

Aromatic Stabilization of the Triarylborirene Ring System by Tricoordinate Boron and Facile Ring Opening with Tetracoordinate Boron¹

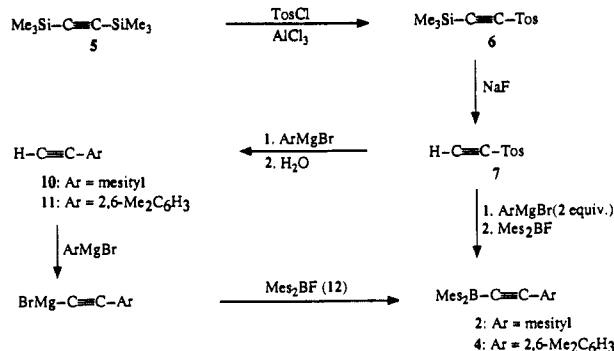
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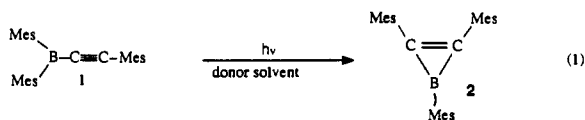
Abstract: To remove uncertainties in the apparent C=C and B—C bond lengths of the borirene ring, as previously estimated from an X-ray crystallographic analysis of trimesitylborirene, the unsymmetrically substituted 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene was prepared by the photorearrangement of ((2,6-dimethylphenyl)ethynyl)dimesitylborane. With such an unsymmetrical borirene there was no disorder in the identity of the ring atoms, and all three ring atom separations could be unambiguously assigned as follows: C=C, 1.380 Å; C₁—B, 1.450 Å; and C₂—B, 1.464 Å. Compared with the reported C=C bond length in cyclopropene (1.304 Å), the C=C bond in the borirene has been lengthened by 0.08 Å, and compared with the reported C—B bond length in trivinylborane (1.558 Å), ring C—B bonds have been shortened by an average of 0.10 Å. These altered bond lengths are fully consistent with those expected if the two ring π -electrons are extensively delocalized among the three sp²-hybridized ring atoms. Therefore, the borirene ring can truly be considered as a Hückel aromatic nucleus. In order to corroborate that cyclic conjugation led to C—C bond lengthening, the open-chain precursor to the borirene ring, namely dimesityl(mesitylethynyl)borane was also examined by X-ray crystallography. In this system the C=C bond showed no unusual lengthening and hence gave no indication of significant conjugation with the tricoordinate boron. When the tricoordinate boron of the borirene ring becomes tetracoordinate by ligation with an amine, such as pyridine, or a sterically suitable alcohol like MeOH or EtOH, the borirene ring is promptly ruptured and, in the presence of a proton source, irreversibly converted into an acyclic borinic ester. Such rupture of the borirene ring by pyridine can be monitored by electronic and multinuclear NMR spectroscopy. These observations corroborate the role of the available 2p_z-orbital on sp²-hybridized boron in stabilizing the borirene ring.

The π -electron delocalization between tricoordinate boron and sp²-hybridized carbon has been especially manifest in the properties of boracyclopolyenes,⁵ where it can produce, in turn, the relative stability of the borepins⁶ or the heightened reactivity of the boroles.⁷ These electronic effects could be attributed to the Hückel aromaticity and antiaromaticity, respectively, of the borepin and borole ring systems.⁸ A natural corollary of the Hückel theory is that the borirene or boracyclopropane ring system ought to possess stabilizing π -electron delocalization and hence should be capable of existing, despite its considerable ring strain.⁹ Indeed, within the last seven years, several syntheses of borirenes have been reported that involve thermal ring closures leading to non-crystalline products.¹⁰ On the basis of mass spectral and multinuclear NMR data, such products were assigned structures as borirene derivatives.¹¹

Scheme I



In order both to verify the existence of the borirene structure and to assess the extent of any π -electron delocalization in such a ring, we sought a route to borirenes that could yield solid derivatives suitable for X-ray crystal structure determination. Such a method was found in the photoisomerization of sterically hindered diaryl(arylethynyl)boranes.¹² Thus, the irradiation of dimesityl(mesitylethynyl)borane (**1**) at 300 nm in donor-containing solvents led to a clean isomerization to the crystalline trimesitylborirene (**2**) (eq 1, Mes = mesityl = 2,4,6-trimethylphenyl).¹³



From the X-ray structure analysis of **2** it appeared that the BC₂ array of borirene ring atoms formed an equilateral triangle with

(12) The photoisomerization of a diaryl(arylethynyl)borirene was first cited as unpublished work of this laboratory in a review in 1977 (ref 5). Subsequently, chemical evidence for the photogeneration of triphenylborirene in solution from diphenyl(phenylethynyl)borirene was published: Eisch, J. J.; Shen, F.; Tamao, K. *Heterocycles* **1982**, *18*, 245. Although the pure borirene could not be isolated, it was intercepted as its cycloadduct with diphenylacetylene, namely the pentaphenylborole-pyridine complex.

(13) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2526.

(1) Part 11 of the series, Bora-Aromatic Systems. Part 10: Eisch, J. J.; Boleslawski, M. P.; Tamao, K. *J. Org. Chem.* **1989**, *54*, 1627.

(2) The State University of New York at Binghamton.

(3) The University of South Carolina.

(4) The University of Delaware.

(5) Eisch, J. J. In *Advances in Organic Chemistry*; West, R., Stone, F. G. A., Eds.; Academic Press: New York, NY, 1977; Vol. XVI, pp 67-109.

(6) (a) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. (b) Ashe III, A. J.; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879.

(7) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379.

(8) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, NY, 1960; pp 256-304.

(9) To the best of our knowledge, the explicit suggestion that the then unknown borirene ring should possess aromatic stabilization was first made by Academician M. E. Vol'pin in his classic review of non-benzenoid aromatic compounds and the concept of aromaticity (Vol'pin M. E. *Russ. Chem. Rev.* **1960**, *29*, 129).

(10) (a) van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem.* **1983**, *95*, 61. (b) Habben, C.; Meller, A. *Chem. Ber.* **1984**, *117*, 2531. (c) West, R.; Pachaly, B. *Angew. Chem.* **1984**, *96*, 96. (d) Berndt, A.; Poes, C. *Angew. Chem.* **1984**, *96*, 306.

(11) In a personal communication, Professor Bernd Wrackmeyer of the Institute of Inorganic Chemistry, University of Bayreuth, has informed us of his unsuccessful attempts to reproduce the preparations of borirenes claimed for the procedures described in refs 10a and 10c. In his hands, such procedures give complex mixtures of boron-containing products, which do not exhibit the expected ¹¹B NMR and mass spectral properties consistent with the presence of borirenes. On the other hand, the data on the borirenes described in refs 10b and 10d do support these authors' claims to have produced borirenes.

an average separation of 1.416 (1) Å. This bond distance would represent a significant shortening of the B—C bond over that in trivinylborane (1.558 Å) and a considerable lengthening of the C=C bond over that in cyclopropene (1.304 Å). Upon this basis, then, we concluded that extensive π -electron delocalization prevailed in the borirene and that the ring could be viewed as having Hückel aromaticity.¹³

However, because of the 3-fold disorder in the crystal lattice, the data did not permit us to discern whether the ring sites were occupied by a given boron atom. This disorder, which arose from the high degree of symmetry of the trimesitylborirene molecule and the small differences in B—C and C—C ring atom separations, left us unsure of whether the observed ring dimensions of **2** were actual bond distances or averaged values arising from boron-carbon atom disorder.

