Organometallics **2008,** *27,* 4844–4846

Diels−Alder Dimerization of a Boracyclohexadiene

Ian A. Cade,[†] Anthony F. Hill,[*,†] and Jörg Wagler[†,‡]

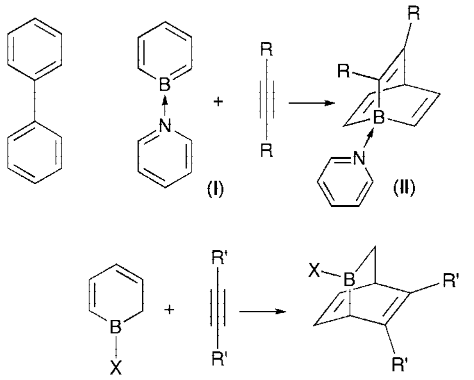
Research School of Chemistry, Institute of Advanced Studies, The Australian National University, Canberra, Australian Capital Territory 0200, Australia, and Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, D-09596 Freiberg, Germany

Received August 21, 2008

Summary: The 7-azaindole adduct of borabenzene is unstable, spontaneously undergoing a Diels−Alder type cycloadditive dimerization to provide a novel diboratricyclo barrelene cage.

The pyridine adduct of borabenzene (**I**, Scheme 1)[1] is isoelectronic with biphenyl and is thermally stable. Indeed, the stability of the N→B linkage underpins the considerable advances in the development of polycyclic variants with the promise of electro-optical applications.[2] The bond-localized Kekule description of the aromatic π system might suggest the possibility of borabenzenes entering into [4 + 2] Diels−Alder type cycloaddition reactions with suitable dienophiles. Remarkably, such processes have only recently been observed and require potent dienophiles (activated alkynes, benzyne, fumaronitrile) to provide 7-borabarrelenes (e.g., **II**; Scheme 1).[3] While boracyclohexadienes do not undergo self-dimerization, they have been shown to react with potent dienophiles via [4 + 2] cycloadditions (Scheme 1).[4]

Scheme 1. Alkyne−Borabenzene and Boracyclohexadiene [2 + 4] Cycloaddition[a] [3,4]



[a] Legend: R = CO$_2$Me, R′ = CF$_3$, X = OMe, NMe$_2$.

Following our isolation of the archetypal "metallaboratrane" [Ru(CO)(PPh$_3$){B(mt)$_3$}] (mt = 1-methyl-2-mercaptoimidazolide),[5a] in which a Ru→B dative bond is housed within a cage structure, we have managed to extend this class of compound to a range of other metallaboratranes based on osmium, rhodium, iridium, and platinum which are nevertheless limited to either two or three methimazolyl heterocycles buttressing the M→B bond.[5] In attempting to extend this chemistry beyond these cage structures, we have now turned our attention to other potential three-atom bridging groups that might constrain a Lewis acidic boron(III) center proximal to a metal center.[6] In this respect, the 7-azaindolyl group appeared a suitable candidate,[7] while the borabenzene motif offered the potential of serving as a novel Lewis acidic functionality. Notably, Fu has presented evidence in support of the boron center possessing electrophilic character that favors associative routes for nucleophilic substitution at boron.[1b,8]

1-Chloro-2-(trimethylsilyl)-1-boracyclohexadiene (**1**)[1b] serves as a convenient precursor to various borabenzene base adducts via nucleophile-induced elimination of Me$_3$SiCl, including pyridine adducts.[1,2] We find that the reaction of **1** with 7-azaindole results in the formation of a red solution that slowly

---

[*] To whom correspondence should be addressed. E-mail: a.hill@anu.edu.au.

[†] Australian National University.

[‡] Technische Universität Bergakademie Freiberg.

(1) (a) Boese, R.; Finke, N.; Henkelmann, J.; Maier, G.; Paetzold, P.; Reisenauer, H. P.; Schmid, G. *Chem. Ber.* **1985**, *118*, 1644. (b) Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315. (c) Fu, G. C. *Adv. Organomet. Chem.* **2001**, *47*, 101. (d) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 1804. (e) Siebert, W. *Adv. Organomet. Chem.* **1993**, *35*, 187.

(2) (a) Bosdet, M. J. D.; Jaska, C. A.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *Org. Lett.* **2007**, *9*, 1395. (b) Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1997**, *16*, 1501. (c) Jaska, C. A.; Emslie, D. J. H.; Bosdet, M. J. D.; Piers, W. E.; Sorensen, T. S.; Parvez, M. *J. Am. Chem. Soc.* **2006**, *128*, 10885. (e) Emslie, D. J. H.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1252.

