1]

Xiaolai Zheng and Gerhard E. Herberich*

Institut für Anorganische Chemie, Technische Hochschule Aachen, 52056 Aachen, Germany

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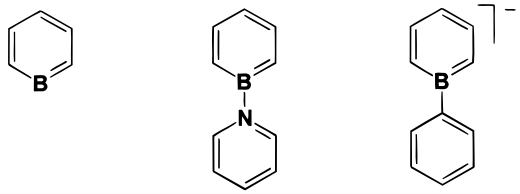
Summary: The stable carbene 1,2,3,5-tetramethylimidazol-2-ylidene forms an adduct with 3,5-dimethylborabenzene. This adduct ***8*** *can readily be made from the carbene and 1-chloro-3,5-dimethyl-2-(trimethylsilyl)-1,2-dihydroborinine (****6****) as colorless crystals. The structure of* ***8*** *is closer to that of the anion in* $NMe_3Ph(C_5H_5BMe)$ *(****9****) than to the structures of known betainic adducts. There is no noticeable conjugation between the borabenzene and the imidazol-2-ylidene moieties.*

Borabenzene **1** is a nonexistent aromatic heterocycle. The elusive nature of **1**, according to quantum chemistry calculations at different levels, is due to the presence of a low-lying in-plane σ-type LUMO which is essentially localized at the boron atom.[2] This highly reactive species, however, can be stabilized either by uncharged donors to afford neutral borabenzene−Lewis base adducts[3,4] (e.g., **2**[3a]) or by anionic groups to give boratabenzene ions[5,6] (e.g., **3**[5a]).



1 **2** **3**

Known neutral borabenzene adducts comprise a pyridine adduct[3a] and adducts with other nitrogen bases,[4] with trimethylphosphine,[4a] and with *tert*-butylisocyanide[4a] and include a thermally unstable dinitrogen adduct observed in matrix isolation[3b] and an enantiomerically pure pyridine adduct of "pinene-fused" borabenzene.[4c] In this communication we report on

(1) Part 32: Zheng, X.; Englert, U.; Herberich, G. E.; Rosenplänter, J. *Inorg. Chem*., submitted.

(2) (a) Karadakov, P. B.; Ellis, M.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Int. J. Quantum Chem.* **1997**, *63*, 441−449. (b) Cioslowski, J.; Hay, P. J. *J. Am. Chem. Soc.* **1990**, *112*, 1707−1710. (c) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733−737. (d) Raabe, G.; Schleker, W.; Heyne, E.; Fleischhauer, J. *Z. Naturforsch.* **1987**, *42A*, 352−360. (e) Raabe, G.; Heyne, E.; Schleker, W.; Fleischhauer, J. *Z. Naturforsch.* **1984**, *39A*, 678−681.

(3) (a) Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644−1654. (b) Maier, G.; Reisenauer, H. P.; Henkelmann, J.; Kliche, C. *Angew. Chem.* **1988**, *100*, 303; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 295−296.

(4) (a) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315−1318. (b) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1997**, *16*, 1501−1502. (c) Herberich, G. E.; Englert, U.; Ganter, B.; Pons, M.; Wang, R. *Organometallics* **1999**, *18*, 3406−3413.

(5) (a) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971**, *93*, 1804−5. (b) For a review of older work see: Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199−236.

(6) For leading references see: (a) Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329−6330. (b) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 466−473. (c) Herberich, G. E.; Englert, U.; Fischer, A.; Ni, J.; Schmitz, A. *Organometallics* **1999**, *18*, 5496−5501.

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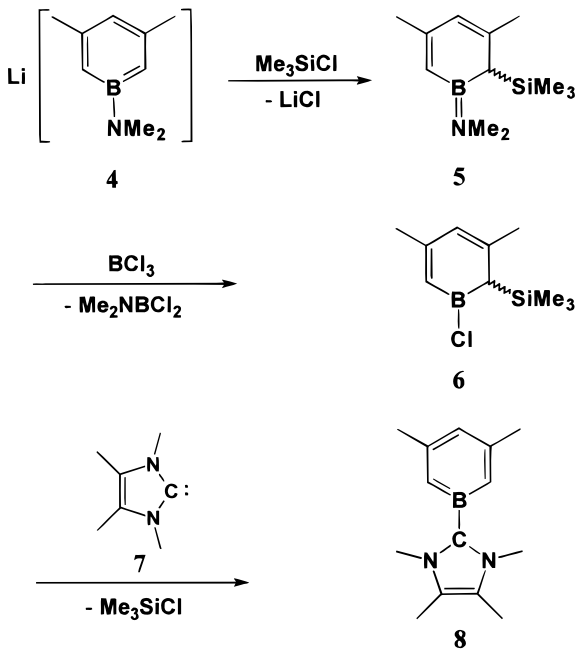
Scheme 1



the synthesis and characterization of the first borabenzene adduct with a carbene. Stable heterocyclic carbenes[7−9] are excellent σ-donors due to their singlet ground state nature. They are known to form adducts with a wide variety of Lewis acids, including several boranes.[8]

