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Electronic and Structural Effects of Stepwise Borylation and Quaternization on Borirene Aromaticity

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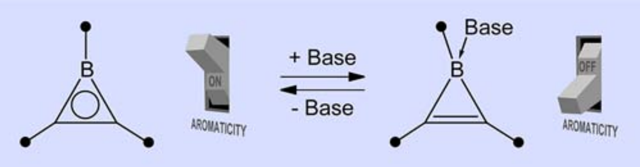
Supporting Information



ABSTRACT: Room-temperature photolysis of the aminoboryl complex $[(OC)_5Cr{=}B{=}N(SiMe_3)_2]$ in the presence of a series of mono- or bis(boryl) alkynes bis{bis(dimethylamino)boryl}ethyne, 1-phenyl-2-bis(dimethylamino)borylethyne, and 1-trimethylsilyl-2-bis(dimethylamino)borylethyne led to the isolation of hitherto unknown borylborirenes in resonable yields, that is, $[(RC{=}CR')(\mu\text{-}BN(SiMe_3)_2)]$ (**7**, R = $B(NMe_2)_2$, R′ = Ph; **8**, R = R′ = $B(NMe_2)_2$; **9**, R = $B(NMe_2)_2$, R′ = $SiMe_3$). The borirenes were isolated and spectroscopically characterized by multinuclear NMR, IR, and UV/vis spectroscopy, crystallography, and elemental analysis. Reactivity studies of the borirenes demonstrated their behavior toward different Lewis bases. The isolated adducts and the parent borirenes were compared to 1,3-mesityl-2-phenylborirene and its adducts. To gain insight into the electronic structure and to evaluate the influence of the exocyclic groups, Density Functional Theory (DFT) calculations were carried out.

INTRODUCTION

Borylated molecular and polymeric species have become of great importance due to their broad application in organic and inorganic synthesis and materials science.[1] In particular, the design of π-conjugated organic compounds displaying three-coordinate boron centers constitutes a highly topical area of research, because functional materials based thereon are promising materials for use in light emitting devices, sensors, and electronic circuits.[1d,e,g,j−l] Syntheses of these important materials rely heavily on classical methods established in organoboron chemistry such as hydroboration,[1a] silicon−boron exchange,[1g] and metal-mediated C−H bond borylation.[1m,n]

Transition metal borylene complexes of the type $[L_nM{=}B{=}N(SiMe_3)_2]$ (M = Cr, Mo, W) serve as facile synthetic sources of $[{:}BN(SiMe_3)_2]$ both under thermal and photochemical conditions.[2] Borylene transfer is also an excellent tool for the functionalization of carbon double[3] and triple bonds,[4] thus providing new synthetic approaches for π-conjugated boron-containing molecules far beyond the conventional methodologies. The borylene-based functionalization of alkynes is not only applicable to a wide range of substrates, including terminal and internal alkynes, diynes, and transition metal-bound alkynyl moieties, but also proceeds with remarkably high yields. This functionalization of carbon−carbon triple bonds upon photolysis provides simple access to borirenes,[4] the boron-containing analogue of the cylopropenylium cation.[5] Although several reports from our laboratories[4] and those of others[6] are available on borirenes, in general little is known about their properties and reactivity. Known reactivity patterns are scarce and commonly result in cleavage of the aromatic ring induced by protic substrates,[4f,6e] hydroboranes,[7] or UV light (Scheme 1).[4f] A highly unusual "partially-cleaved" borirene was observed upon reaction of 1,3-mesityl-2-phenylborirene with $[Pt(PEt_3)_3]$ yielding a B−C σ-complex.[8]

If borirenes and the borylene transfer reaction are to play any part in the construction of useful boron-containing materials, methods of functionalization and modulation of the π system that do not involve rupture of the ring, will need to be developed. For these reasons, we explored the synthesis of borirenes with both one and two boryl substituents, which are well-known to be excellent σ-donor groups (as well as π-acceptors, although only when coplanar), as well as potential points of further chemistry via cross-coupling protocols. Filling the empty p orbital of boron by the addition of a Lewis base is a well-known reaction, but in boron-containing heterocycles, such adduct formation disrupts any π-conjugation involving the boron atom, and thus also "switching off" any aromaticity or antiaromaticity in the ring. This phenomenon has recently proven useful for modulating the photophysical properties of boroles.[9] Thus, herein we have attempted to quaternize borirene boron atoms using Lewis bases, a possibility hinted at but only briefly explored by Eisch in an early report.[6a]

In this Article, we present the photochemical borylene transfer from borylene complex **1** to a set of alkynes substituted by different functional groups, for example, $B(NMe_2)_2$, Ph, and $SiMe_3$. The results of the reaction of borylene complexes with substituted alkynes led to the isolation of the new boryl-functionalized borirenes **7**−**9**. We then investigated the reactivity of aminoborirenes (**7**−**9**) in a comparative study

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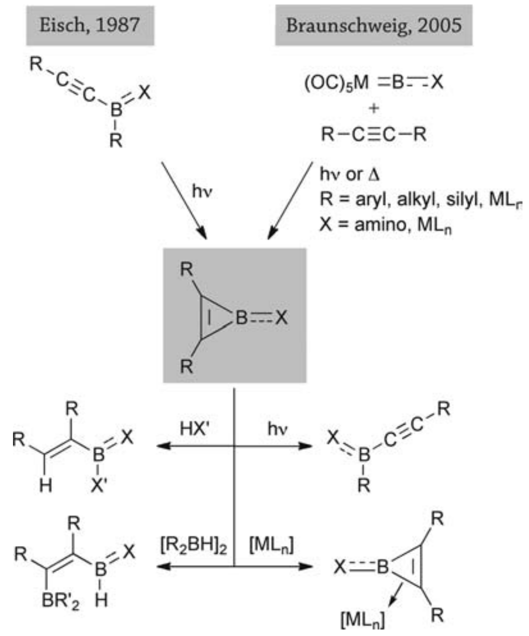
Scheme 1. Two Syntheses of Borirenes and Their Key Reactivity Patterns



with 1,3-dimesityl-2-phenylborirene (**5**). Once these borirenes were available in sufficient quantities, theoretical calculations combined with spectroscopic data were employed to elucidate the electronic structure of these species, particularly with respect to the extent of π-delocalization within the BCC ring and the exocyclic groups. The quaternization and dequaternization of a number of borirenes was accomplished with a range of Lewis bases, and a number of the adducts were structurally characterized.