(3) Wood, T. K.; Piers, W. E.; Keay, B. A.; Parvez, M. *Org. Lett.* **2006**, *8*, 2875.

(4) Maier, G.; Henkelmann, J.; Reisenauer, H. P. *Angew. Chem., Int. Ed.* **1985**, *24*, 1065.

(5) (a) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759. (b) Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Organometallics* **2003**, *22*, 4446. (c) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913. (d) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221. (e) Crossley, I. R.; Hill, A. F.; Humphrey, E. R.; Willis, A. C. *Organometallics* **2005**, *24*, 4083. (f) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2006**, *25*, 289. (g) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062. (h) Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656. (i) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2007**, *26*, 3891. (j) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2008**, *27*, 312. (k) Crossley, I. R.; Hill, A. F. *Dalton Trans.* **2008**, 201. (l) Crossley, I. R.; Foreman, M. R.; Hill, A. F.; Owen, G.; White, A. J. P.; Williams, D. J.; Willis, A. C. *Organometallics* **2008**, *27*, 381.

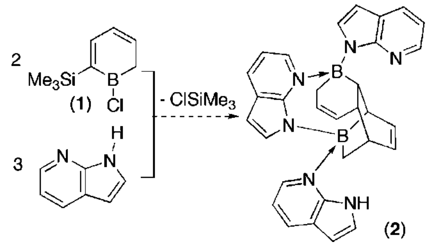
(6) For an alternative approach involving the coordination chemistry of (2-phosphinoaryl)boranes see: (a) Bontemps, S.; Gornitzka, H.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1611. (b) Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 12056. (c) Bontemps, S.; Sircoglou, M.; Bouhadir, G.; Puschmann, H.; Howard, J. A. K.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem. Eur. J.* **2008**, *14*, 731. (d) Sircoglou, M.; Bontemps, S.; Mercy, M.; Saffon, N.; Takahashi, M.; Bouhadir, G.; Maron, L.; Bourissou, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 8583. (e) Bebbington, M. W. P.; Bouhadir, G.; Bourissou, D. *Eur. J. Org. Chem.* **2007**, 4483. (f) Bontemps, S.; Bouhadir, G.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1481.

(7) (a) Hill, A. F.; Wagler, J. *Organometallics* **2008**, *27*, 2350. (b) Song, D.; Jia, W. L.; Wu, G.; Wang, S. *Dalton Trans.* **2005**, 433. (c) Saito, T.; Kuwata, S.; Ikariya, T. *Chem. Lett.* **2006**, *35*, 1224.

(8) Qiao, S.; Hoic, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **1996**, *118*, 6329.

10.1021/om800814n CCC: $40.75

Scheme 2. Formation of 2



decolorizes to provide the colorless product **2**[9] (Scheme 2). Within 8 min of mixing, the ^{1}H NMR spectrum of the reaction mixture indicates that all the azaindole (δ_H(C_6D_6) 12.30 (NH), br) has been consumed (replaced by broad resonances at δ_H 10.2, 8.5), while the ^{11}B{^{1}H} spectrum also indicates complete consumption of **1** (δ_B 53.6) and formation of an intermediate (δ_B 5.17, 2.59), the chemical shifts of which are suggestive of four-coordinate boron. Beyond these observations, the ^{1}H NMR spectra (7 min intervals over 80 min) were too complex to yield further information about the structures of intermediates. The red coloration is consistent with the initial formation of the desired azaindole adduct **III** of borabenzene, given that the simple pyridine adducts of borabenzene and boranaphthalene have absorptions (472 and 486 nm, respectively) corresponding to charge transfer from the boraarene-centered HOMO to the pyridine-centered LUMO.[1a] Simple pyridine adducts are, however, stable under these conditions, in contrast to the case for the initial azaindole adduct.

The nature of the final colorless product **2** did not follow unequivocally from spectroscopic and elemental composition data. Accurate mass spectrometry (ESI-MS) indicated a composition corresponding to [H(azaindole)$_3$(borabenzene)$_2$]$^+$; however, the ^{1}H and ^{13}C{^{1}H} spectra were cluttered and somewhat uninformative, though they eventually yielded to analysis (see Supporting Information), while the ^{11}B{^{1}H} NMR spectrum comprised two poorly resolved resonances (δ_B ca. 4.8, 5.3, hhw = 830 Hz) of little diagnostic value, beyond suggesting on the basis of chemical shift that the boron centers were four-coordinate.

