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# 1-Borabarrelene Derivatives via Diels–Alder Additions to Borabenzenes

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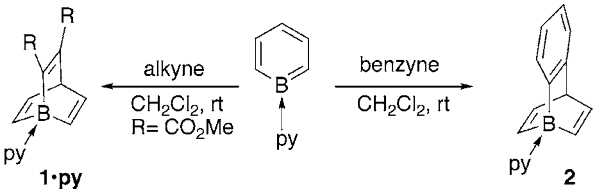
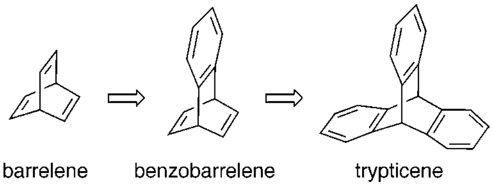
## ABSTRACT



**Borabenzene reacts with strong dienophiles such as dimethylacetylenedicarboxylate or benzyne to afford substituted borabarrelenes and borabenzobarrelene, respectively. The resultant Diels–Alder adducts display high stability due to increased Lewis acidity at boron.**

Barrelene[1] and benzobarrelene[2] are parent compounds in a family of hydrocarbons with highly directional bicyclic cores that comprise the iptycenes, of which trypticene is an example. Although they have long been of theoretical interest, they and their derivatives have recently found application as ROMP monomers[3] and as photoactive building blocks in fluorescent materials.[4] The incorporation of heteroatoms into such hydrocarbon frameworks represents a means to alter the photophysical properties of the group and potentially provide bonding handles for further chemistry.



Although 1-elementa derivatives of both barrelenes and trypticenes have been made using members of groups 14[5] and 15,[6] examples from group 13 are to our knowledge unknown.[7] Such compounds might be expected to possess enhanced Lewis acidity over typical triaryl boranes because of the pyramidal geometry enforced at boron by the [2.2.2] bicyclic core of the molecule,[8] providing linkages strong enough to sustain macromolecular structures.[9] Because iptycenes are typically prepared via Diels−Alder (DA) reactions, we surmised that the borabarrelene framework may be accessible via such a methodology. Although bora- and boratabenzenes have been known for many years,[10] it appears that their susceptibility to DA chemistry has not been investigated,[11] despite the fact that the HOMO of the pyridine

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[1] (a) Zimmerman, H. E.; Grunewald, G. L.; Paufler, R. M.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 2330. (b) Taylor, G. N. *J. Org. Chem.* **1972**, *37*, 2904. (c) Cossu, S.; Battaggia, S.; De Lucchi, O. *J. Org. Chem.* **1997**, *62*, 4162.

[2] (a) Friedman, L.; Lindow, D. F. *J. Am. Chem. Soc.* **1968**, *90*, 2329. (b) Johnson, R. P.; Exarchou, A.; Jefford, C. W.; Hahn, R. C. *J. Org. Chem.* **1977**, *42*, 3758. (c) Pu, L.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 1351.

[3] (a) Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138. (b) Wagaman, M. W.; Grubbs, R. H. *Synth. Met.* **1997**, *84*, 327.

[4] See, for example: Chen, Z.; Amara, J. P.; Thomas, S. W.; Swager, T. M. *Macromolecules* **2006**, *39*, 3202.

[5] (a) Dam, M. A.; Akkerman, O. S.; de Kanter, F. J. J.; Bickelhaupt, F.; Veldman, N.; Spek, A. L. *Chem.−Eur. J.* **1996**, *2*, 1139. (b) Dam, M. A.; Hoogervorst, W. J.; de Kanter, F. J. J.; Bickelhaupt, F.; Spek, A. L. *Organometallics* **1998**, *17*, 1762.

[6] (a) Ashe, A. J., III; Bellvill, D. J.; Friedman, H. S. *Chem. Commun.* **1979**, 880. (b) Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693. (c) Moores, A.; Ricard, L.; LeFloch, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4940.