RESULTS AND DISCUSSION

Synthesis of Borirene Precursors. $[(Me_2N)_2BC{\equiv}CPh]$ (**2**) was prepared according to a literature procedure.[10] Treatment of $[LiC{\equiv}CSiMe_3]$ in hexane with 1 equiv of $ClB(NMe_2)_2$ yielded **3**. Compound **4** was obtained by reaction of $[BrMgC{\equiv}CMgBr]$ with 2 equiv of $ClB(NMe_2)_2$. After workup, **3** was isolated as a colorless liquid, showing spectroscopic characteristics similar to those reported for an analogous compound,[11] and **4** as a colorless solid (Figure 1). Single crystals of **4** suitable for X-ray analysis were obtained by storing a concentrated pentane solution at −30 °C for 3 weeks.

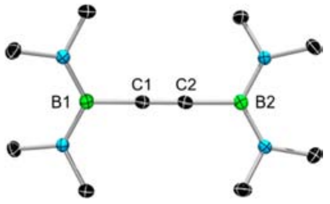
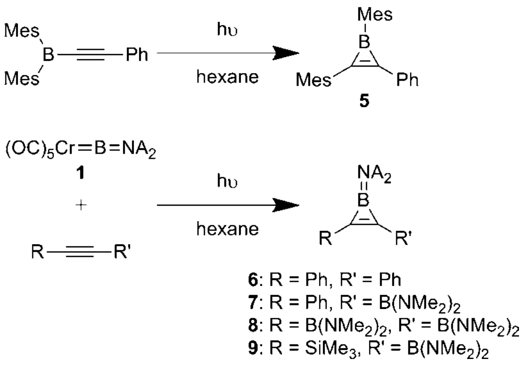


Figure 1. Molecular structure of **4**. Ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å): C1−C2 1.211(1), B1−C1 1.556(1).

Scheme 2. Synthesis of the Borirenes 5–9[a]



[a] A = $SiMe_3$.

Synthesis of the Borirenes. Compound **5**[8] was synthesized according to the literature. The borirenes **6**,[4e] **7**, **8**, and **9** were prepared by photochemical borylene transfer. As shown in Scheme 2, a pale yellow hexane solution of **1** was irradiated in the presence of the requisite alkynes for 12 h at room temperature, which resulted in the formation of the aminoborirenes **6**–**9**.

All reactions were monitored by multinuclear NMR spectroscopy, which revealed gradual consumption of the starting materials and quantitative formation of the borirenes, as indicated by the presence of new resonances in the ^{11}B NMR spectrum at δ = 30–23 ppm. Compounds **7**–**9** were purified by distillation under reduced pressure. The compounds were isolated as air- and moisture-sensitive light yellow solids (**7** and **8**) or a light yellow oil (**9**) in yields between 56% and 86%. The borirenes **7** and **9** show considerably decreased stability indicated by the change of their color to black-yellow/black-red after elongated storage under argon in a glovebox or a Schlenk tube at ambient temperature. Nervertheless, **7** and **8** can be stored at low temperatures without decomposition. Borirene **8** was found to be stable under the same conditions as the triaryl borirene **5**.

Table 1. Relevant Bond Lengths (Å) and Angles (deg) for 6–8

	compound		
	6	7	8
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
C1−C2	1.357(2)	1.366(2)	1.382(2)
B1−C1	1.487(2)	1.478(2)	1.478(3)
B1−C2	1.490(2)	1.498(2)	1.476(2)
C1−C3/B3	1.469(2)	1.462(2)	1.564(2)
∠BCC plane−C3Ph/B3NN plane	44.9(1)	12.4(2)	68.8(1)
C2−B2/C4	1.462(2)	1.558(2)	1.560(2)
∠BCC plane−C4Ph/B2NN plane	37.7(1)	72.0(2)−78.9(2)	77.7(1)
B1−N1	1.419(2)	1.423(2)	1.430(2)
∠C1−B1−C2	54.2(1)	54.7(1)	55.8(1)

Differential thermal analysis showed melting points below 100 °C for the borirenes **5**–**8** and in all cases decomposition over 200 °C. The data indicate that borirenes **5**–**8** are thermally very stable. The ^{11}B NMR signals of the borirenes are in the expected region. The borirenes **8** (δ = 31.6 ppm) and **9** (δ = 31.9 ppm) show only one resonance indicating isochronism for the ring boron atom and the exocyclic boron atom, whereas **7** shows two signals (δ = 31.3 ppm, 27.9 ppm). The signals of **7**–**9** are downfield shifted by 5 ppm in comparison to bis(borirenes).[4e] Surprisingly, the signal of the triarylborirene **5** (δ = 32.8 ppm)[8] has nearly the same shift, suggesting that the group at the ring boron atom has a negligible influence on the chemical shift in the ^{11}B NMR spectrum. The basic structural features of **7**−**9** are very similar to those reported for borirenes with other substituents. The ^{1}H and ^{13}C NMR spectra of **7**−**9** showed only one signal for the $N(SiMe_2)_2$ moiety, indicating free rotation around the B−N bond at room temperature in solution. In addition, the ^{13}C NMR spectra of these compounds show the presence of ring carbon resonances (**7**, δ = 175.95, 166.23; **8**, δ = 186.46; **9**, δ = 182.25) observed as broad singlets. The values are downfield-shifted as compared to those reported in the literature.[4a,12] Other NMR spectroscopic data are consistent with proposed structures.

