

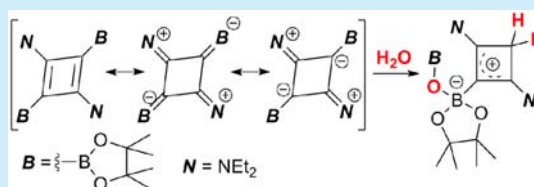
Rhombic Cyclobutadiene with a Boryl/Amino-Substitution Pattern: Boryl Group Migration Induced by Reaction with Water

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S Supporting Information

ABSTRACT: The synthesis of a donor–acceptor cyclobutadiene featuring a boryl/amino-substitution pattern is presented together with its characteristic reactivity toward water. On the basis of the results of X-ray crystallography, theoretical studies, and spectroscopic analyses, the observed rhombic structure of the cyclobutadiene was attributed to a charge-separated electronic structure. Reaction of this boryl-substituted cyclobutadiene with water induced a characteristic migration of the boryl group, due to the Lewis acidity of the boryl-substituent.



Cyclobutadienes (CBDs) are cyclic molecules with four π -electrons. A large number of theoretical and experimental studies on this fundamental class of molecules have revealed that CBDs do not adopt a square but rectangular structure in order to avoid an unstable antiaromatic electronic configuration with four π -electrons (Figure 1).¹ Despite the high reactivity of most

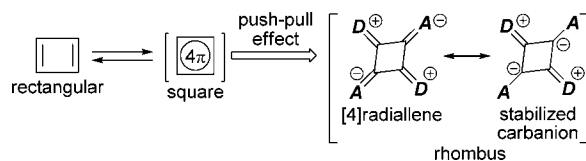


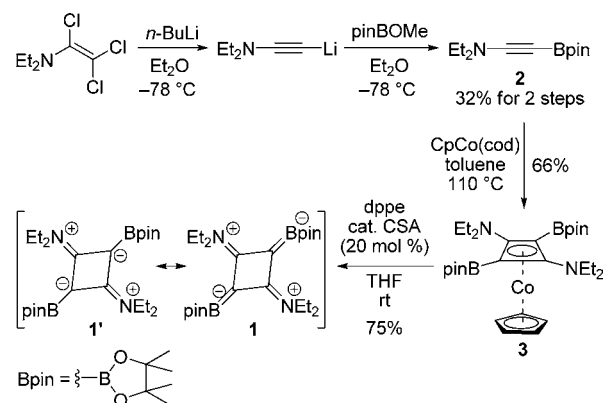
Figure 1. Structural deviation of CBDs.

CBDs, some examples could be isolated after kinetic stabilization with suitable protecting groups.^{2–7} It is even possible to replace one of the four bulky substituents in these CBDs by smaller substituents, e.g., ester,⁵ aryl,⁶ or sulfonyl groups.⁷ In contrast to the rectangular structure of CBDs protected by bulky substituents, the captodative (push–pull) effect of a combination of donor and acceptor substituents in an alternating order leads to the formation of a rhombic CBD structure.⁸ There, the four π -electrons of the rhombic CBD interact with the donor and acceptor groups, resulting in a [4]radialene-type structure.⁹ However, for this substitution pattern, only carbonyl- (ester- or acyl-) and amino-substituted CBDs have been reported so far, and therefore, the exact properties of rhombic CBDs still remain unclear.

Herein, we report the synthesis of a CBD with a push–pull substitution pattern arising from the presence of alternating boryl- and amino-substituents as the acceptor and donor groups. On the basis of X-ray crystallography, theoretical calculations, and spectroscopic studies, a rhombic structure was assigned to this CBD, and the coexistence of the resulting charge-separated character and Lewis acidic boryl-substituent gave rise to a characteristic reactivity of this CBD toward water.

Boryl/amino-substituted CBD **1** was synthesized as described in Scheme 1. According to our previous report for the synthesis

Scheme 1. Synthesis of CBD 1



of the similar boryl/amino-substituted acetylene,¹⁰ a reaction of the *in situ*-generated diethylaminoacetylide¹¹ with 2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (MeOBpin) gave boryl/amino-substituted acetylene **2** in the form of colorless crystals in 32% yield. A subsequent reaction with CpCo(cod) induced a head-to-tail dimerization of **2**, affording complex **3** in 66% yield. An ensuing ligand exchange reaction between **3** and 1,2-bis(diphenylphosphino)ethane (dppe) in the presence of a Brønsted acid catalyst (10-camphersulfonic acid) furnished the targeted CBD **1** as orange crystals in 75% yield. Compounds **1**, **2**, and **3** were exhaustively characterized by multinuclear NMR spectroscopy (¹H, ¹³C, and ¹¹B) and elemental analysis. The solid-state structures of **1** and **3** were moreover determined by X-ray crystallography.