[7] BN analogues of barrelene have been studied computationally: Zhang, J.; Zhang, S.; Li, Q. S. *Chem. Phys. Lett.* **2005**, *407*, 315.

[8] (a) Yasuda, M.; Yoshioka, S.; Yamasaki, S.; Somyo, T.; Chiba, K.; Baba, A. *Org. Lett.* **2006**, *8*, 761. (b) Livant, P. D.; Northcott, D. J. D.; Shen, Y.; Webb, T. R. *J. Org. Chem.* **2004**, *69*, 6564.

[9] (a) Wagner, C. E.; Shea, K. J. *Org. Lett.* **2001**, *3*, 3063. (b) Wagner, C. E.; Shea, K. J. *Org. Lett.* **2004**, *6*, 313.

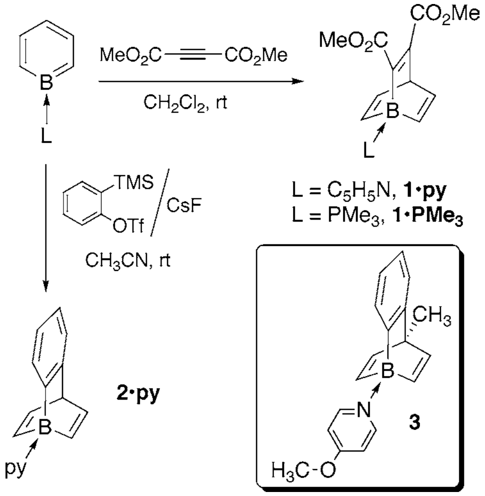
[10] (a) Herberich, G. E.; Ohst, H. *Adv. Organomet. Chem.* **1986**, *25*, 199. (b) Fu, G. C. *Adv. Organomet. Chem.* **2001**, *47*, 101. (c) Fu, G. C. *J. Org. Chem.* **2004**, *69*, 3245.

10.1021/ol061201w CCC: $33.50

adduct of borabenzene (see Supporting Information) is associated with the boron containing heterocycle and has the appropriate symmetry to engage in a regiochemical DA reaction.

Accordingly, reactions of pyridine and trimethylphosphine-stabilized borabenzenes, prepared by the method of Fu et al.,[12] with the strong dienophile dimethylacetylenedicarboxylate proceed smoothly at room temperature to afford the 1-borabarrelene products **1·py** and **1·PMe$_3$** (Scheme 1). Their formation was indicated spectroscopically by a characteristic triplet of triplets for the bridgehead proton at 5.3−5.5 ppm and an upfield shift of the $^{11}B\{^{1}H\}$ resonance of about ≈35 ppm in comparison to those associated with the borabenzene precursors. The $^{11}B\{^{1}H\}$ chemical shifts of −0.6 ppm for **1·py** and −16.1 ppm for **1·PMe$_3$** are in the range associated with neutral, four-coordinate boron centers with these Lewis bases.[13] Light orange compounds **1** are air and moisture tolerant and can be purified via column chromatography and recrystallization or sublimation, affording them in 90% isolated yield.

**Scheme 1**



Use of a somewhat more aggressive dienophile, in situ generated benzyne,[14] allows access to the 1-borabenzobarrelene **2·py** in moderate (23%) yield using the protocol shown in Scheme 1. Given the surfeit of aromatic protons in this derivative, the $^{1}H$ NMR spectrum is complex, but the signature triplet of triplets pattern for the bridgehead proton at 5.09 ppm and a $^{11}B\{^{1}H\}$ signal at 0.1 ppm are indicative of successful installation of the benzyne moiety.

These structural assignments were augmented by X-ray structural determinations of both **1·py** and a derivative of **2·py** prepared from *p*-$MeC_5H_4B\leftarrow NC_5H_4$-*p*-OMe (**3**, inset Scheme 1). All attempts to obtain suitable crystals of **2·py** met with failure, so the more well-behaved analogue **3** was prepared.[15] Thermal ellipsoid Crystalmaker diagrams of **1·py** and **3** are shown in Figures 1 and 2, respectively, along with selected metrical data.