The infrared spectra of **7**−**9** showed a medium absorption in the range of 1685−1614 cm^{-1}, characteristic for the BCC ring breathing of the borirenes (Table 2).[12] The values measured in the solid state are about 50 cm^{-1} lower than the values calculated for the molecules in the gas phase. To establish a trend, the frequencies of bis(trimethylsilyl)- and 1-trimethylsilyl-2-phenyl-aminoborirene (1693 cm^{-1}, 1633 cm^{-1}) were calculated. Comparison of the values indicates that the bond strength in the BCC ring seems to be influenced by the exocyclic groups over the following series: aryl > boryl > silyl, which can probably be explained by the extent of electron donation by the functional groups.

Table 2. Experimental and Calculated IR Data of the Ring Breathing Mode of Representative Borirenes (cm^{-1})

	5	6	7	8	9
exp	1708	1685	1663	1641	1617
calcd	1759	1732	1711	1696	1671

Single crystals of **6** and **8** suitable for X-ray analysis were obtained by storing a pentane solution at −30 °C for 1 week, and of **7** by slow evaporation of a saturated pentane solution in the freezer of a glovebox at −35 °C (Figure 2). The C1−C2 bonds of **6**−**8** are minimally longer than those in free ethylene (1.339 Å)[13] and *cis*-stilbene (1.339(5) Å).[14] They are similar to those of triaryl cyclopropenylium cations[7] (∼1.37 Å), triarylborirenes[8] (1.370(4) Å), bis(silyl)aminoborirenes[4a] (1.376(4) Å), bis(borirenes)[4e] (e.g., 1.362(3) Å, 1.367(2) Å), metal borirene complexes[4b,d,f] (e.g., 1.367(4) Å, 1.363(2) Å), the one known ferroborirene[4g] (1.371(3) Å), and a *cis*-1,2-bis(boryl)alkene[15] (1.354(9) Å). The elongation from 1.19(2) Å in diphenylacetylene[16] and 1.211(1) Å in **4** to 1.357(2) Å in **6** and 1.382(2) Å in **8** is typical for the change of hybridization of the two carbon atoms from sp to sp^{2}. Comparison of the C1−C2 bonds of **6**−**8** reveals that the more $B(NMe_2)_2$ groups are bound to the BCC ring, the longer is the C1−C2 bond. The B1−C1 and B1−C2 bonds show lengths between 1.476(2) and 1.498(2) Å, again comparable with those of triarylborirenes (1.474(4) Å, 1.459(4) Å),[8] bis(silyl)aminoborirenes[4a] (1.485(3) Å), bis(borirenes)[4e] (e.g., 1.473(3) Å, 1.498(2) Å), metal borirene complexes[4b,d,f] (e.g., 1.501(2) Å, 1.474(2) Å), and the one known ferroborirene[4g] (1.49(4) Å). Comparison of the ring B−C bonds of **6**, **7**, and **8** reveals a shortening upon augmentation of the number of $B(NMe_2)_2$ groups, a trend closely related to that for the C1−C2 bonds. Only in **7** does the B1−C2 bond show a slight elongation as compared to that of **6**.

Presumably due to steric hindrance, the exocyclic phenyl groups of **6** are not in plane with the BCC ring (44.9(2)°, 37.7(2)°), a fact that is also found for all three aryl groups in **5**. In contrast, the phenyl group in **7** is nearly coplanar with the BCC ring with the distortion being only 12.4(2)°. This has also been observed in a platinum borirene complex[4b,f] and indicates conjugation with the BCC ring. The distance between the BCC ring and the exocyclic boryl groups in **7** and **8** is typical for a diaminoboryl group conjugated with an alkene[17] and is close to the sum of covalent radii of boron and carbon (1.57 Å).[18] These distances in **8** are longer than in **7** and the B1C1 distance (1.556(1) Å) in the parent alkyne **4**. The disordered exocyclic boryl group (B2NN plane) of **7** is distorted between 72(2)° and 78.9(2)° from the BCC ring, thus minimizing steric congestion. For **8** the same effect is found; the distortions are 68.8(1)° (B2NN plane) and 77.7(1)° (B3NN plane). The B1−N1 distance in **6**, **7**, and **8** is also influenced by the number of $B(NMe_2)_2$ groups, thus showing a greater elongation the more $B(NMe_2)_2$ groups are attached to the BCC ring.

These structural findings for **6**, **7**, and **8** have been interpreted as indicative of extensive delocalization of the two π-electrons over a three-centered bonding molecular orbital comprised of the p_z atomic orbitals of boron and carbon.[19] The number of $B(NMe_2)_2$ groups in **6**, **7**, and **8** influences the bond lengths in a clear trend, which indicates stronger delocalization in the BCC ring the more $B(NMe_2)_2$ groups are attached to it. As the boryl groups are quasi-orthogonal to the BCC ring, no π-conjugation between them and the BCC ring can be postulated. To better understand these facts, we performed DFT calculations, which are discussed below.

To gain insight into the electronic structure of the borirenes, UV/vis spectroscopic measurements were performed in hexane. In the case of **5**, peaks at 260 and 248 nm (19 548, 19 536 L

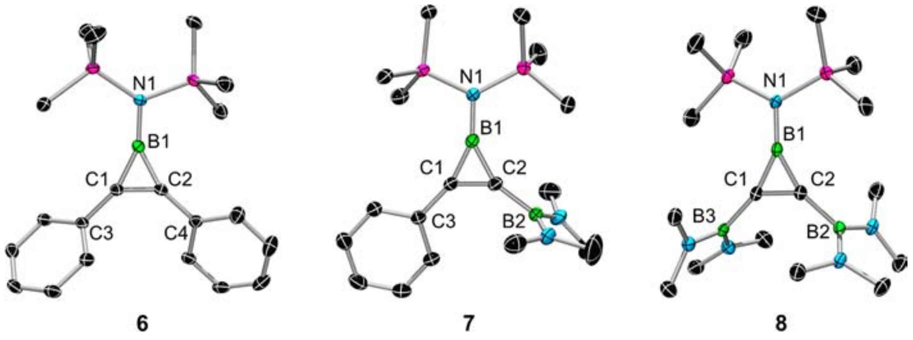
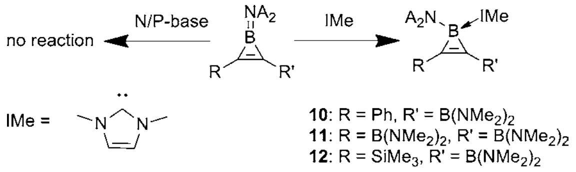


Figure 2. Molecular structures of **6**−**8**. Ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg) are shown in Table 1.

mol^{-1} cm^{-1}), which are characteristic for the aryl groups, and another at 208 nm (65 297 L mol^{-1} cm^{-1}) were observed. Also, the spectra of **7** showed a characteristic absorption (248.5 nm; 18 164 L mol^{-1} cm^{-1}) for the phenyl group. In the spectra of **8** a shoulder at 225 nm was identified, whereas that of **9** shows no characteristic absorptions.