Our synthesis of a carbene borabenzene adduct is summarized in Scheme 1. The solvent-free lithium aminoboratabenzene **4**[6c] was silylated to give **5** as a distillable liquid.[10] Treatment of **5** with BCl_3 produced the highly reactive chloro compound **6**.[11] When a toluene solution of 1,3,4,5-tetramethylimidazol-2-ylidene[9] **7** was added to a toluene solution of **6** at ambient temperature, a white precipitate of adduct **8** formed immediately in high yield.[12] Recrystallization from hot toluene afforded colorless platelets of **8**, suitable for an X-ray structure determination.[13]

The molecule of **8** (Figure 1) in the crystal consists of a planar borabenzene ring and a planar imidazolylidene ring with an interplanar angle of 34.75(6)°.[15] The deviation from coplanarity is enforced by a repulsive interaction between the *N*-Me groups and the α-CH groups of the borabenzene ring. A comparison with the structures of the pyridine adduct **2**,[3a] the PMe_3 adduct,[4a] and the salt $NMe_3Ph(C_5H_5BMe)$[16] (**9**) shows, perhaps unexpectedly, that the bonding situation of the carbene adduct **8** is more similar to that in the anion of **9** than to that in other betainic adducts.[17] We relate this observation to the fact that the charge compensation in **8** is more remote than, for example, in **2**. The length of the excyclic bond C1−B [159.6(2) pm] is the same as the corresponding bond in **9** [159.9(2) pm] within the error of structural determination. This indicates that

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(7) (a) Carmalt, C. J.; Cowley, A. H. *Adv. Inorg. Chem.* **2000**, *50*, 1−32. (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91. (c) Arduengo, A. J., III. *Acc. Chem. Res.* **1999**, *32*, 913−921. (d) Bourissou, D.; Bertrand, G. *Adv. Organomet. Chem.* **1999**, *44*, 175. (e) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162.

(8) (a) Wacker, A.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.* **1999**, 789. (b) Wacker, A.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.* **1998**, 843. (c) Padilla-Martínez, I. I.; Martínez-Martínez, F. J.; López-Sandoval, A.; Giron-Castillo, K. I.; Brito, M. A.; Contreras, R. *Eur. J. Inorg. Chem.* **1998**, 1547. (d) Weber, L.; Dobbert, E.; Stammler, H.-G.; Neumann, B.; Boese, R.; Bläser, D. *Chem. Ber.* **1997**, *130*, 705. (e) Tamm, M.; Lügger, F. E.; Hahn, F. E. *Organometallics* **1996**, *15*, 1251. (f) Okada, K.; Suzuki, R.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2069. (g) Padilla-Martínez, I. I.; Rosalez-Hoz, M. de J.; Contreras R.; Kerschl, S.; Wrackmeyer, B. *Chem. Ber.* **1994**, *127*, 343. (h) Kuhn, N.; Henkel, G.; Kratz, T.; Kreutzberg, J.; Boese, R.; Maulitz, A. H. *Chem. Ber.* **1993**, *126*, 2041. (i) Alcaraz, G.; Reed, R.; Baceiredo, A.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1354.

(9) (a) Kuhn, N.; Kratz, Th. *Synthesis* **1993**, 561. (b) Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5531.

(10) Preparation of **5**: Me_3SiCl (3.8 g, 35 mmol) in THF (10 mL) was added dropwise to a solution of lithium 3,5-dimethyl-1-(dimethylamino)boratabenzene[6c] (3.74 g, 24.1 mmol) in THF (10 mL) at 0 °C. After the reaction mixture was stirred at ambient temperature for 2 h, all volatiles were removed under vacuum. Hexane (30 mL) was then added to the residue, and the white precipitate of LiCl was filtered off. Hexane was removed under vacuum, and condensation (70 °C, 10^{-2} mbar) afforded **5** (4.59 g, 86%) as a colorless oil. Anal. Calcd for $C_{12}H_{24}BNSi$: C, 65.15; H, 10.94; N, 6.33. Found: C, 64.88; H, 11.15; N, 6.31. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.68 (dd, J = 2.5, 1.5 Hz, 4-H), 5.67 (s, 6-H), 2.81 (s, NMe), 2.71 (s, NMe), 2.22 (s, 2-H), 1.96 and 1.90 (s, 3-/5-Me), −0.01 (s, $SiMe_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.6 (C-5), 146.6 (C-3), 121.9 (C-4), 120.5 (br, C-6), 39.6 (NMe), 38.6 (br, C-2), 38.4 (NMe), 26.2 and 25.6 (3-/5-Me), 0.2 ($SiMe_3$). ^{11}B NMR (160 MHz, $CDCl_3$, external $BF_3{\cdot}Et_2O$): δ 41.4. MS (70 eV): m/z (I_{rel}) 221 (20, M^+), 148 (30, $M^+ - SiMe_3$), 73 (100, $SiMe_3^+$).