In order to remove such uncertainty, we set out to synthesize a borirene having a lower degree of symmetry but still maintaining similar steric and electronic properties for the substituents attached to the borirene ring. To this end, we have undertaken to prepare 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene (**4**) by the photoisomerization of ((2,6-dimethylphenyl)ethynyl)dimesitylborane (**3**). Having established in this manner that significant π -electron delocalization was in fact operative in stabilizing the borirene ring, we have now also investigated and evaluated the destabilizing effect of Lewis bases on such strained rings.

Results

Synthesis of Borirene Precursors. The requisite diaryl(aryl-ethynyl)boranes, **1** and **3**, were both prepared from the multistep procedure summarized in Scheme 1. Bis(trimethylsilyl)acetylene (**5**) was converted into trimethyl(*p*-tolylsulfonyl)ethynylsilane (**6**) by the action of *p*-toluenesulfonyl chloride and AlCl₃. Then **6** was desilylated to (*p*-tolylsulfonyl)acetylene (**7**) by NaF. Thereafter, **7** could be treated either with mesityl Grignard reagent (**8**) or with 2,6-dimethylphenyl Grignard reagent (**9**) to produce mesitylacetylene (**10**) or (2,6-dimethylphenyl)acetylene (**11**), respectively, by a reaction discovered by Truce.¹⁴ The magnesium bromide Grignard reagent of **10** or **11** was then coupled with dimesitylboron fluoride (**12**) to produce precursors **1** or **2**, respectively (Scheme 1).

Photoisomerization to the Borirenes. Irradiation at 300 nm proved to be more effective for the isomerization than irradiation of shorter wavelength. Tetrahydrofuran or benzene containing small amounts of pyridine proved to be the most suitable media for the photoreaction (yields ~70%). Toluene or benzene alone gave distinctly lower conversion (~35%), and alkanes permitted no reaction.

X-ray Crystal Structure Determination. Since the detailed data for the structure of trimesitylborirene has already been published or is available as Supplementary Material,¹³ no repetition of these data is reported here. The analysis of the unsymmetrically substituted borirene, 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene (**4**) proceeded satisfactorily: no atom disorder was encountered in the crystal lattice, and all ring carbon and boron atoms could be located unambiguously. Selected bond distances and bond angles observed with **4** are given in Figure 1. The borirene ring B—C bonds have been determined to have separations of 1.450 (10) and 1.464 (11) Å, and the C—C ring bond has a distance of 1.380 (9) Å.

In order to learn whether there was any comparable changes in the B—C and C≡C bond lengths for the precursor to the borirene ring system, an X-ray crystal structure analysis was also carried out on dimesityl(mesitylethynyl)borane (**1**). Selected bond distances and bond angles found for **1** are listed in Figure 2. Noteworthy are the boron-ethynyl carbon bond length of 1.529 (6) Å and the C≡C bond length of 1.217 (6) Å. Moreover, the bond angle of the B—C≡C array is 176.1 (5) Å.

Properties of Trimesitylborirene (2). (a) **Spectral Characteristics.** In hydrocarbon solution **2** displays a maximum in the UV absorption spectrum at about 300 nm (290 in C₅H₁₄ and 312 in

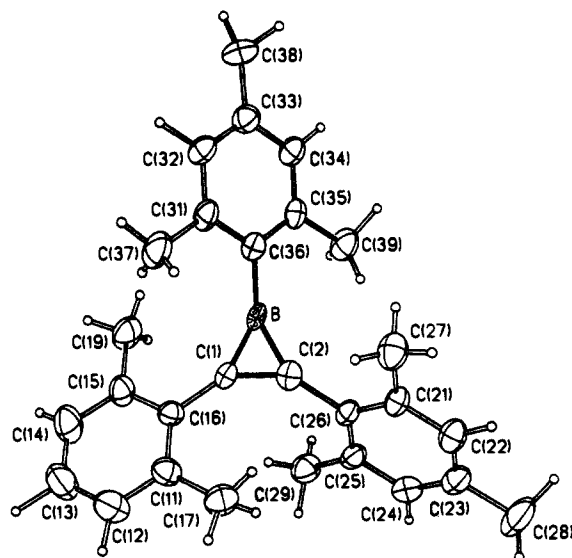
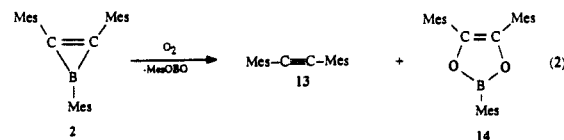


Figure 1. The molecular structure and labeling scheme for 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene (**4**) is shown, drawn with hydrogen atoms of arbitrary radius. Selected bond distances (Å) are as follows: B—C(1), 1.450 (10); B—C(2), 1.464 (11); C(1)—C(2), 1.380 (9); B—C(36), 1.535 (9); C(1)—C(16), 1.463 (8); C(2)—C(26), 1.506 (9). Selected bond angles (deg) are as follows: C(1)—B—C(2), 56.6 (5); B—C(1)—C(2), 62.2 (5); C(1)—C(2)—B, 61.2 (5); C(1)—B—C(36), 150.3 (7); C(2)—B—C(36), 153.1 (6); B—C(1)—C(16), 151.5 (6); C(2)—C(1)—C(16), 146.2 (6); C(1)—C(2)—C(26), 146.7 (6); B—C(2)—C(26), 152.0 (6). Dihedral angles (deg) are as follows: [B, C(1), C(2)]—[C(11)—C(16)] = 36.0, [B, C(1), C(3)]—[C(21)—C(26)] = 46.9, [B, C(1), C(3)]—[C(31)—C(36)] = 38.2.

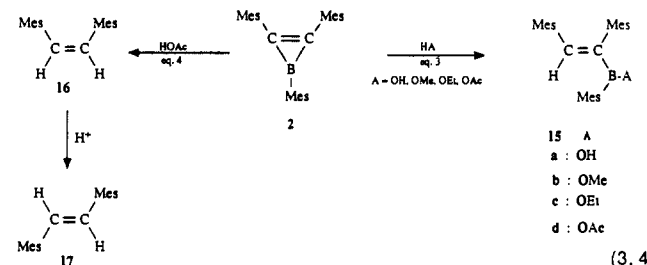
C₆H₆). In the presence of pyridines, however, the long wavelength absorption shifts to 350 nm, and the solutions of **2** take on a distinctly yellow color.

Similarly, pronounced changes are to be noted in the ¹³C NMR spectrum: the spectrum of **2** in CD₂Cl₂ consists of four peaks in the methyl region and seven peaks in the aromatic region; in the presence of pyridine, eight peaks are now discernible in the methyl region and 31 peaks in the aromatic region. Likewise, the ¹¹B NMR absorption for **2** in pure CD₂Cl₂ lies at 34.8 ppm but is shifted to 21.8 ppm in the presence of pyridine.

(b) **Chemical Stability of the Borirene Ring.** Borirene **2**, which melts at 218 °C, could be heated briefly in the air at 250 °C without any apparent decomposition, and it could be irradiated for 48 h in toluene at 300 nm without undergoing further change. However, prolonged treatment of a solution of **2** in toluene at 25 °C with dry dioxygen converted about a third of **2** into dimesitylacetylene (**13**). Small amounts of a C₂₉H₃₃BO₂ product detected by mass spectrometry suggest the formation of 2,4,5-trimesityl-1,3-dioxa-2-borole (**14**) as a side product (eq 2).