Reactivity of the Borirenes. A huge variety of reports about partial or total quaternization of boron centers exist in the literature. These reactions are useful for, among other things, the sensing of anions.[11] This reaction is restricted to electron deficient boranes, thus quaternization of aminoboranes is much more rare, as the p orbital of boron is significantly filled by the π-basic amino group. To gather more information about the reactivity of borirenes and to probe the degree of aromaticity, we investigated the reactivity of **5** and **7**,**8** toward Lewis bases as shown in Scheme 3.

Scheme 3. Reactivity of Aminoborirenes toward Lewis Bases[a]

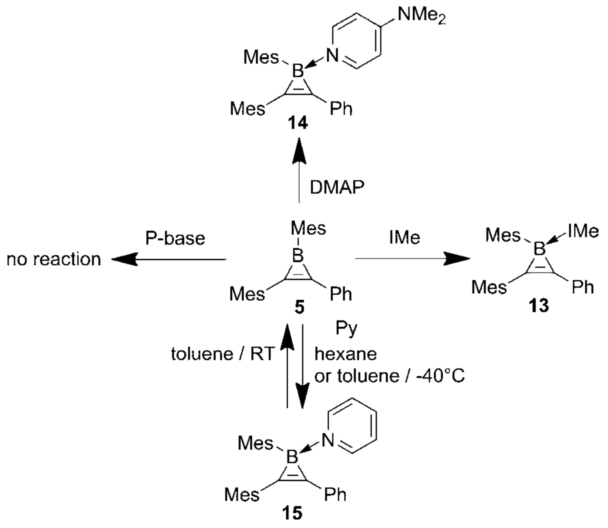


[a] A = SiMe$_3$.

The aminoborienes **7**–**9** did not react with DMAP (4-(dimethylamino)pyridine), pyridine, PCy$_3$, or PMe$_3$ at ambient temperature or at 80 °C, whereas NMR spectroscopy showed immediate reaction with IMe (1,3-dimethyl-2,3-dihydro-1*H*-imidazole) at ambient temperature. The base adducts **10**–**12** were isolated after workup as colorless solids in resonable yield. In the case of **7**–**9**, no quaternization of the exocyclic boryl groups was observed even upon addition of an excess of IMe.

The triaryl borirene **5** does not react with phosphorus-centered Lewis bases, but it forms stable adducts with IMe (**13**) and DMAP (**14**), whereas pyridine does not form an adduct at ambient temperature. Upon cooling to −40 °C, adduct formation (**15**) was observed (Scheme 4, Figure 3). Nevertheless, **15** can be precipitated as a pale yellow solid by addition of pyridine to a hexane solution of **5**. The base can be removed from adducts **10**–**14** by addition of BPf$_3$ (Pf = C$_6$F$_5$, pentafluorophenyl), yielding the parent borirene and corresponding base adduct of BPf$_3$ (Scheme 5). This reaction suggests that borirenes are weaker Lewis acids than BPf$_3$.

Scheme 4. Reactivity of 5 toward Lewis Bases



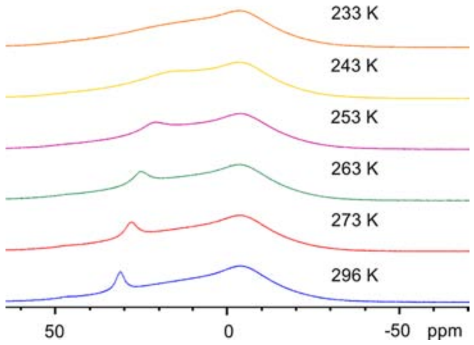
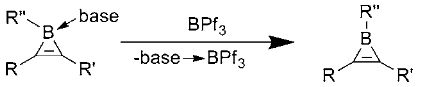


Figure 3. Temperature-dependent formation of **15** as noted by 11B NMR.

Scheme 5. Dequaternization of Borirenes



	R	R'	R''	base
5	Mes	Ph	Mes	-
7	Ph	B(NMe$_2$)$_2$	N(SiMe$_3$)$_2$	-
8	B(NMe$_2$)$_2$	B(NMe$_2$)$_2$	N(SiMe$_3$)$_2$	-
9	SiMe$_3$	B(NMe$_2$)$_2$	N(SiMe$_3$)$_2$	-
10	Ph	B(NMe$_2$)$_2$	N(SiMe$_3$)$_2$	IMe
11	B(NMe$_2$)$_2$	B(NMe$_2$)$_2$	N(SiMe$_3$)$_2$	IMe
12	SiMe$_3$	B(NMe$_2$)$_2$	N(SiMe$_3$)$_2$	IMe
13	Mes	Ph	Mes	IMe
14	Mes	Ph	Mes	DMAP

The melting and decomposition points of **10**–**15** determined by differential thermal analysis indicate a reduced thermal stability of the borirenes quaternized with IMe in comparison to the parent borirenes, whereas the DMAP (**14**) and pyridine (**15**) adducts of **5** show no decomposition <320 °C.