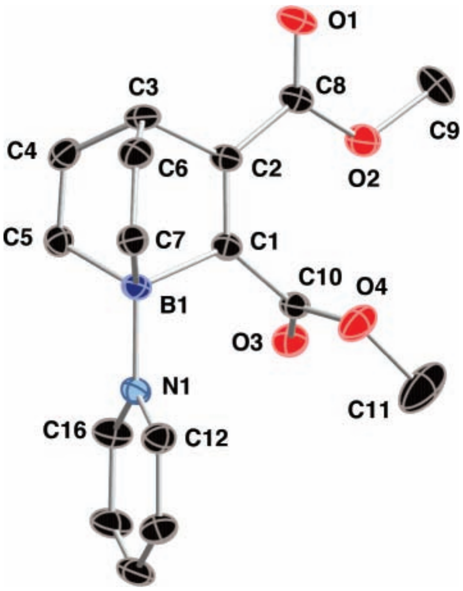


**Figure 1.** Thermal ellipsoid diagram of **1**·py (50%), with hydrogens omitted. Selected bond distances (Å): B(1)−N(1), 1.584(3); B(1)−C(1), 1.646(3); B(1)−C(5), 1.624(3); B(1)−C(7), 1.616(3); C(1)−C(2), 1.348(3); C(4)−C(5), 1.322(3); C(6)−C(7), 1.326(3). Selected bond angles (deg): C(1)−B(1)−C(5), 103.01(15); C(1)−B(1)−C(7), 103.35(17); C(5)−B(1)−C(7), 105.66(17).

The highly constrained nature of the borabarrelene core of these molecules is apparent in the pyramidalization

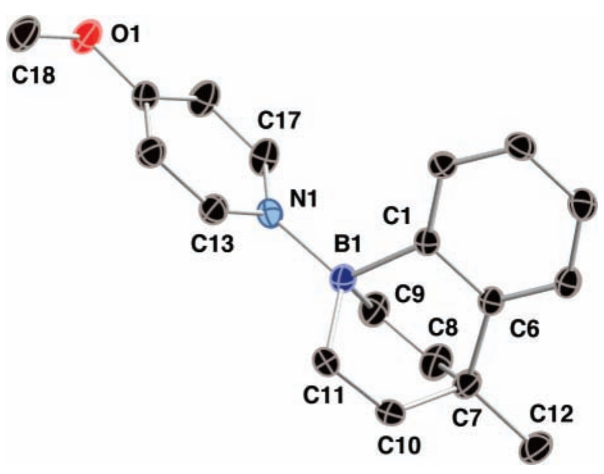


**Figure 2.** Thermal ellipsoid diagram of **3** (50%), with hydrogens omitted. Selected bond distances (Å): B(1)−N(1), 1.589(2); B(1)−C(1), 1.630(2); B(1)−C(9), 1.619(2); B(1)−C(11), 1.617(2); C(1)−C(6), 1.412(2); C(8)−C(9), 1.325(2); C(10)−C(11), 1.328(2). Selected bond angles (deg): C(1)−B(1)−C(9), 103.27(12); C(1)−B(1)−C(11), 103.56(12); C(9)−B(1)−C(11), 105.00(14).

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[11] DA reactions with related boracycles: Maier, G.; Henkelmann, J.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1065.

[12] Hoic, D. A.; Wolf, J. R.; Davis, W. M.; Fu, G. C. *Organometallics* **1996**, *15*, 1315.

[13] Kidd, R. G. In *NMR of the Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic: London, 1983; Vol. 2.