(c) **Protodeboronation.** Borirene **2** underwent facile cleavage of one B—C ring bond when treated with water, methanol, ethanol, or acetic acid at 25 °C (eq 3). Complete removal of boron from



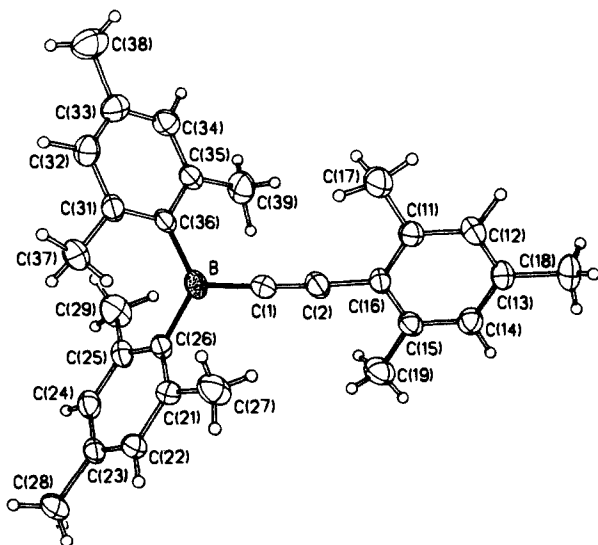


Figure 2. The molecular structure and labeling scheme for dimesityl(mesitylethynyl)borane (**1**) is shown, drawn with hydrogen atoms of arbitrary radius. Selected bond distances (Å) are as follows: B—C(1), 1.529 (6); B—C(26), 1.599 (6); B—C(36), 1.594 (6); C(1)—C(2), 1.217 (6); C(2)—C(16), 1.424 (5); C(11)—C(17), 1.520 (5); C(13)—C(18), 1.514 (6); C(15)—C(19), 1.510 (6); C(21)—C(27), 1.514 (5); C(23)—C(28), 1.519 (8); C(25)—C(29), 1.510 (6); C(31)—C(37), 1.513 (6); C(33)—C(38), 1.538 (7); C(35)—C(39), 1.504 (5). Selected bond angles (deg) are as follows: C(1)—B—C(26), 117.3 (4); C(1)—B—C(36), 117.9 (4); C(26)—B—C(36), 124.9 (3); B—C(1)—C(2), 176.1 (5); C(1)—C(2)—C(16), 177.7 (5); C(12)—C(11)—C(17), 118.6 (2); C(16)—C(11)—C(17), 121.4 (2); B—C(26)—C(21), 121.3 (2); B—C(26)—C(25), 118.6 (2).

2 could be achieved by heating with glacial acetic acid. Under these conditions, (*Z*)-dimesitylethene (**16**) was formed and partly isomerized to its *E* isomer (**17**). In contrast with the behavior of these Brønsted acids, *tert*-butyl alcohol was unable to cleave **2** without assistance from a pyridine.

(d) Pyridine-Assisted Protodeboronation by *tert*-Butyl Alcohol. When a mixture of 1 equiv of **2** was treated with 0.25 equiv of 4-(dimethylamino)pyridine in THF, a bright yellow solution was formed. Addition of an excess of *tert*-butyl alcohol caused a prompt discharge of the yellow color and cleavage of the borirene. The corresponding borinate ester was thereby formed (eq 3, **15**; A = *O-t*-Bu).

Discussion

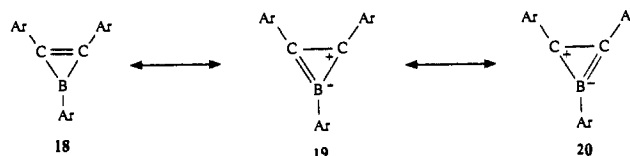
Dimensions of the Borirene Ring. The photorearrangement of ((2,6-dimethylphenyl)ethynyl)dimesitylborane (**3**) led to the formation and isolation of 2-(2,6-dimethylphenyl)-1,3-dimesitylborirene (**4**) as a stable, colorless solid melting at 177 °C. The X-ray crystallographic analysis of **4** did not encounter the disorder in ring atom identity exhibited by trimesitylborirene (**2**), and all ring carbon and boron atoms of **4** could be located unambiguously. The borirene ring B—C bonds have been determined to have a separation of 1.450 (10) and 1.464 (11) Å, and the ring C—C bond (Table I and Figure 1) has a distance of 1.380 (9) Å. These results establish that the experimentally observed, apparent B—C and C—C bond distance of 1.416 (6) Å of the borirene ring in trimesitylborirene (**4**) is an average value arising from the 3-fold disorder.

Even though the B—C and C—C ring bonds actually differ by 0.07 Å from each other, there is still no doubt that the ring B—C bond is significantly shorter than that found in open-chain vinylic boranes. For comparison, it can be noted that the B—C bond length in trivinylborane is 1.558 Å,¹⁵ longer by 0.10 Å. In a complementary manner, the ring C—C bond of **4** at 1.38 Å is considerably longer than that found in the structurally similar cyclopropene ring, whereas the C=C bond length is 1.304 Å.¹⁵

(15) Vilkov, L. V.; Mastruyukov, V. S.; Sadova, N. D. *Determination of the Geometrical Structure of Free Molecules*; Mir: Moscow, 1983.

Such alterations in bond lengths for the borirene ring support the conclusion that two π -electrons of the ring are extensively delocalized among the boron and carbon p-orbitals in a three-center bonding molecular orbital. Thus the ring can be viewed as having Hückel aromaticity, quite analogous to that of the triphenylcyclopropenium cation.^{16,17}

The alternative valence-bond description of such π -electron delocalizations invokes resonance structures (**18–20**) with considerable π -electron density on boron.



Further experimental support for resonance contributions **19** and **20** can be drawn from the ¹¹B NMR spectrum of trimesitylborirene, where the ¹¹B resonance peak is observed at 34.8 ppm. Relative to the corresponding ¹¹B peak for trivinylborane at 55 ppm, the ¹¹B borirene resonance is at much higher field and thus is consistent with a boron center having a higher electron density.

That delocalization between the 2p_z-orbital of boron and adjacent carbon-carbon unsaturation is especially fostered by the cyclic array of the borirene ring is evident by a comparison with B—C bond lengths in open-chain boranes. As already noted, the B—C bond in trivinylborane is 1.558 Å and that in trimethylborane is 1.578 Å.¹⁸ Another open-chain borane, the precursor to **2**, namely dimesityl(mesitylethynyl)borane (**1**) was determined to have a boron-alkynyl carbon bond length of 1.529 Å and C≡C separation of 1.217 Å. Neither bond length shows any significant alteration that would indicate the existence of π -electron delocalization (**21** and **22**).



Chemical Stability of Borirenes. Despite their considerable ring strain,¹⁹ these triarylborirenes exhibit significant kinetic stability toward heat, light, and dry oxygen. Judging by the earlier failures to isolate triphenylborirene from the photoisomerization of diphenyl(phenylethynyl)borane,¹² it seems clear that the ortho-disubstituted aryl groups of borirenes **2** and **4** provide decisive steric hindrance to decomposition and oxidation pathways. The slow attack of oxygen on trimesitylborirene is reminiscent of the

(16) Sundaralingam, M.; Jensen, L. H. *J. Am. Chem. Soc.* **1966**, *88*, 198.

(17) Molecular orbital calculations of varying levels of refinement have been carried out on the borirene ring system, B₂H₃, over the last 10 years, principally by Professor Paul von Raguë Schleyer and co-workers. Ab initio calculations at the STO-3G level gave values of 1.340 and 1.440 Å for the C—C and B—C ring distances, respectively. Other values for the C—C bond by other levels of refinement are 1.347 (4-31G), 1.348 (3-21G), 1.340 (6-31G), and 1.358 (MP2/6-31G, latest value) and for the B—C bond 1.476 (4-31G), 1.485 (3-21G), 1.465 (6-31G), and 1.473 (MP2/6-31G, latest value) (personal communication to the author by Professor Schleyer). Depending upon which calculated values are compared with the experimental distances, the agreement is within 0.01–0.03 Å for the B—C and within 0.02–0.04 Å for the C—C bond.