The ^{11}B{^{1}H} NMR spectra showed in all cases new resonances at $\delta \approx -20$ ppm, which is high-field shifted by about 50 ppm in comparison to the parent borirenes, thus indicating the formation of a quaternized boron center. The exocyclic boryl groups of **10** (δ = 33.9 ppm), **11** (δ = 33.8 ppm), and **13** (δ = 34.8 ppm) are only slightly high-field shifted with respect to the parent borirenes. The signals for **14** and **15** are found at around δ = 0 ppm and obscured by the signal of the borosilicate glass tube. The presumed shifts are consistent with the lower Lewis basicity of pyridine bases as compared to NHCs (*N*-heterocyclic carbene) and literature ^{11}B NMR data of other pyridine adducts of simple alkyl- and arylboranes, which are close to 0 ppm.[20] The carbon atoms of the BCC ring were detected at δ = 165.94 ppm (**11**) and δ = 178.84, 165.94 ppm (**12**). For the carbene carbon atom coordinated to the ring boron atom, resonances were found for **11** and **12** at δ = 172.05 ppm. In both cases, the signal is a quartet with a $^1J_{BC} \approx 71$ Hz coupling. Other NMR spectroscopic data are consistent with proposed structures.

IR spectra of **10**−**15** showed typical absorptions between 1693 and 1573 cm^{-1} in the solid state for CC double bonds (Table 3). The experimental values fit to those predicted via computational methods well. The values for the CC stretch decrease over the series aryl > boryl > silyl, thus resembling the trend observed for the nonquaternized borienes. The influence of the base seems not to be as great as that of the exocyclic groups. Even so, the values for **13**−**15** show that a stronger base yields higher frequencies for the CC stretch, thus indicating reduced delocalization in the ring.

Table 3. Experimental and Calculated IR Data of the C═C Stretch in Quaternized Borirenes (cm^{-1})

	10	11	12	13	14	15
exp	1650	1615	1573	1693	1687	1680
calcd	1705	1661	1686	1763	1733	

The C1−C2 bonds of the quaternized borirenes **10**−**14** are very similar, regardless of the functional groups or base on the BCC ring (Figure 4, Table 4). They are shorter than in the parent borirenes, indicating a lesser degree of delocalization over the ring and the electron density being more centered between C1−C2. The intracyclic B−C bonds have lengths near the sum of the covalent radii of boron and carbon (1.57 Å);[20c] however, they are elongated with regard to the parent borirenes. An aryl or amino group at the ring boron atom has no effect on the ring B−C bonds, whereas the ring B−C bonds adjacent to a boryl or mesityl group are slightly longer than those next to a phenyl or silyl group. The exocyclic boryl and mesityl groups are distorted from the plane of the BCC ring, whereas the phenyl groups are in plane with the BCC ring except for that in **13**. The orientation of the exocyclic groups in **10**, **11**, and **13** does not differ from those of the parent borirenes, whereas in **14** the aforementioned coplanarization of the phenyl group takes place. If the exocyclic group on the boron is an amino group, the distance matches the sum of covalent radii of boron and nitrogen (1.55 Å);[18] if it is a mesityl group, the bonds are somewhat longer than the sum of the covalent radii (ΣBC(sp^2) = 1.57 Å). The distance between the ring boron and the base is minimally influenced by the base or the functional groups at the borirene. The average distance of 1.62 Å fits to those observed in the pyridine base adducts of boroles.[20c] These structural findings for **10**−**14** are interpreted as indicative for annihilation of delocalization of the two π-electrons over the three-centered bonding molecular orbital comprised of the p$_z$ atomic orbitals of boron and carbon.[19]

The compounds **10**−**14** were also investigated by UV/vis spectroscopy. Compound **10** shows a maximum at 250 nm (13 425 L mol^{-1} cm^{-1}) typical for a phenyl group and nearly identical to the absorption in the parent borirene **7** (248.5 nm; 18 164 L mol^{-1} cm^{-1}). In the spectrum of **11**, a shoulder at 224 nm was identified, again similar to the parent borirene **8**, which shows one at 225 nm. The spectrum of **12** shows no characteristic absorption. The same fact is found in the parent borirene **9**. This can be explained by the lack of chromophores that absorb in the appropriate range. The absorption spectra of **13** and **14** are quite similar. That of **13** shows a maximum at 245 nm (13 011 L mol^{-1} cm^{-1}) and a shoulder at 285 nm. That of **14** shows a striking maximum at 258 nm (34 345 L mol^{-1} cm^{-1}) and a shoulder at 281 nm.

Computational Studies. To analyze the bonding situations in the synthesized borirenes and the adducts in more detail, we performed DFT calculations at the B3LYP/6-311G* and OLYP/TZP levels. The so-called "fragment approach" as implemented in the Amsterdam Density Functional (ADF) program was employed for the bonding analysis.

The major aim of the analysis was to quantify the relative ease with which charge flux is contained in the simplest borirene center, the BCC ring. We thus systematically compared the effects of various side-chains on the energy of bonding for some strategically selected bonds. Although the dynamics of polarity in molecular systems have been traditionally related to charge delocalization on extended π-systems, boron possesses the unusual property of acting as multi-symmetry charge flux "adapter"; that is, it is able to