(11) Preparation of **6**: A CH_2Cl_2 solution of boron trichloride (2.0 M, 8.6 mL, 17.2 mmol) was added dropwise to **5** (3.42 g, 15.5 mmol) in CH_2Cl_2 (40 mL) at −78 °C. The reaction mixture was slowly warmed to 0 °C, and stirring was continued for 2 h. After complete removal of the volatiles under reduced pressure, vacuum distillation (50−52 °C, 5 mbar) of the residue using a Vigreux column (10 mL) afforded **6** (3.01 g, 91%) as a pale yellow oil. Anal. Calcd for $C_{10}H_{18}BClSi$: C, 56.49; H, 8.53. Found: C, 56.64; H, 8.56. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.12 (s, 4-H), 6.00 (s br, 6-H), 3.34 (s br, 2-H), 2.14 and 2.06 (s br, 3-/5-Me), 0.09 (s, $SiMe_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 164.4 (br, C-5), 155.5 (br, C-3), 126.7 (br, C-6), 124.6 (C-4), 57.5 (br, C-2), 26.2 (3-/5-Me), 0.3 ($SiMe_3$). ^{11}B NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}Et_2O$): δ 57.5. MS (70 eV): m/z (I_{rel}) 212 (5, M^+), 73 (100, $SiMe_3^+$).

(12) Preparation of **8**: 1,3,4,5-Tetramethylimidazol-2-ylidene[9] (0.25 g, 2.01 mmol) in toluene (10 mL) was added to a solution of **6** (0.44 g, 2.07 mmol) in toluene (5 mL). A white precipitate formed immediately. The mixture was stirred at room temperature for 30 min, and hexane (20 mL) was then added to the reaction system. The solid formed was collected by filtration, washed with hexane (2 × 10 mL), and dried under high vacuum to give **8** (0.38 g, 83%) as an air- and moisture-sensitive colorless powder; mp 224−226 °C. A crystal suitable for X-ray diffraction work was grown by slowly cooling a saturated toluene solution of **8** from 80 °C to ambient temperature. Anal. Calcd for $C_{14}H_{21}BN_2$: C, 73.70; H, 9.28; N, 12.28. Found: C, 73.61; H, 9.18; N, 12.31. ^{1}H NMR (500 MHz, CD_2Cl_2, −40 °C): 6.25 (dd, J = 1.2, 0.6 Hz, 2-/6-H), 6.18 (t, J = 0.6 Hz, 4-H), 3.77 (s, 2 NMe), 2.25 (s, 4′-/5′-Me), 2.19 (s, 3-/5-Me). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, −40 °C): δ 160.4 (br, C-2′), 141.7 (C-3, 5), 126.4 (br, C-2, 6), 124.6 (C-4′,5′), 117.9 (C-4), 33.7 (2 NMe), 25.0 (4′-/5′-Me), 8.8 (3-/5-Me). ^{11}B NMR (160 MHz, CD_2Cl_2, external $BF_3{\cdot}Et_2O$, 20 °C): δ 23.9. MS (70 eV): m/z (I_{rel}) 228 (100, M^+), 213 (75, $M^+ - Me$), 198 (10, $M^+ - 2$ Me), 123 (4, $C_7H_{11}N_2^+$).

(13) (a) Crystal data for **8**: $C_{14}H_{21}BN_2$, colorless platelet, 0.55 × 0.50 × 0.15 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 1179.8(3) pm, b = 745.8(2) pm, c = 1597.6(5) pm, β = 108.82(2)°, V = 1.3307(6) nm^3, Z = 4, d_{calc} = 1.139 g cm^{-3}, μ = 4.70 cm^{-1}, $F(000)$ = 496. Data collection: Enraf-Nonius CAD4, Cu Kα radiation, graphite monochromator, $\omega-2\theta$ scans (4° < θ < 70°) at 180 K; 6417 reflections measured, 2506 unique reflections (R_{int} = 0.050) of which 1761 observed [$I > 2\sigma(I)$], no absorption correction applied. Structure solution and refinement:[13c] 238 parameters, R_1 = 0.047 and wR_2 = 0.101 for observed data, R_1 = 0.069 and wR_2 = 0.107 for all data, GOF = 0.945; largest peak in the final difference map, 0.36 × 10^{-6} e pm^{-3}; non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically. (b) Further details on the crystal structure determination are available on request from the Cambridge Crystallographic Data Center, on quoting the depository number CCDC-148125. (c) Sheldrick, G. E. *SHELX-97*, Program for Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, 1997.