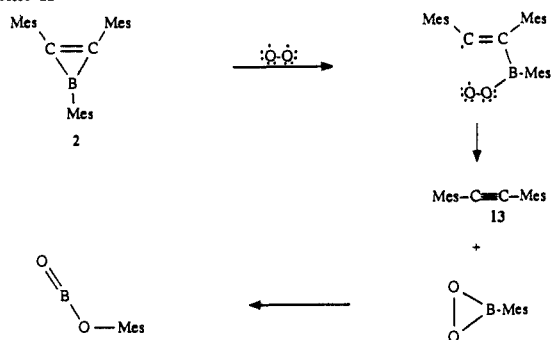
SCF calculations on borirene yield a C—C separation of 1.346 Å and a B—C separation of 1.473 Å. Finally, a parameterized version of the Extended Hückel Molecular Orbital Method (ASED-MO) yields C—C and B—C lengths of 1.38 and 1.43 Å, respectively (personal communication to the author by Professor Alfred B. Anderson; the ASED-MO calculations were performed by Professor Anderson of Case Western University, and the SCF calculations were performed by Professor Jeffrey A. Nichols of Cleveland State University).

Since the two B—C bond lengths of the unsymmetrical borirene **3** differ by 0.14 Å and the experimental error of any B—C or C—C bond length is ± 0.01 Å, the agreement between any of the aforementioned calculated values can be considered to be reasonably good. Therefore, in future research on potentially aromatic heterocycles, MO calculations should serve as a useful guide for the extent of π -electron delocalization.

(18) Onak, T. *Organoborane Chemistry*; Academic Press: New York, 1975; pp 3–4.

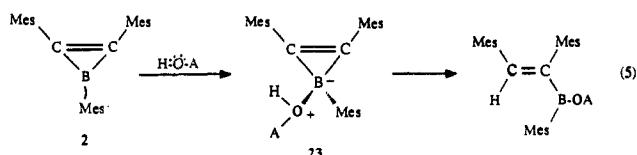
(19) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; von Raguë Schleyer, P. *Organometallics* **1985**, *4*, 429.

Scheme II



air-stability of trimesitylborane, compared with the oxidizability of triphenylborane.²⁰ The principal oxidation product eventually formed from trimesitylborirene is dimesitylacetylene, accompanied by small amounts of a dioxaborole (eq 2). A reasonable mechanism for the alkyne formation is offered in Scheme II.

In sharp contrast to their low reactivity toward oxygen, these bulky substituted borirenes are readily cleaved by Brønsted acids, such as water, certain alcohols, and acetic acid. For reasons to be discussed in the next section, such cleavage most likely requires prior coordination of the Brønsted acid at the boron center and subsequent proton transfer within the zwitterionic complex (**23**) (eq 5). Examination of a space-filling representation of **2** (Figure



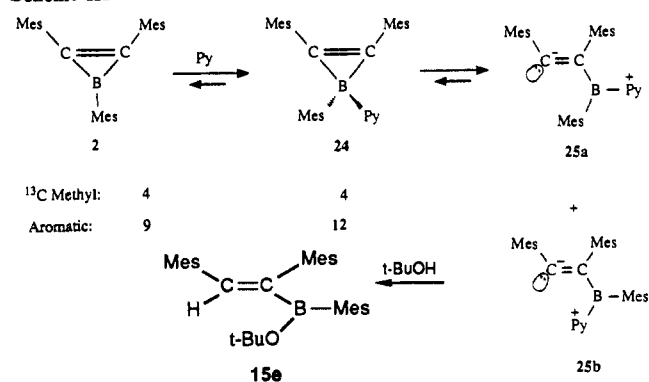
2 in ref 13) reveals that the ring boron is accessible through a cavity formed by the propeller-like array of the three mesityl groups. If the Brønsted acid cannot fit into this cavity, no cleavage ought to occur. In fact, *tert*-butyl alcohol failed to cleave the borirenes **2** under conditions where the smaller methanol or ethanol reagents did so readily.

Spectral and Chemical Changes of Borirenes upon Coordination.

As would be expected of tricoordinate organoboranes having a sterically accessible orbital, these borirenes form coordination complexes with pyridines. Such coordination is evident by the pronounced changes that occur in the electronic and NMR spectra: colorless borirene solutions become a vivid yellow, the ¹³C NMR spectrum becomes greatly enriched in signals, and the ¹¹B peak of the borirene at 34.8 ppm is shifted further upfield to 21.82 ppm. Such complexation with pyridine or 4-(dimethylamino)pyridine appears to be reversible, for attempts to remove solvent or excess pyridine from such solutions and to isolate the pure complex led to recovery of the borirene.

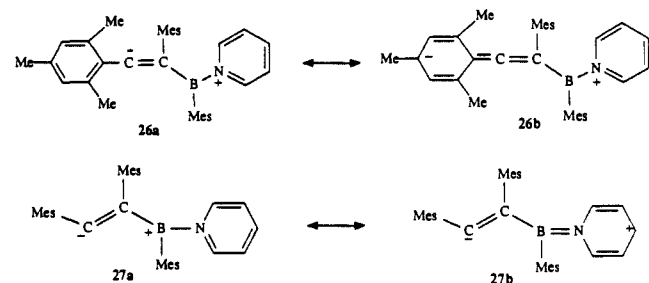
From the complexity of the ¹³C NMR spectrum of borirene **2** in the presence of pyridine, it is evident that no single adduct, such as **24**, is responsible for the observed spectrum. Uncoordinated **2** would be expected to display a maximum of four different methyl and nine aromatic ¹³C signals. The observed spectrum shows four methyl and seven aromatic carbon signals.²¹ Complex **24** should have a maximum of four methyl and 12 aromatic carbon signals. But the complex of **2** with pyridine actually shows eight methyl and 31 aromatic carbon signals. The only way conceivable to us to account for such a multiplicity of signals is to propose a ring-opening of **24** and the formation of the two conformers **25a** and **25b** of the zwitterion **25** (Scheme III). If all methyl and aromatic carbon signals in **25a** and **25b** displayed separate signals of different chemical shifts, then 12 methyl and 34 aromatic carbon signals would be observable. If one assumes that only the methyl carbons of the *B*-mesityl group (endo in **25a**, exo in **25b**) would have different chemical shifts, then the observed number of methyl signals (8) would correspond

Scheme III

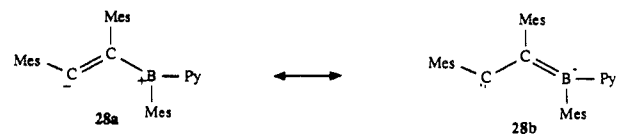


to the presence of **25a** and **25b**. The observed number of aromatic carbon signals (31) would be lacking only three signals of the 34 that could arise from **25a** and **25b**, a difference easily arising from accidental degeneracy of signals.²¹

Further support for the formation of the zwitterionic isomers, **25a** and **25b**, upon coordination of **2** with pyridine comes from the ¹³C and ¹¹B chemical shifts observed from 1:1 mixtures of **2** and pyridine: the ¹¹B signal of **2** is shifted from +34.8 ppm (downfield from BF₃·OEt₂) to +21.8 ppm, indicating a change to a greater tetracoordination character at boron. In the ¹³C NMR spectrum five new signals appear upfield (123–124 ppm) from those of **2** (127–144 ppm) and six new signals appear downfield (150–151 ppm). The upfield signals could stem from the shielding of the carbanionic carbon and the ortho- and para-ring carbons of the mesityl groups at C₃ in **25a** and **25b** (**26**). Conversely, the downfield shifts could arise from the deshielding of the α- and γ-carbons of the coordinated pyridine in **25a** and **25b** (**27**).