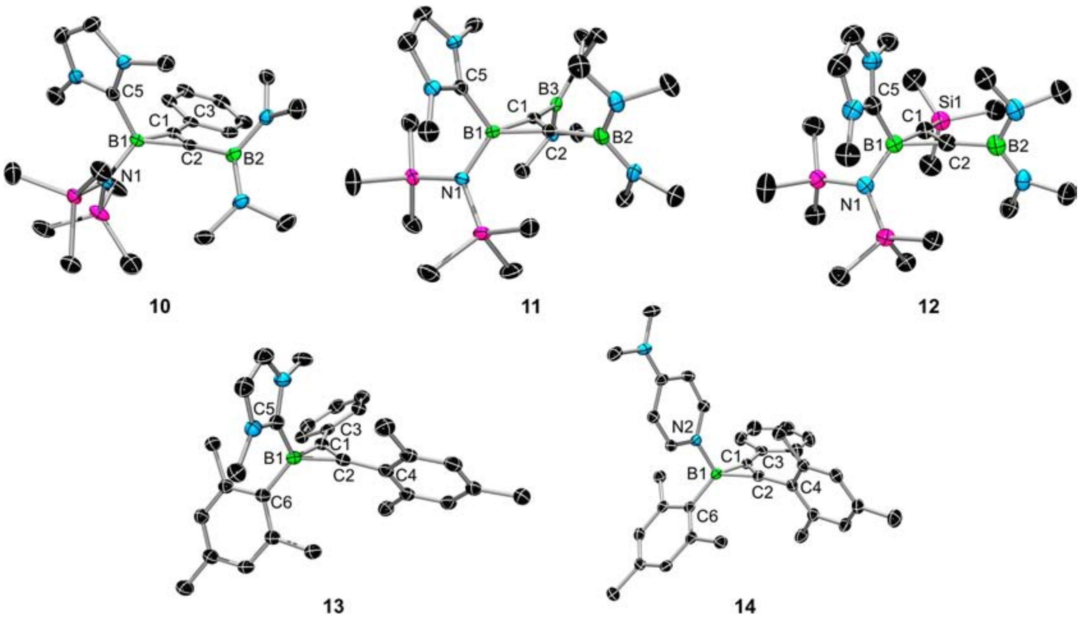
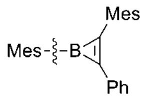
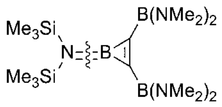
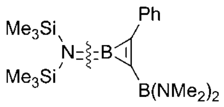
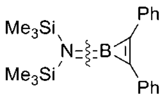


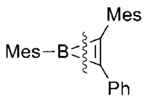
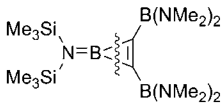
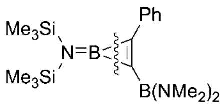
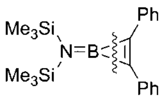
Figure 4. Molecular structures of **10**−**14**. Ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Relevant bond lengths (Å) and angles (deg) are mentioned in Table 4.

Table 4. Relevant Bond Lengths (Å) and Angles (deg) of 10−14

	compound				
	10	11	12	13	14
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
C1−C2	1.330(2)	1.339(2)	1.341(2)	1.315(2)	1.327(2)
B1−C1	1.561(2)	1.590(2)	1.581(3)	1.589(2)	1.563(2)
B1−C2	1.628(2)	1.584(2)	1.608(2)	1.619(2)	1.619(2)
C1−C3/B3/Si1	1.469(2)	1.556(2)	1.843(2)	1.458(2)	1.460(2)
∠BCC plane−C3Ph/B3NN plane	18.3(1)	66.3(1)		36.4(1)	3.2(1)
C2−B2/C4	1.553(2)	1.556(2)	1.556(2)	1.460(2)	1.463(2)
∠BCC plane−C4Mes/B2NN plane	63.4(1)	67.7(1)	77.00(1)	56.2(1)	68.9(1)
B1−N1/C6	1.560(2)	1.569(2)	1.554(3)	1.614(2)	1.609(3)
B1−C5/N2	1.626(2)	1.629(2)	1.612(3)	1.612(2)	1.621(2)
C1−B−C2	49.24(8)	49.7(1)	48.89(9)	48.39(7)	49.9(1)

Table 5. Bonding Energy Decomposition Participation (kcal mol^{-1}) and N/C−B Bond Distance (Å) for Some Selected Borirene Systems

				
Compound	5	8	7	6
ΔE_{orb}	-180.63	-365.59	-374.43	-385.14
ΔE_{elstat}	-161.32	-244.17	-247.14	-259.38
ΔE_{int}	-113.64	-118.32	-118.85	-117.61

				
Compound	5	8	7	6
ΔE_{orb}	-477.27	-468.52	-679.42	-452.98
ΔE_{elstat}	-264.46	-281.62	-320.34	-289.53
ΔE_{int}	-205.33	-212.70	-385.66	-211.65
d(C/N-B)	1.554	1.445	1.440	1.437

bidirectionally convey charge flow between two different elements simultaneously through both σ and π symmetry bonds.[21] In the model molecule $(H_3Si)_2NBC_2(SiH_3)_2$, for instance, the N−B bond is composed of σ and π bonds, the latter to a smaller extent. In the BCC core, the π covalent contribution to bonding energy indicates cyclic delocalization, suggesting some aromatic character, which is also supported by computed NICS(0) and NICS(1) values. The lone pair (LP) donation of N and of the π-(C═C) bond to the empty p_z orbital on the ring boron was also quantified by Natural Bonding Analysis (NBO), revealing that the extent of the donation process can be modulated through modification of the substituents on the C═C linkage.[4e]

Table 5 shows the different values of bonding energy contribution to the N/C−B and the B−C2 bonds. In all cases, the orbital interaction is predominant with respect to the electrostatic contribution; thus electron delocalization in the BCC core does take place. Orbital interaction is much larger in the R−B bond when R is an amino group, due to the LP(N)→$p_z(B_{borirene})$ donation, and is commensurate with a shorter N−B bond. This orbital interaction is modified upon change of the substituents bound to C═C. When the C═C unit is bound to two $B(NMe_2)_2$ units, the $E_{orb}(N{-}B_{borirene})$ is smaller as compared to the case when one of the $B(NMe_2)_2$ groups is replaced by a phenyl group, in line with a longer N−B bond. This reflects the reduced LP(N)→$p_z(B_{borirene})$ donation that can be ascribed to the increased $p_z(B)\leftarrow\pi(C{=}C)$ donation, which in turn is due to the fact that the $\pi(C{=}C)\rightarrow B(NMe_2)_2$ charge flux is suppressed. Indeed, the $B(NMe_2)_2$ unit cannot accept charge from π(C═C) because either the $p_z(B_{exocyclic})$ orbital is perpendicular to the π(C═C) or if an overlap can occur, the LP(N) on the other side is already donating to the $p_z(B_{exocyclic})$ orbital (see Figure 5). Moreover, it is interesting to

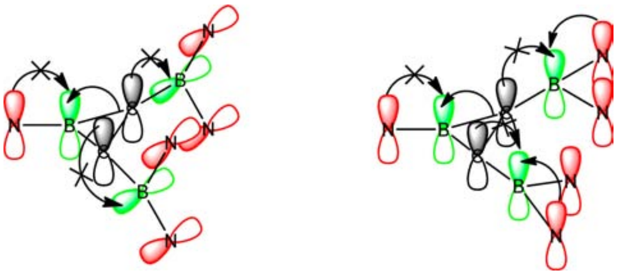


Figure 5. The proposed donations and suppressed donations in isomers of **8** in which the boryl [BN2] plane is perpendicular to (left) or coplanar with (right) the borirene π system.