[14] Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.

observed at boron; the sums of the C−B−C angles are 311.9(3)° for **1·py** and 311.7(2)° for **3**. This high level of pyramidalization compares to that observed for several pyridine adducts of the borane $B(C_6F_5)_3$ ($\Sigma_{C-B-C} \approx 333°$[16]) and is significantly more severe than another constrained borane−pyridine adduct, 2-spiro-1-boraadamantane ($\Sigma_{C-B-C} \approx 328.3°$[8b,17]). Accordingly, the B−N distances of 1.584(3) Å (**1·py**) and 1.589(2) Å (**2·py**) are the shortest such bond lengths so far observed in borane−pyridine adducts; the average B−N distance for 33 adducts in the Cambridge Structural Database[18] is 1.650 Å. The majority of these distances falls in the 1.60−1.69 Å range; one example shows a distance comparable to the present cases. The highly constrained 1,2,3-triphenylborirane derivative reported by Denmark et al. exhibits a distance of 1.594 Å.[19]

Taken together, these metrical data suggest that the pyridine ligands in the 1-borabarrelenes are strongly bound to the forcibly pyramidalized boron centers. This notion is supported by the observed thermal stability of the compounds and our inability to induce ligand exchange. For example, heating solutions of **1·py**, **1·PMe$_3$**, or **2·py** in the presence of excess $d_5$-pyridine to temperatures of up to 200 °C in toluene solution did not lead to production of free proteo pyridine or $PMe_3$. Indeed, the spectra indicated that the compounds were stable under these conditions.

DSC/TGA analysis of solid samples of the three compounds indicated thermal stability to ≈210 °C (Figure 3).

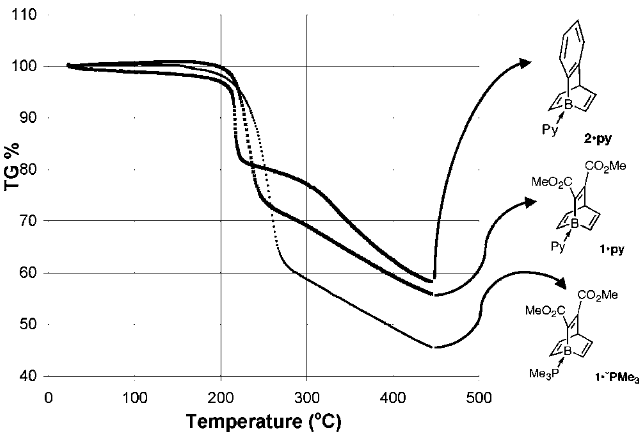
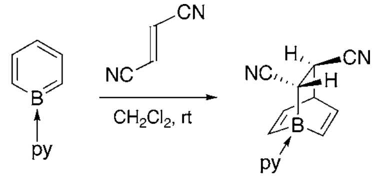


**Figure 3.** Thermal gravimetric analysis of compounds **1**·py, **1**·PMe$_3$, and **2**·py. Melting points for the three compounds as measured by differential scanning calorimetry are 222 °C (**1**·py), 162 °C (**1**·PMe$_3$), and 216 °C (**2**·py).

Compounds **1** undergo ill-defined mass loss beginning at 222 °C; for **1·py**, this is the melting point of the compound, whereas **1·PMe$_3$** melts well before this temperature regime (162 °C). Although the mass loss for **1·py** of ≈27% is consistent with that expected for dissociation of pyridine (26.7%), it occurs over a wide temperature range. The situation is even less clear for **1·PMe$_3$**, which loses ≈38% of its mass over a 60° temperature range; this value is between that expected for loss of $PMe_3$ (25.8%) or $MeO_2CC{\equiv}CCO_2Me$ (48.0%) and may indicate competing exothermic decomposition processes. Compound **2·py**, on the other hand, melts at 216 °C before rapidly losing ≈14% of its mass in an exothermic process; this is close to the 11.3% reduction expected upon loss of acetylene, suggesting that retro DA expulsion of HC≡CH is favored over pyridine dissociation.