An additional spectral argument favoring the formation of ring-opened zwitterions **25a** and **25b**, upon coordination, is the bathochromic shift in the spectrum of **2** and the development of the yellow color. Since **2** itself is colorless, there is no apparent reason why the simple coordination of pyridine to yield **24** should lead to a bathochromic absorption shift. In actuality, the opposite effect is observed: deep blue pentaphenylborole turns to pale yellow when complexed with pyridine.⁸ On the other hand, our proposal that coordination of the borirene with pyridine leads to **25** not only makes the ¹³C spectrum understandable but also offers in structure **25** a system of conjugation considerably extended over that present in **2**. Such greater π-electron delocalization (**26** ↔ **27** ↔ **28**) would be expected to cause a bathochromic absorption shift in the electronic spectrum.



A final cogent chemical corroboration can be adduced to support the formation of **25** from **2** and pyridine: although *tert*-butyl

(20) Brown, H. C.; Dodson, V. H. *J. Am. Chem. Soc.* 1957, 79, 2302.

(21) Failure to observe the maximum expected number of aromatic carbons could be due to accidental degeneracy of signal positions. However, aromatic carbons in organoboranes not bonded to hydrogens often display low signal intensity and thus are frequently difficult to locate (personal communication from Professor B. Wrackmeyer).

alcohol alone cannot cleave **2** in THF solution, this same alcohol with catalytic amounts of a pyridine promptly does cleave the borirene ring. The most obvious interpretation of these observations is that *tert*-butyl alcohol itself is too bulky to coordinate with the boron center in **2**, but it is readily able to donate a proton to the more accessible carbanionic center in zwitterion **25**. Pyridine would be required only in catalytic amounts, because it would dissociate from boron once the borinate ester (**15e**) was formed (Scheme III).

Thermodynamic Stability of Uncoordinated Borirenes. The foregoing cleavage reactions of borirenes with dioxygen, hydroxyl derivatives, and Lewis bases serve to show how important the tricoordinate boron center is to the integrity of this strained ring. Estimates for the ring strain of the parent borirene, BC_2H_5 , have ranged up to 69 kcal/mol;¹⁹ all that such a ring can counter this strain with is its thermodynamic aromatic stabilization energy¹⁹ and any kinetic stabilization it may have due to steric shielding of the ring bonds. Regardless of the actual magnitude of such π -electron stabilization,¹⁹ it is clear from this study that the boron $2p_z$ -orbital must be available for such stabilization of the strained borirene. As soon as electron density from a coordinated O_2 , ROH, or R_3N makes this boron orbital unavailable for π -overlap, the aromatic character is disrupted, and the ring opens readily. Complexation of borirenes with pyridine provides a manifest illustration of this electronic effect.²⁸

Experimental Section

General Manipulation and Analytical Techniques. All operations involved in the preparation, transfer, and analyses of organometallic compounds were conducted under an atmosphere of pure, anhydrous nitrogen or argon.²² Similarly, all the solvents and liquid reagents employed in organometallic reactions were made anhydrous and then freed of dissolved oxygen and peroxides by heating with the appropriate reductant or desiccant under nitrogen and then distilling through moisture-free glassware.²³

The following known purification procedures were employed for the principal liquids used in this study: (a) tetrahydrofuran (THF) via LiAlH_4 treatment; (b) CH_2Cl_2 , CHCl_3 and CCl_4 with phosphorus pentoxide, with CH_2Cl_2 then being treated with calcium hydride; (c) hydrocarbons by refluxing over LiAlH_4 ; (d) pyridine by refluxing and distilling, consecutively, from KOH pellets and from barium oxide; and (e) methanol, ethanol, and *tert*-butyl alcohol by distilling from magnesium turnings that were previously activated with iodine.

Gas chromatographic (GC) analyses were carried out on an F&M dual column instrument, Model 720, for collection of samples and on a Hewlett-Packard chromatograph, Model 5880A, for quantitative analyses. Thin-layer chromatography (TLC) and column chromatography (CC) were employed, where appropriate, with silica gel as the stationary phase and hexane-methylene chloride mixtures as the mobile phase.

Melting points were measured in a Thomas-Hoover oil-bath apparatus and are uncorrected. The melting points of air-sensitive compounds were determined on samples sealed in capillaries under nitrogen.

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded with a Varian Anaspect spectrometer, Model AM-360, equipped with an EM-3630 lock/decoupler. Multinuclear spectra (^1H , ^{13}C , and ^{11}B) were recorded on a Bruker spectrometer, Model AM-300, at the Department of Chemistry, University of South Carolina, Columbia, SC by Professor Jerome D. Odom. As spectral solvents anhydrous samples of carbon tetrachloride, chloroform-*d*, benzene-*d*₆, pyridine, and methylene chloride were employed. The chemical shifts for protons are reported on the delta scale (δ) in parts per million downfield from an internal tetramethylsilane (TMS) reference. For ^{13}C and ^{11}B spectra internal TMS and external $\text{BF}_3\cdot\text{OEt}_2$ served as references, respectively.

Infrared (IR) spectra were measured either with a Model 457 or a Model 238B Perkin-Elmer spectrophotometer on samples dispersed in mineral oil between sodium chloride plates or on samples dissolved in deoxygenated and dry solvents in air-tight matched solution cells. The latter solution cells were carefully purged with nitrogen before filling with air-sensitive solutions.

Electronic spectra were measured with a Hewlett-Packard spectrophotometer, Model 8452A, on carefully deoxygenated and dry solutions of the organometallic compounds, and such solutions were maintained under nitrogen before and after the recording of the spectrum.

Photochemical Reactions. All photoreactions described in this report were conducted in a Rayonet reactor, Model RPR-100, which consists of a cylindrical array of 16 phototubes having a diameter of 25.4 cm and a height of 38 cm. The quartz photoreactor situated at the center of this bank of phototubes was provided with magnetic stirring and external cooling by a fan that kept the chamber temperature at 35 °C. The contents of the photoreactor was loaded and maintained during irradiation under a pure, dry atmosphere of nitrogen.

In the 16-lamp bank, two types of lamps were used: either all low-pressure mercury lamps with an emission at 253.8 nm with a band width of 2 nm or all 300-nm lamps having a coating that limits the band width to 30 nm.

X-ray Crystallographic Measurements on 2-(2,6-Dimethylphenyl)-1,3-dimethylborirene (4). Data were collected on a Nicolet R37 diffractometer, $4^\circ \leq 2\theta \leq 45^\circ$, at the Department of Chemistry, The University of Delaware. Despite searching many samples, only partially twinned crystals were found. Data were collected on the specimen displaying the least twin contributions. With all non-hydrogen atoms anisotropic, all aromatic rings constrained to rigid, planar hexagons, all a mix of found and idealized isotropic hydrogen atom contributions: $R(F) = 9.35\%$, $R(F) = 9.57\%$, $\text{GOF} = 2.182$, $\Delta/\sigma(\text{final}) = 0.03$, $\Delta(\rho) = 0.21 \text{ e } \text{\AA}^{-3}$. SHELXTL (5.1) software was used for all computations (Sheldrick, G. Nicolet XR1, Madison, WI).

Crystal data for **4**: $\text{C}_{28}\text{H}_{31}\text{B}$, triclinic, $P\bar{1}$, $a = 8.215(3) \text{ \AA}$, $b = 8.377(5) \text{ \AA}$, $c = 18.146(6) \text{ \AA}$, $\alpha = 102.17(3)^\circ$, $\beta = 95.27(3)^\circ$, $\gamma = 107.05(3)^\circ$, $V = 1151.3(9) \text{ \AA}^3$, $Z = 2$, $D(\text{calcd}) = 1.13 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.7 \text{ cm}^{-1}$, $T = 293 \text{ K}$. Of 3115 reflections collected, 3005 were independent ($R_{\text{merge}} = 3.7\%$), and 1576 were observed ($F_o \geq 3\sigma(F_o)$). Selected bond distances and angles are given in Figure 1. Further data are compiled in the Supplementary Material.