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The molecular structure of **1** in the solid state is shown in Figure 2. Two crystallographically independent molecules are

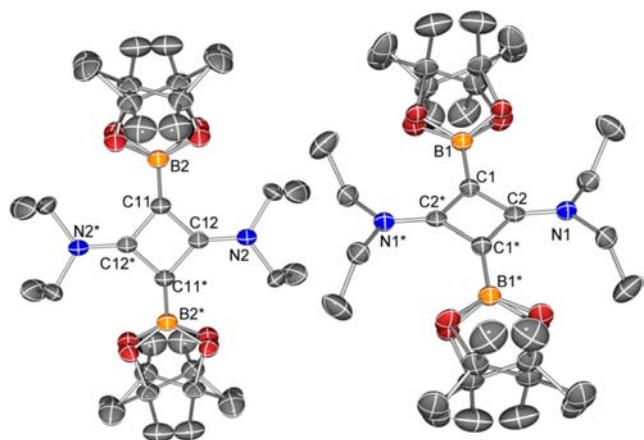


Figure 2. Molecular structure of **1** (thermal ellipsoid probability: 50%). The two independent molecules in the asymmetric unit are shown. The disordered pinacolate moieties are disordered over two positions with relative occupancies of 1:1. All hydrogen atoms are omitted for clarity.

contained per asymmetric unit, and both molecules adopt planar rhombic structures with C_{2h} symmetry, resulting in four identical carbon–carbon bond lengths within the CBD moieties. A C_2 axis is located on the coaxial of the N1–C2 and C2*–N1* bonds, and a mirror plane involving the B1–C1 and C1*–B1* bonds is oriented perpendicular to the CBD ring with disordered pinacolate moieties. As a result of the distortion into rhombus structure, the internal bond angles of boryl-substituted carbons [84.73(19)° for C2–C1–C2* and 84.26(19)° for C12–C11–C12*] were smaller than those of the amino-substituted carbons [95.27(19)° for C1–C2–C1* and 95.74(19)° for C11–C12–C11*]. Whereas the substituted nitrogen atoms are arranged in a coplanar fashion with respect to the CBD ring, the two boron atoms lie below and above the CBD plane. The boryl-substituted C1 and C11 atoms exhibit a pyramidalized coordination geometry (sum of the angles around C1 and C11 = 357° and 358°), adopting bent angles of 11.85(16)° and 9.74(16)°, respectively.¹² The sides of the rhombic CBD [1.468(2) Å/1.461(2) Å] are intermediate between carbon–carbon single and double bonds¹³ and comparable to those of previously reported carbonyl/amino-substituted CBDs.^{8d,e} The boron–carbon bond lengths in **1** [1.505(3) Å/1.504(4) Å] are shorter than the B–C bonds of the CBD precursor **3** [1.530(5) Å/1.539(5) Å] (Figure S2) or the sum of the covalent radii between boron and carbon atoms (1.65 Å).¹⁴ The nitrogen–carbon bonds are also shorter than the corresponding single bonds in complex **3**. According to these results, the *exo*-B–C and *exo*-N–C bonds of **1** would have the unsaturated character.

To provide further insights into the electronic structure of **1**, we performed DFT calculations at the M06-2X/6-31G(d) level of theory, using Gaussian 09 (rev. C.01).¹⁵ The structural optimization of **1** was able to closely reproduce the rhombic structure obtained from the X-ray crystallographic analysis. Frontier orbitals of **1** are shown in Figure 3. The HOMO and LUMO are localized at the B–C and N–C bonds in the form of π - and π^* -type orbitals, suggesting that the captodative electronic effect of the boryl/amino substitution pattern induces a [4]radialene-type structure in **1'** as illustrated in Scheme 1. In fact, the natural population analysis (NPA) charge distribution of

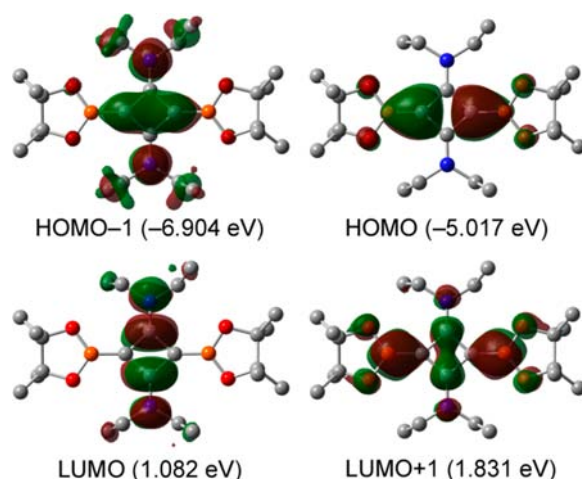


Figure 3. Frontier orbitals of **1** calculated at the M06-2X/6-31G(d) level of theory.