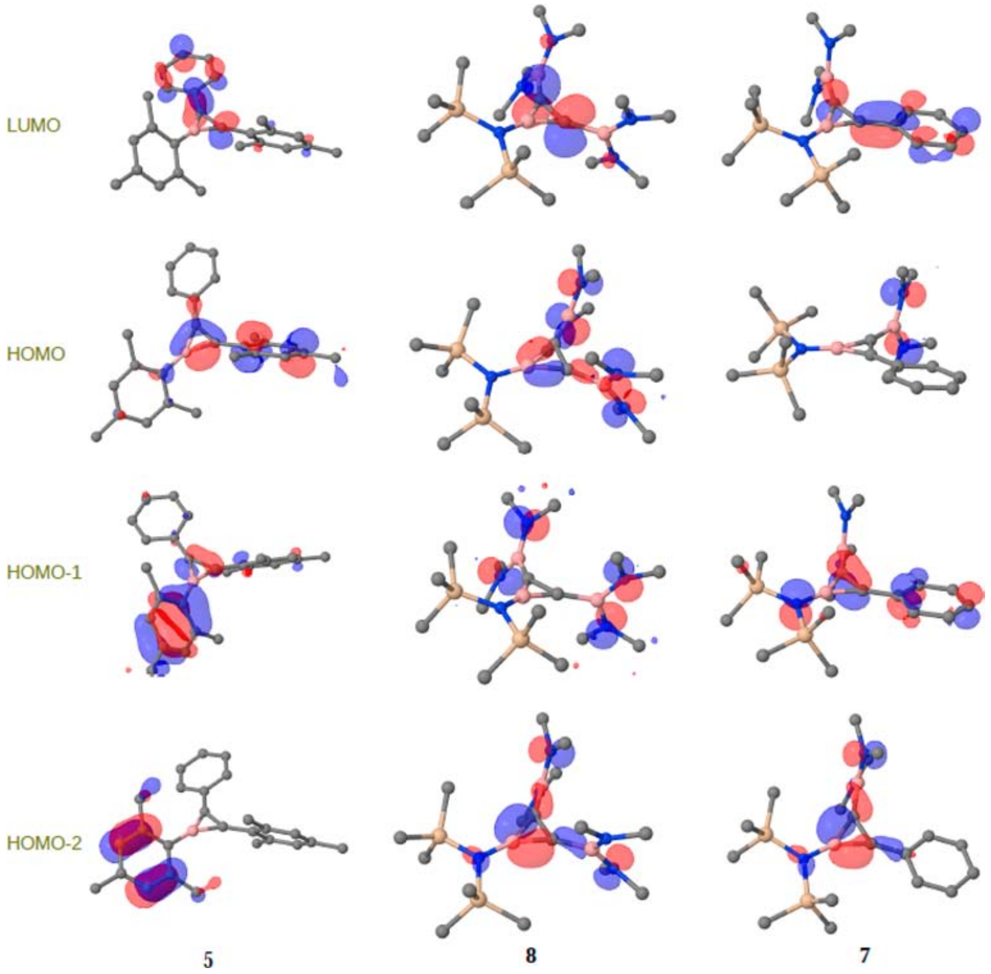


Figure 6. The LUMO (lowest unoccupied molecular orbital) (top) to HOMO−2 (bottom) levels in **5**, **8**, and **7**.

note that in the N−B−C−Ph chain the orbitals of each atom are prone to extensive π-electron delocalization, in agreement with the shorter NB−CPh bond as compared to the NB−CB$(NMe_2)_2$ bond, amounting to 1.481 and 1.499 Å, respectively.

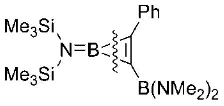
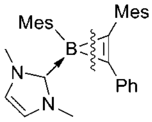
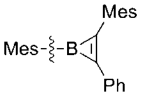
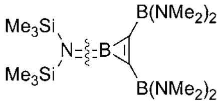
Inspection of molecular orbitals indicates that in the borirene core, there are substantial B−C_2 σ-like bonds generated from the boron-centered p orbital parallel to the borirene plane. In **7**, the borirene clearly exhibits a strong additional stabilization from the C═C π system (see its HOMO−1 in Figure 6), which is additionally antiphase to the LP(N); thus the π(C═C)→p_z(B) donation is not countered by the LP(N)→p_z(B) stabilization. Second-order perturbation analysis in NBO basis indicates an energy of 100 kcal/mol corresponding to the π(C═C)→p_z(B) donation. However, for **8** (Tables 5−7), the π(C═C)→p_z(B) stabilization amounts to 104 kcal/mol; it is thus likely that inductive effects are responsible for the observed higher ΔE_{orb}(B−C2) value in **7**. Moreover, for the all-aryl borirene **5**, the π(C═C)→p_z(B) donation is also of the same value (105 kcal/mol), which, when compared to **8**, suggests that the inductive effect in the borirene core is independent of any lone pair donation to the boron (e.g., LP(N)→p_z(B), p(aryl)→p_z(B)). One thus sees here the capacity of boron to behave as what could be called a three-way multisymmetry charge flux bridge; that is, boron's unique feature of having an unoccupied p_z orbital allows it to simultaneously accommodate and donate charge density by way of both resonance and induction.