X-ray Crystallographic Measurements on Dimesityl(mesitylethynyl)borane (1). Data collection was conducted in a manner similar to that employed for **4**. A colorless crystal mounted on a glass fiber was photographed, and cell reduction routines failed to reveal a lattice symmetry higher than triclinic. The centrosymmetric space group, $P1$, was assumed throughout. No corrections for absorption or decay were required.

The structure was solved by direct methods. A sufficient number of methyl-group hydrogen atoms were located to determine unambiguously the groups rotations relative to the aromatic planes. Each methyl group is a composite of found and calculated hydrogen-atom positions. The three mesitylene rings were constrained to rigid hexagonal planes to conserve data. Again, computations used SHELXT (5.1).

Crystal data for **1**: $\text{C}_{29}\text{H}_{33}\text{B}$, triclinic, $P\bar{1}$, $a = 8.224(2) \text{ \AA}$, $b = 8.357(2) \text{ \AA}$, $c = 19.553(4) \text{ \AA}$, $\alpha = 78.03(2)^\circ$, $\beta = 79.41(2)^\circ$, $\gamma = 68.26(2)^\circ$, $V = 1212.6(5) \text{ \AA}^3$, $Z = 2$, $D(\text{calcd}) = 1.075 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.55 \text{ cm}^{-1}$, $T = 294 \text{ K}$. Of 3130 reflections collected, 3031 were independent ($R_{\text{merge}} = 3.37\%$), and 2127 were observed. Selected bond distances and angles are given in Figure 2. Further data are compiled in the Supplementary Material.

Starting Materials and Reagents. 2-Bromomesitylene was either prepared by a published procedure or purchased from Lancaster Synthesis, and it was then fractionally distilled just prior to use (purity > 99.5%). Phenylacetylene, bis(trimethylsilyl)acetylene, 2-bromo-1,3-dimethylbenzene, and 4-(dimethylamino)pyridine were obtained from commercial sources and purified before use.

Trimesitylborirene (2). (a) **Trimethyl(*p*-tolylsulfonyl)ethynyl)silane (6).** A 500-mL, three-necked, round-bottomed flask, whose necks were respectively provided with a reflux condenser surmounted by a gas inlet, a motor-driven sealed stirrer with a Teflon paddle, and a pressure-equalized addition funnel, was flame-dried and thoroughly flushed with dry nitrogen. After temporarily capping the flask, the funnel was removed and was charged in a nitrogen-filled glove bag with 15.0 g (0.11 mol) of fresh anhydrous aluminum chloride, 21.0 g (0.11 mol) of *p*-toluenesulfonyl chloride, and 150 mL of freshly distilled nitrobenzene, and the contents were shaken to form an orange solution. The funnel was reconnected to the three-necked flask, which had previously been charged with 17.0 g (0.10 mol) of bis(trimethylsilyl)acetylene (**5**) and 150 mL of methylene chloride. With stirring and maintaining the reaction mixture at 0 °C in an ice bath, the contents of the funnel was added dropwise to the flask over a 1-h period. After the addition was complete, the ice bath was removed from the dark reaction mixture, and the temperature was allowed to attain 25 °C. Thereafter, the mixture was stirred at reflux for 40 h, cooled, and then cautiously poured onto 400 g of crushed ice. The lower, dark organic phase of the thawed mixture was separated, and the upper, aqueous phase extracted with 3 100-mL portions of CH_2Cl_2 . The combined organic extracts were dried over anhydrous MgSO_4 , and then most of the solvent was removed successively on the rotary evaporator and by distillation under reduced pressure (to remove $\text{C}_6\text{H}_5\text{NO}_2$). The dark distillation residue was extracted repeatedly with hot hexane, which extracts upon cooling yielded up to 22.5 (90%) of colorless tri-

(22) Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1980; Vol. 2, pp 7-20.

(23) Reference 22; pp 75-80.

methyl(*p*-tolylsulfonyl)ethynyl)silane (6), mp 77–78 °C. IR (mineral oil) 2100 cm⁻¹ (lit.²⁴ 81–82 °C). The foregoing procedure, which is a modification of a published report, gave consistently pure product in yields of 75–90%.

(b) (*p*-Tolylsulfonyl)acetylene (7). A solution of 20.0 g (0.075 mol) of trimethyl(*p*-tolylsulfonyl)ethynyl)silane (6) in 400 mL of 95% ethanol was cooled with stirring to 0 °C and then treated dropwise with a chilled solution of 10.0 g (0.22 mol) of sodium fluoride dissolved in 150 mL of water. The ice bath was removed, and the reaction mixture was then kept at 25 °C for 3 h. A sample of the mixture was extracted with CH₂Cl₂, the extract was derived over anhydrous MgSO₄, and the solvent was evaporated. The IR spectrum of the resulting residue displayed intense bands at 2070 and 3300 cm⁻¹ (C≡C–H) but lacked the band at 2100 cm⁻¹ due to 6; the reaction had thus gone to completion.

The entire reaction mixture was worked up analogously, and the organic residue thereupon was extracted with 3 100-mL portions of hot hexane. Upon cooling the extracts 16.2 g (90%) of reasonably pure 7 crystallized out, mp 62–64 °C. This product could be purified in two ways: Soxhlet extraction with a hexane to give pure white crystals, mp 74.5–75 °C, in a recovery of 50% or slow recrystallization from hexane to give crystals with a yellowish tint, mp 74–75 °C (lit.²⁴ 75–76 °C), in a 75% recovery.

(c) Mesitylmagnesium Bromide. The preparation of this Grignard reagent in diethyl ether according to the procedure of Brown and Dodson²⁰ proved to be unsatisfactory in our hands. However, the use of tetrahydrofuran instead gave very good results.

In a 200-mL, three-necked, round-bottomed flask maintained under nitrogen and provided with a reflux condenser whose top was connected to a nitrogen inlet, a motor-driven stirrer, and a pressure-equalized addition funnel were placed 2.4 g (0.10 g-atom) of magnesium turnings and 19.9 g (0.10 mol) of 2-bromomesitylene. With stirring and an ice bath at hand, 50 mL of anhydrous THF was added in one portion. The mixture had to be warmed to initiate reaction, but the ice bath was necessary to control frothing once the exotherm had begun. After heat evolution had subsided, the mixture was heated under reflux for another 2 h. Titration of a hydrolyzed 1-mL aliquot with 0.10 N HCl indicated a yield of Grignard reagent of >96%.

(d) Fluoro(dimesityl)borane (12). To the foregoing Grignard reagent, which was stirred in a dry ice–acetone bath at –78 °C, was added dropwise a solution of 7.1 g (0.05 mol) of redistilled boron trifluoride etherate in 50 mL of anhydrous THF. Thereafter the reaction mixture was stirred at 25 °C for 12 h. This solution of 12 could be used directly for preparing alkynyl(mesityl)boranes, or pure 12 could be isolated by reduced-pressure distillation.

In the latter operation, considerable thermal decomposition led to a lower yield of product. Thus, the reaction mixture was filtered under nitrogen to remove residual magnesium, and the solvent was removed in vacuo. Distillation of the solid residue from a short-path still gave a colorless distillate that solidified, 67%: bp 130–132 °C at 0.5 mmHg, mp 75–76 °C (lit.²⁰ 75.5 °C); ¹H NMR (CCl₄) 2.16 (s, 12 H), 2.20 (s, 6 H), 6.6 (s, 4 H). Treatment of a sample of 12 with methanolic water and recrystallization of the product from petroleum ether gave dimesitylborinic acid, mp 139–140 °C (lit.²⁰ 140–141 °C).