The identity of **2** was ultimately established by a crystallographic study, the results of which are summarized in Figure 1.[9b]

The asymmetric unit includes two independent molecules of the same diastereomer of **2** (enantiomers generated by $P2_1/c$ symmetry), the geometric features of which are comparable. The core of the structure comprises an annulated barrelene motif resulting from the [4 + 2] combination of two borahexadiene units, the boron centers of which are appended by a bridging azaindolide (B3, B4) and terminal azaindole (B4) and azaindolide (B3) heterocycles. Bond lengths and angles within the cage structure are unremarkable, with those between C34−C35 (1.327(3) Å) and C39−C40 (1.319(3) Å) corresponding to double bonds and the remaining carbon and boron atoms adopting tetrahedral sp^3 geometries. Some strain associated with the bridging azaindolide group is indicated by the following (i) the dihedral angle B4−N10−N9−B3 (14.8°) displaces B3 and B4 to opposite sides of the azaindolyl plane; (ii) the B4−N10−C55 (135.1(2)°) and B3−N9−C55 (129.4(2)°) angles are each opened relative to the internal references provided by B3−N7−C48 (126.6(2)°) and B4−N11−C62 (126.1(2)°), in which the heterocycles are bound to sp^3 boron via nitrogen in the 1- (pyrrolyl) or 7-position (pyridine). In each case, the dative bonds between the pyridine donors and boron are significantly longer than the covalent pyrrolyl−boron bonds.

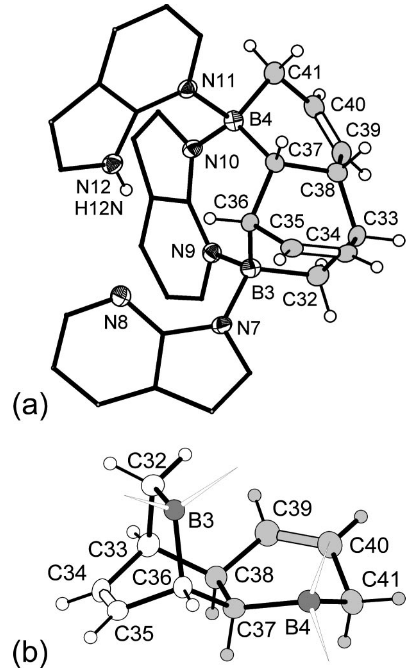


Figure 1. (a) Molecular structure of **2** in the crystal of **2**$\cdot$0.5CH$_2$Cl$_2$ (50% displacement ellipsoids, 7-azaindolyl groups simplified, CH$_2$Cl$_2$ molecules omitted). (b) Alternative view of the (B3)-borabarrelene core of **2** with constituent boracycles indicated in white and light gray. Selected bond lengths (Å): N7−B3 = 1.565(3), N9−B3 = 1.641(3), N10−B4 = 1.576(4), N11−B4 = 1.660(4).

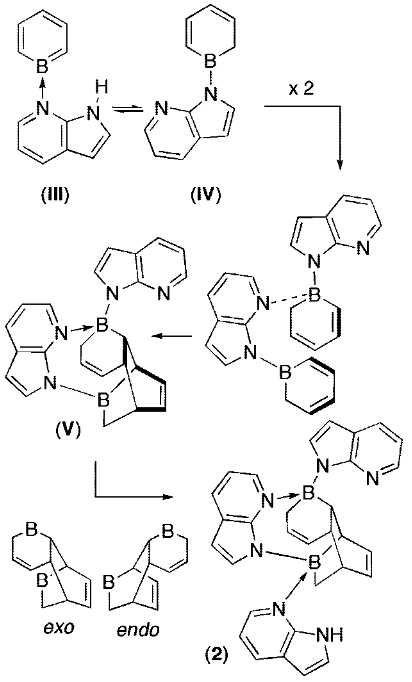
The mechanism by which **2** forms calls for comment in that (i) the pyridine adduct of borabenzene does not spontaneously cyclodimerize[1] and (ii) potent dienophiles undergo 1,4-addition with borabenzenes while the skeleton of **2** arises from 2,5-addition. We therefore suggest that the pyrrolic hydrogen of the initially formed azaindole adduct **III** (Scheme 3) transfers to the 2-position of the borabenzene to provide the boracyclohexadiene **IV**. Precedent for such a process has recently been provided by Piers, who has described the 1,2-addition of pyridinium chloride to the pyridine adduct of borabenzene.[10] The electron-withdrawing nature of the azaindolyl group presumably activates one molecule in the role of dienophile to