**Scheme 2**



**4·py**

Given the Lewis acidic nature of the boron center in the borabenzene “dienes”, the mechanism of the DA cycloaddition process could conceivably proceed via a nonconcerted pathway.[20] This question was probed by carrying out a reaction between borabenzene pyridine and *trans*-1,2-dicyanoethylene, which proceeded rapidly at room temperature (Scheme 2). The reaction produced a single diastereomer, which was assigned the structure **4·py** on the basis of NMR spectroscopy and X-ray crystallographic analysis, which clearly demonstrates retention of the trans configuration in the dienophile. Figure 4 shows a thermal ellipsoid plot of **4·py**, along with selected metrical data; these data do not differ significantly from those discussed above for **1·py** and

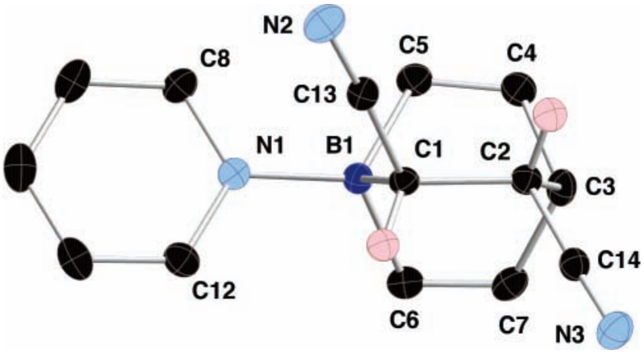


**Figure 4.** Thermal ellipsoid diagram of **4**·py (50%), with hydrogens omitted. Selected bond distances (Å): B(1)−N(1), 1.586(2); B(1)−C(1), 1.699(2); B(1)−C(5), 1.603(2); B(1)−C(6), 1.595(2); C(1)−C(2), 1.560(2); C(4)−C(5), 1.333(2); C(6)−C(7), 1.334(2). Selected bond angles (deg): C(1)−B(1)−C(5), 104.8(1); C(1)−B(1)−C(6), 102.6(1); C(5)−B(1)−C(6), 108.7(1). Selected torsion angle: C(13)−C(1)−C(2)−C(14), 110.7(1).

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(15) The requisite boracyclic precursor to $p$-$MeC_5H_4B{\leftarrow}NC_5H_4$-$p$-OMe was prepared using a methodology described in: Emslie, D. J. H.; Piers, W. E.; Parvez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1251.

(16) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1.

(17) Mikhailov, B. M.; Cherkasova, K. L. *Zh. Obshch. Khim.* **1972**, *42*, 128.

(18) The Cambridge Structural Database; Version 5.27, November 2005.

**3**, apart from a lengthened C(1)−C(2) distance resulting from its single-bond nature. Notably, treatment of **4·py** with dimethylacetylenedicarboxylate results in slow conversion to **1·py**, indicating the reversible nature of the addition of *trans*-1,2-dicyanoethylene to a borabenzene pyridine.

In conclusion, we have discovered a new mode of reactivity for the borabenzene family of heterocycles, which leads to highly Lewis acidic 1-borabarrelene and 1-borabenzobarrelene frameworks. The compounds are remarkably thermally stable toward loss of the stabilizing Lewis base ligand, suggesting these compounds might be viable building blocks for oligomeric materials. This stability is also manifested in the observation that exposure of **2·py** to ruthenium-based olefin metathesis catalysts[21] does not lead to ROMP of this monomer, in contrast to the situation observed in all-carbon analogues.[3] Nonetheless, the facility of the route into these compounds reported here opens the opportunity to explore the chemistry and applications of these compounds further as well as the preparation of other boron-containing frameworks; this work is ongoing.

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**Supporting Information Available:** Experimental procedures, characterization data, and representative NMR spectra for all new compounds (15 pages). Crystallographic information files (.cif) for **1**·py, **3**, and **4**·py are also included and have been deposited into the Cambridge Crystallographic Data Center under the reference numbers CCDC 605945−605946 for **1**·py and **3** and 607628 for **4**·py. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Denmark, S. E.; Nishide, K.; Faucher, A.-M. *J. Am. Chem. Soc.* **1991**, *113*, 6675.

(20) Hermitage, S.; Howard, J. A. K.; Jay, D.; Pritchard, R. G.; Probert, M. R.; Whiting, A. *Org. Biomol. Chem.* **2004**, *2*, 2451.

(21) (a) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (b) Romero, P. E.; Piers, W. E.; McDonald, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6161.