(e) Mesitylacetylene (10). The following procedure was developed upon the basis of Truce's method for converting acetylenic sulfones into arylacetylenes. In a 250-mL, three-necked flask equipped as in part (a) and maintained under a nitrogen atmosphere was placed 0.136 mol of mesitylmagnesium bromide in 75 mL of THF, and the solution was then cooled to –78 °C. Then a solution of 6.0 g (34 mmol) of (*p*-tolylsulfonyl)acetylene in 30 mL of THF was introduced dropwise over 20 min, whereupon the mixture turned dark. After a further 30 min, the mixture was brought to 25 °C and then heated at reflux for 50 h. Hydrolysis, separation, and drying of the organic layer, solvent removal, and distillation of the organic residue gave 4.2 g (85%) of 10: bp 210–215 °C; IR (neat) 2090, 3310 cm⁻¹; ¹H NMR (CCl₄) 1.9 (s, 3 H), 2.2 (s, 6 H), 3.2 (s, H), 6.7 (s, 2 H).

(f) Dimesityl(mesitylethynyl)borane (1). Instead of hydrolyzing and isolating the mesitylacetylene, the reaction mixture in part (e) could be directly treated with 0.50 mol (or 13.4 g) of fluoro(dimesityl)borane dissolved in 50 mL of THF. After 24 h of stirring at reflux the reaction mixture was cooled to 25 °C and quenched with 50 mL of dry methanol. All succeeding steps of the work were also conducted under nitrogen.

Then 150 mL of dry heptane was added to precipitate the salts. This mixture was filtered, and the filtrate was freed of volatile solvent. The resulting dark residue was redigested with 200 mL of warm heptane, and the suspension was again filtered. Final removal of the solvent from the filtrate and recrystallization of the residue from 200 mL of acetonitrile and a little decolorizing charcoal gave 8.1 g (62%) of 1, mp 123–125 °C. Repeated recrystallization from a CH₃CN–CH₂Cl₂ pair gave pale yellow 1, mp 126.0–126.5 °C; IR (mineral oil) 1610 and 2125 cm⁻¹; ¹H NMR

(CCl₄) 2.28 (s, 6 H), 2.38 (s, 12 H), 6.80 (s, 4 H), 6.90 (s, 2 H); MS (70 eV, *m/e*), 392 (48), 272 (43), 257 (100); UV (CH₂Cl₂) 356, (hexane) 388, (hexane–pyridine) 324, (benzene) 318 nm. Anal. Calcd for C₂₉H₃₃B: C, 88.76; H, 8.47; B, 2.75. Found: C, 88.86; H, 8.62; B, 2.83.

(g) Trimesitylborirene (2). In a quartz photoreactor tube maintained under nitrogen were placed 1.0 g (2.55 mmol) of dimesityl(mesitylethynyl)borane and 100 mL of anhydrous, deoxygenated THF. The Rayonet reactor was equipped with a full bank (16) of 300-nm phototubes, and the quartz reactor was irradiated for up to 22 h. This irradiation period was established as optimal by monitoring the reaction in the following manner: periodically the irradiation was interrupted, an aliquot of the solution was withdrawn, the solvent was evaporated under nitrogen, and the residue was examined by infrared spectroscopy. Isomerization was indicated by the progressive decrease in the sharp C≡C band of 1 at 2125 cm⁻¹.

The photolysate was transferred to a Schlenk flask, and the solvent was evaporated in vacuo. Recrystallization of the residue from 30 mL of dry, deoxygenated heptane gave 650 mg (65%) of colorless trimesitylborirene, mp 217–218 °C; ¹H NMR (CCl₄) 2.0 (s, 12 H), 2.2 (s, 15 H), 6.9 (s, 6 H); ¹¹B NMR (CCl₄) 34.8 ppm, relative to BF₃·OEt₂ as 0; ¹³C NMR (CD₂Cl₂) 20.692, 21.299, 21.546, 22.996, 127.670, 128.538, 132.91, 136.335, 138.131, 140.239, 144.230; IR (CCl₄) 1100, 1440, 1610, and 3000 cm⁻¹; MS (70 eV, *m/e*), 392 (48), 272 (43), 257 (100); UV (hexane) 290, (benzene) 312, (pyridine) 350 nm. Anal. Calcd for C₂₉H₃₃B: C, 88.76; H, 8.47. Found: C, 88.81; H, 8.58.

Photolyses conducted on the same scale, but in different solvents, gave the following yields (%): toluene (21); heptane (0); toluene–heptane, 1:2 (v/v) (35).

2-(2,6-Dimethylphenyl)-1,3-dimesitylborirene (4). (a) (2,6-Dimethylphenyl)acetylene (11). Analogous to the preparation of mesitylmagnesium bromide, 2-bromo-1,3-dimethylbenzene (Lancaster Synthesis, 99%) was converted into the corresponding Grignard reagent on a 150-mmol scale. This reagent in THF was allowed to reflux with 38 mmol of (*p*-tolylsulfonyl)acetylene for 60 h. The usual hydrolytic workup provided 70% of (2,6-dimethylphenyl)acetylene, bp 200–202 °C; IR (neat) 2105 and 3315 cm⁻¹.²⁵

(b) ((2,6-Dimethylphenyl)ethynyl)dimesitylborane (3). As in part (a), the unhydrolyzed reaction solution from 3 equiv of (2,6-dimethylphenyl)magnesium bromide and 1 equiv of (*p*-tolylsulfonyl)acetylene (38 mmol) was treated with 60 mmol of fluoro(dimesityl)borane. After 24 h at reflux the reaction mixture was cooled and quenched with 560 mL of dry methanol. While maintaining a nitrogen atmosphere, 150 mL of dry heptane was added, and the mixture was filtered. The filtrate was freed of volatile solvent, and the resulting residue was redigested with 200 mL of warm heptane. The hot suspension was again filtered, and the filtrate was evaporated to dryness. Recrystallization from acetonitrile gave 40% pure 3, mp 130–130.5 °C; IR (mineral oil) 1615 and 2140 cm⁻¹; ¹H NMR (CCl₄) 2.25 (s, 6 H), 2.30 (s, 12 H), 2.40 (s, 6 H), 6.6 (s, 4 H), 6.9 (m, 3 H). Anal. Calcd for C₂₈H₃₁B: C, 88.88; H, 8.26; B, 2.86. Found: C, 88.90; H, 8.38; B, 2.4.

(c) 2-(2,6-Dimethylphenyl)-1,3-dimesitylborirene (4). Irradiation of 1.00 g of 3 in 100 mL of anhydrous, deoxygenated THF for 22 h at 300 nm and usual workup gave 430 mg (43%) of the colorless borirene 4, after several recrystallizations from heptane, mp 175–177 °C; ¹H NMR (CDCl₃) 2.07 (s, 12 H), 2.25 (s, 6 H), 2.35 (s, 6 H), 6.83 (s, 4 H), 7.0 (s, 3 H); IR (mineral oil) 1615 and 1695 cm⁻¹. Anal. Calcd for C₂₈H₃₁B:

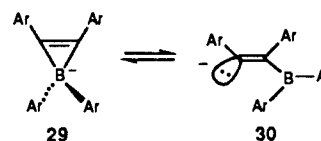
(24) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Syn.* 1970–1971, 1, 145.

(25) Yates, K.; Mandrapilas, G. *J. Org. Chem.* 1980, 45, 3892.

(26) Fuson, R. C.; Horning, E. C.; Ward, M. L.; Rowland, S. P.; Marsh, J. L. *J. Am. Chem. Soc.* 1942, 64, 30.

(27) Fuson, R. C.; Southwick, P. L.; Rowland, S. P. *J. Am. Chem. Soc.* 1944, 66, 1109.