---

(9) (a) Preparation of **2**: a solution of 2-(trimethylsilyl)-1-chloroboracyclohexadiene (2:1 mixture of 2,4- and 2,5-isomers, 0.184 g, 1.01 mmol) in diethyl ether (8 mL) was treated with 7-azaindole (0.180 g, 1.52 mmol) under an atmosphere of dry purified dinitrogen. A colorless precipitate began to form after 40 min, while the initial red coloration faded over a period of 16 h to provide a colorless solution, the concentration of which afforded a white solid which was isolated by filtration and recrystallized from a mixture of dichloromethane and hexane as a CH$_2$Cl$_2$ hemisolvate. N.B.: although the reaction proceeds in essentially quantitative spectroscopic yield, losses attend removal by fractional recrystallization or sample washing (diethyl ether) of residual 7-azaindole. Yield: 0.101 g (41%). Anal. Found: C, 70.16; H, 5.30; N, 15.24. Calcd. for $C_{31}H_{28}B_2N_6(CH_2Cl_2)_{0.5}$: C, 68.95; H, 5.33; N, 15.32. ESI-MS (low res): *m/z* 507.1 [HM]$^+$, 389.1 [HM−azaindole]$^+$, 273.1 [HM−2(azaindole)]$^+$. ESI-MS (high res): acc mass (calcd for $^{12}C_{31}{}^1H_{29}{}^{11}B_2{}^{14}N_6$) *m/z* 507.270 093 (507.263 981). NMR (CDCl$_3$, 25 °C): ^{11}B{^{1}H} δ_B 4.8, 5.3. For ^{1}H and ^{13}C{^{1}H} data (HMQC, HSBC, DQF-COSY) see the Supporting Information. (b) Crystal data for **2**$_2\cdot$CH$_2$Cl$_2$: $C_{63}H_{58}B_4Cl_2N_{12}$, M_r = 1097.35, T = 100(2) K, colorless needle, 0.43 × 0.08 × 0.04 mm, monoclinic, space group $P2_1/c$, a = 10.4817(2) Å, b = 30.2472(9) Å, c = 16.7978(5) Å, β = 98.561(2)°, V = 5266.3(2) Å^3, Z = 4, ρ_{calcd} = 1.384 Mg m^{-3}, μ(Mo Kα) = 0.181 mm^{-1}, 46 070 collected reflections, 9243 unique reflections, R1 ($I > 2\sigma(I)$) = 0.0546, wR2 = 0.1295 (F^2 refinement for all 5997 unique reflections, $2\theta_{max}$ = 50.0°), 748 parameters, CCDC 698269.

(10) Ghesner, I.; Piers, W. E.; Parvez, M.; MacDonald, R. *Chem. Commun.* **2005**, 2480.

Scheme 3. Suggested Mechanism for the Formation of 2



a second, resulting in the observed regiochemistry of addition. The electrophilic three-coordinate boron center that remains in the initially formed cycloadduct **V** then captures a third (free) azaindole to provide the final product. As noted above, the boracyclohexadienes XBC_5H_6 (X = F, Cl, Br, OMe, OH, NMe_2) have been previously reported and do not dimerize via cycloaddition, although Diels–Alder reactions ensue (for X = OMe, NMe_2) with the superlative dienophile hexafluorobut-2-yne.[4] Thus, the azaindolyl group appears to be unusual in activating **IV** toward cycloaddition. Alternatively, the pendant pyridyl group on one molecule of substrate might in principle coordinate to the boron of a second, thereby assisting in preorganizing the two components for cycloaddition. The templation of the cycloaddition would thereby account for the less commonly observed exo regiochemistry that is adopted in the case of **2**.

While our initial aim of obtaining azaindole–borabenzene for applications in coordination chemistry was confounded by the formation of **2**, we note that the topology of **2** (and presumably it is conjugate base) appears to be well suited for chelation of various metals, a feature we are currently exploring.

Acknowledgment. This work was supported by the Australian Research Council (DP0771497) and through a fellowship within the Post-Doctoral Programme of the German Academic Exchange Service (to J.W.). We are grateful to Professor Gottfried Otting for helpful discussion relating to the NMR characterization of **2**.

Supporting Information Available: A CIF file giving full details of the crystal structure determination of **2**·$0.5CH_2Cl_2$ (CCDC 698269) and text and a figure giving a discussion of the NMR characterization of **2** (HMQC, HSBC, DQF-COSY). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800814N