(14) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(15) Max. deviation from best borabenzene plane 1.5(2) pm for C12; distance for C1 11.4(2) pm. Max. deviation from best carbene plane 0.4(2) pm for C3; distance for B 12.1(2) pm.

(16) Herberich, G. E.; Schmidt, B.; Englert, U. *Organometallics* **1995**, *14*, 471−480.

(17) Cf. especially the C−B bonds in **2** [146.5(4), 148.5(4) pm], $C_5H_5B{\cdot}PMe_3$ [147(1), 147(1) pm], **8** [149.1(3), 150.3(3), and 159.6(2) pm], and **9** [149.8(3), 150.3(3), and 159.9(2) pm].

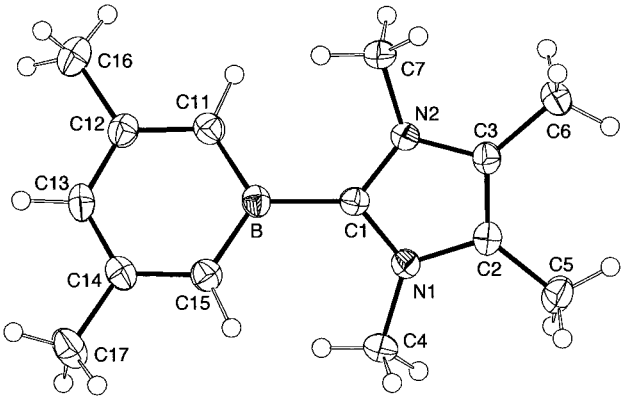

Figure 1. Platon plot[14] of **8** (at the 50% probability level). Selected bond distances (pm) and angles (deg): C1−B 159.6(2); imidazolylidene fragment, N1−C1 135.1(2), N2−C1 135.6(2), N1−C2 138.8(2), N2−C3 138.5(2), C2−C3 135.0(2); borabenzene fragment, C11−B 149.1(3), C15−B 150.3(3), C11−C12 139.9(2), C12−C13 140.4(2), C13−C14 139.2(2), C14−C15 139.6(2); N1−C1−N2 104.6(1), N1−C1−B 127.9(1), N2−C1−B 127.3(1), C11−B−C15 116.4-(2), C11−B−C1 120.8(2), C15−B−C1 122.7(2), C1−N1−C2 111.25(1), C1−N2−C3 110.93(1), N1−C2−C3 106.37(1), N2−C3−C2 106.81(1), C12−C11−B 120.50(2), C14−C15−B 119.60(2), C11−C12−C13 119.67(2), C12−C13−C14 123.11-(2), C13−C14−C15 120.69(2).

the conjugation between the two heteroaromatic rings, if there is any, is rather weak.

It may seem surprising that adduct **8** is colorless, while the pyridine aduct **2** is deep yellow to red, depending on the polarity of the medium. The color of **2** can be understood as resulting from a $\pi\pi^*$ transition; the HOMO is mainly the π_3 orbital of the borabenzene moiety, the LUMO is mainly the empty π_4 orbital of the pyridine moiety, and the HOMO/LUMO transition assumes considerable charge-transfer character.[3a] DFT calculations[18] reproduced the structure of **8** quite well.[19] The HOMO of **2** (−4.750 eV) and the HOMO of **8** (−4.377 eV) are of similar energy, but the LUMO energy of **2** (−2.440 eV) with the six-membered heterocycle pyridine is much lower than that of **8** (−0.324 eV) with the five-membered imidazolyl ring. The calculated HOMO/LUMO gaps of 2.31 eV for **2** and of 4.05 eV for **8** place the longest wavelength $\pi\pi^*$ transition of **2** (537 nm) into the visible region, while **8** (306 nm) is expected to be colorless, as observed.

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Supporting Information Available: Tables of bond distances and angles, anisotropic thermal parameters, and atomic coordinates for **8**.[13b] This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) DFT[18a] caculations were performed at the Becke3LYP[18b,c]/6-311G(d)[18d] level using the Gaussian 98 suite of programs.[18e] (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (d) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (e) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; and Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Cf. calculated distances: C1−B 1.579, C11−B 1.502, C1−N1 1.360, N1−C2 1.395, C2−C3 1.362 pm; the only exception is the interplanar angle of 45.8°, which corresponds to a soft normal mode and, not surprisingly, is much lower in the crystalline state.

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