There is a tendency for the B−C2 bonds to have a larger E_{orb} when the boron is sp^2 hybridized, except for the case, although not by much, when both carbons in the C═C unit are bound to B(NMe_2) side chains. Furthermore, the C═C bond is longer when bound to sp^2 boron, reflecting the existence of π(C═C)→p_z(B) donation relative to the quaternary boron case, in which NBO analysis accordingly indicates no considerable π(C═C)→p_z(B) interaction. The lack of LP(N)→p_z(B) donation in the case of **8** is also supported by the fact that the B−C_2 orbital interaction energy value for either sp^2 or sp^3 hybridized boron is of the same order of magnitude.

In a borirene unit, charge flux does not depend solely on π delocalization, and thus aromaticity plays a minor role due to boron's multisymmetry charge flux bridging capabilities; that is, the boron atom can convey charge flow even through induction and not only through resonance. The two forms of electron donation to boron, LP→p_z and π→p_z, are complementary and highly coupled, which in turn depend on the borirene side-chains; this dependency is due to geometrical and electronic reasons.

To determine the effect of substitution of the borirene ring on the π and σ delocalization in the borirene ring, nucleus-independent chemical shift (NICS) values were calculated for the sequentially borylated borirenes **6**−**8** (Table 7) and the adduct **11** at the ring centroid (NICS(0))[22] and 1.0 Å above

Table 6. Bond Lengths (Å), Natural Charge (e), and Energy Contribution (kcal/mol) in a Range of Borirenes and Base-Stabilized Borirenes

				
Compound	7	13	5	8
ΔE_{orb}	-679.42	-345.78	-477.27	-468.52
ΔE_{elstat}	-320.34	-238.09	-264.46	-281.62
ΔE_{int}	-385.66	-146.85	-205.33	-212.70
d($B_{borirene}$-substituent)	1.440	1.641	1.554	1.445
d(intracyclic B-C (top))	1.491	1.635	1.494	1.494
d(intracyclic B-C (bottom))	1.508	1.598	1.486	1.494
d(C=C)	1.376	1.325	1.370	1.387
q(B)	0.70	0.26	0.61	0.70

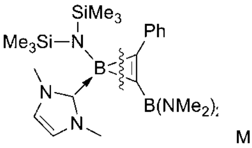
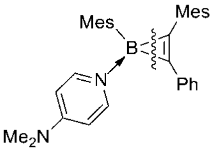
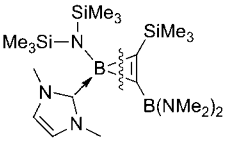
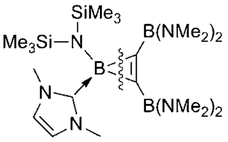
				
Compound	10	14	12	11
ΔE_{orb}	-411.54	-398.22	-354.14	-473.51
ΔE_{elstat}	-269.03	-265.32	-251.07	-277.25
ΔE_{int}	-165.45	-158.28	-159.85	-177.78
d($B_{borirene}$-substituent)	1.578	1.626	1.580	1.590
d(intracyclic B-C (top))	1.578	1.597	1.606	1.610
d(intracyclic B-C (bottom))	1.640	1.566	1.641	1.613
d(C=C)	1.336	1.336	1.340	1.343
q(B)	0.49	0.53	0.48	0.48

Table 7. Nucleus-Independent Chemical Shift (NICS) Values for 6−8 and 11

	compound			
	6	7	8	11
NICS(0)	−19.48	−20.15	−19.68	−21.92
$\text{NICS}_{zz}(0)$	−14.58	−19.82	−25.23	−30.20
NICS(1)	−10.47	−11.67	−13.10	−9.48
$\text{NICS}_{zz}(1)$	−13.41	−16.04	−19.83	−17.02

the ring (NICS(1)).[23,24] The $\text{NICS}_{ZZ}(1)$[25] value, which represents the tensor *z*-components of the value rather than the isotropic NICS value, is considered to give the best measure of aromaticity in *π* systems. Our results show that aromaticity increases regularly with increasing replacement of phenyl by boryl substituents (**6**→**8**), which is in line with our above finding (Figure 5) that the perpendicular and relatively electronically saturated diaminoboryl groups do not significantly communicate with the borirene *π* system. Somewhat counterintuitively, this indicates that the phenyl groups are effectively stronger *π*-acids than the $B(NMe_2)_2$ groups in this case. Unsurprisingly, the "aromaticity" is lowest for the carbene adduct **11**. The $\text{NICS}_{ZZ}(0)$[25] values, which give a measure of the extent of delocalization in the *σ*-system, also increase as strongly *σ*-donating boryl groups are successively added (**6**→**8**). The *σ* delocalization of **11**, which has suffered a loss of delocalization in its *π* system, is even higher than in **6**−**8**.

■ CONCLUSIONS

This Article describes the synthesis of borirenes by photochemical borylene transfer to a series of different functionalized alkynes in high yield. The series of borirenes synthesized allowed us to systematically compare the properties of borirenes depending on the functional groups in 1, 2, and 3 positions. All borirenes were found to possess remarkable thermal stability. We were also able to identify the ring-breathing band in the IR spectrum, giving us an additional tool to identify borirenes and to evaluate the bonding situation in the ring. The X-ray structures of the borirenes **6**−**8** showed clearly that the replacement of the phenyl groups by the $B(NMe_2)_2$ group yields more conjugation in the BCC ring. To evaluate the reactivity of borirenes, we reacted amino- and arylborirenes with different Lewis bases. The reaction yielded borirenes with a quaternized ring boron atom. The formation of the adduct was obviously influenced by the strength of the base and the extent of electronic saturation of the ring boron atom. The base can be removed by addition of BPf_3, thus making the quaternization process a reversible method for switching the borirene aromaticity on and off. The joint computational−experimental study reveals that in a borirene unit charge flux does not depend solely on *π*-delocalization, and thus aromaticity plays a minor role thanks to boron's ability to convey charge flux through induction with the same ease as through resonance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, UV/vis spectra of **7**−**14**, crystallographic data of complexes **4**, **6**−**8**, and **10**−**14** in cif format, and details about DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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