(28) Note Added in Proof: A recent communication (Kropp, M. A.; Schuster, G. B. *J. Am. Chem. Soc.* 1989, 111, 2316) has appeared in which a salt of the anionic complex of triphenylborirene and phenylpotassium has been described (29) and some details of its X-ray crystal structure reported. Although the authors ascribe the yellow-orange color of this complex as arising from the intact, tetracoordinate borirene ring, there is the equally likely possibility that the color may be due to the ring-opened, isomeric anion (30). Consider the similarity of the following to that given in Scheme III:



This uncertainty has been the subject of a recent communication (Eisch, J. *J. Chem. Eng. News* 1989, 67, 3).

C, 88.88; H, 8.26. Found C, 89.02; H, 8.36.

Reactions of Trimesitylborirene (2). (a) **Protodeboronation.** A 75-mg sample of **2** was heated at reflux in glacial acetic acid for 24 h. Quenching the reaction mixture with aqueous NaHCO₃, extraction with hexane, and the separation, drying, and evaporation of the hexane extract left a pale yellow oil, which was principally the (*Z*)-1,2-dimesitylethene (**16**) (MS, 264). Dissolving this oil in hot methanol and allowing the solution to stand for 2 weeks caused 21 mg (43%) of long colorless needles of (*E*)-1,2-dimesitylethene (**17**) to precipitate, mp 130–131 °C (lit.²⁶ 131 °C): ¹H NMR (CDCl₃) 1.75 (s, 12 H), 2.0 (s, 6 H), 6.25 (s, 2 H), 6.35 (s, 4 H); MS, 264 (52), 249 (50), 234 (100), 144 (40), 129 (58).

(b) **Air Oxidation.** A sample of **2** in a test tube open to the air was placed in an oil bath at 250 °C and was maintained at that temperature for 5 min. Although a slight darkening in the melted sample was observed, the infrared and ¹H NMR spectra of the recovered sample indicated no new absorptions.

A 100-mg sample of **2** was dissolved in 70 mL of anhydrous toluene, and a stream of dry air (obtained by previously passing air through a column of anhydrous CaSO₄) was allowed to bubble through the solution for 14 h at 25 °C. The solvent was then evaporated, and the residue was recrystallized from 10 mL of heptane. About 55% of the starting **2** crystallized from the cooled solution. Evaporation of the mother liquor and dissolution of the residue in hot methanol gave, upon cooling, 20 mg of dimesitylacetylene (**13**); mp 127–127 °C (lit.²⁷ 127.5–128.5 °C); MS, 262 (3), 175 (33), 161 (94), 147 (100).

In the mass spectrum of the recrystallization residues, a prominent peak at 424 was observed. This is consistent with the presence of 2,4,5-trimesityl-1,3-dioxa-2-borole (**14**).

(c) **Complexation with Pyridines.** A colorless solution of **2** in CD₂Cl₂ became vivid yellow upon the addition of 1 or more equiv of pyridine. The ¹³C NMR spectrum of the latter proton-decoupled spectrum exhibited the following signals: 20.627, 20.807, 21.017, 21.256, 21.364, 21.496, 22.741, 23.260, 123.679, 123.978, 124.066, 124.162, 124.398, 127.366, 127.844, 128.557, 128.756, 128.894, 134.880, 135.259, 135.307, 135.793, 135.915, 135.947, 135.979, 136.157, 136.508, 136.779, 136.928, 137.153, 138.282, 139.157, 143.865, 149.878, 150.165, 150.253, 150.350, 150.602, 150.706.

In 20 mL of anhydrous cyclohexane 0.75 mmol each of **2** and 4-(dimethylamino)pyridine were heated to reflux. A clear, bright yellow solution resulted. Upon cooling, however, the color faded somewhat, and the pyridine selectively reprecipitated. No precipitate containing the borirene could be detected.

(d) **Alcoholysis.** In a typical experiment 500 mg of **2** dissolved in 10 mL of anhydrous THF under nitrogen was treated with a 2-fold excess of the alcohol or water, and then the mixture stirred for 14 h at 25 °C. The volatile components were then removed in vacuo, and the residue was recrystallized from the parent alcohol.

(1) **Methanolysis.** The methyl (*Z*)-(1,2-dimesitylethenyl)mesitylbo-

rinane (**15b**) melted at 121–123 °C: ¹H NMR (CDCl₃) 1.8 (s, 6 H), 1.9 (s, 6 H), 2.0 (s, 3 H), 2.1 (s, 3 H), 2.2 (s, 3 H), 2.3 (s, 6 H), 3.4 (s, 3 H), 6.5 (s, 2 H), 6.6 (s, 2 H), 6.7 (s, 2 H), 7.0 (s, 1 H); MS, 438 (s), 175 (37), 161 (100), 147 (79).

(2) **Ethanolysis.** The ethyl (*Z*)-(1,2-dimesitylethenyl)mesitylborinate (**15c**) melted at 136–138 °C: ¹H NMR (CDCl₃) 1.0 (t, 3 H), 1.6 (s, 6 H), 1.8 (s, 6 H), 1.9 (s, 3 H), 2.0 (s, 3 H), 2.1 (s, 3 H), 2.2 (s, 6 H), 3.5 (q, 2 H), 6.2 (s, 2 H), 6.3 (s, 2 H), 6.4 (s, 2 H), 6.7 (s, 1 H); MS; 452 (5), 173 (33), 147 (100).

(3) **Hydrolysis.** The (*Z*)-(1,2-dimesitylethenyl)mesitylborinic acid (**15a**) could not be obtained in crystalline form: ¹H NMR (CDCl₃) 1.7 (2, 3 H), 1.9 (s, 6 H), 2.0 (s, 3 H), 2.1 (s, 3 H), 2.2 (s, 3 H), 2.3 (s, 6 H), 6.55 (s, 2 H), 6.65 (s, 2 H), 6.8 (s, 2 H), 7.15 (s, 1 H), 7.45 (s, 1 H); MS, 410 (1), 394 (22), 379 (60), 274 (21), 249 (97), 248 (100).

(4) **Attempted Cleavage with *tert*-Butyl Alcohol.** Stirring a THF solution of **2** with *tert*-butyl alcohol at 25 °C or heating **2** in refluxing pure *tert*-butyl alcohol gave no appreciable amount of any product upon removal of solvent. The borirene could largely be recovered by recrystallization from heptane.

(5) **Pyridine-Assisted Cleavage from *tert*-Butyl Alcohol.** A 800-mg sample of **2** (2.0 mmol) and 62 mg (0.5 mmol) of 4-(dimethylamino)pyridine dissolved readily in 10 mL of anhydrous THF to form a bright yellow solution. Then 20 mL of anhydrous *tert*-butyl alcohol was added in one portion. After a few seconds the yellow color began to fade, and the solution turned cloudy. After stirring for 30 min, an amorphous white precipitate settled out. The mixture was briefly brought to gentle reflux. The cooled supernatant solution was analyzed by mass spectrometry: a prominent peak at 466 was consistent with the presence of *tert*-butyl (*Z*)-(1,2-dimesitylethenyl)mesitylborinate (**15e**) at this stage.

The volatiles were removed from the reaction mixture in vacuo, and successive attempts were made to recrystallize the residue from heptane and then from acetonitrile. From the hot acetonitrile extract an oily sample of (*Z*)-(1,2-dimesitylethenyl)mesitylborinic acid (**16**) was obtained as was verified by ¹H NMR and mass spectral measurements.

(6) **Attempted Photolysis.** Irradiation of a 250-mg sample of **2** for 48 h in 70 mL of toluene at 300 nm led to no change in the starting material.

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Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates and isotropic thermal parameters, and atomic coordinates and isotropic thermal parameters for **4** and **1** (8 pages); tables of observed and calculated structure factors for **4** and **1** (22 pages). Ordering information is given on any current masthead page.