1 showed four alternately charged carbon atoms within the CBD ring (Figure 4a). In addition to the charge-separated

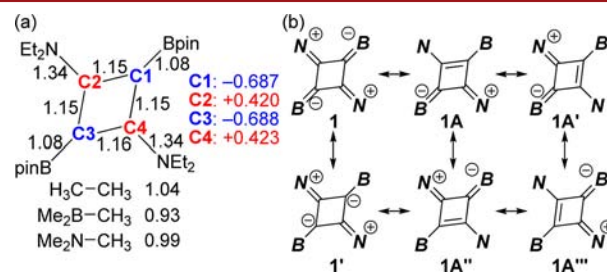


Figure 4. (a) NPA charges of the carbon atoms in the ring (blue, negative; red, positive); Wiberg bond indexes for C–C, B–C, and N–C bonds in **1** and in reference compounds (black); (b) possible resonance structures of **1**.

[4]radialene structure, a C–C multiple bond character was proven to contribute to the electronic structure of the CBD. The analysis of Wiberg bond indexes (WBIs) showed bond orders of 1.15–1.16 for the ring C–C bonds, which is slightly higher compared to C–C single bonds (Figure 4a). However, bond orders of 1.08 for the C–B bonds and 1.33 for the C–N bonds indicated unsaturated character for these bonds in comparison with corresponding saturated reference compounds such as trimethylborane and trimethylamine (Figure 4a). According to the results of WBI, one can expect that **1** may have a set of the resonance structures described in Figure 4b.

The ¹H and ¹³C NMR spectra of **1** in THF-*d*₈ showed only one signal for Bpin, as well as signals associated with the ethyl-substituents. The resonances of the ring carbon atoms were observed at 76 and 185 ppm for the boryl- and amino-substituted carbon atoms, respectively. At room temperature, these values are significantly shifted relative to those of the reported rectangular CBDs in solution (173.4–132.1 ppm).^{2–7} The calculated negative charges on the boryl-substituted carbon atoms (–0.687/–0.688) may contribute to the high-field shifted resonance of them. The gauge-independent atomic orbital (GIAO) calculation at the M06-2X/6-311+G(2d,p) level of theory predicted chemical shifts for rhombic **1** at 87 ppm (B–C) and 211 ppm (N–C), which is in conformity with the experimental results.

The UV–vis absorption spectrum of **1** in THF exhibited absorption maxima at $\lambda = 407$ ($\epsilon = 300$) and $\lambda = 302$ nm ($\epsilon = 30000$) (Figure 5; $[1] = 7.8 \times 10^{-5}$ M). The time-dependent

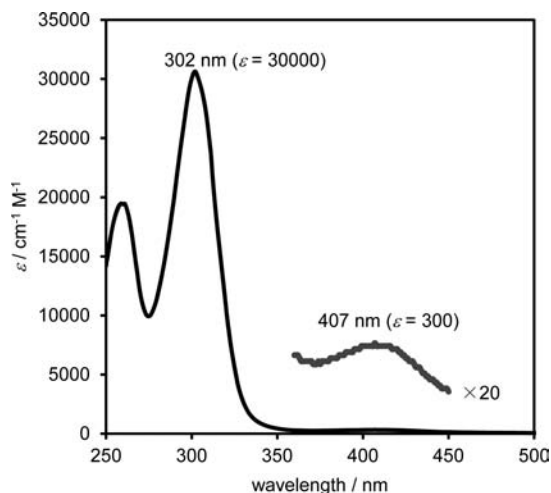
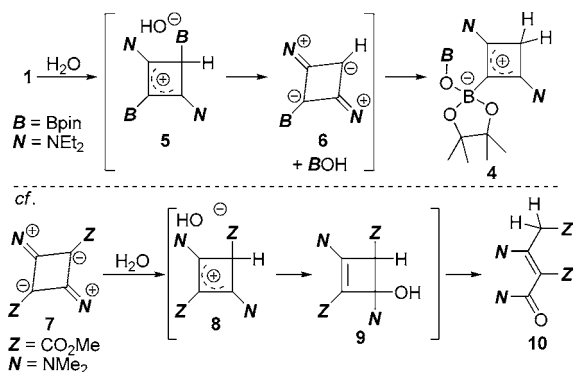


Figure 5. UV–vis absorption spectrum of **1** in THF at room temperature.

DFT (TD-DFT) calculations at the M06-2X/6-31G(d) level of theory suggested a HOMO–LUMO transition energy of 445 nm (2.79 eV, Table S2). The calculation using higher level basis sets [M06-2X/6-311+G(2d,p)] with the solvent effect by the polarizable continuum model (PCM)¹⁶ in THF showed an absorption at 422 nm (2.94 eV, Table S3) between the molecular orbitals having the same topology. Thus, the weak absorption at 407 nm could accordingly be assigned to the HOMO–LUMO transition. Since the HOMO and LUMO of **1** adapt the gerade-type symmetry, the HOMO–LUMO transition may be symmetry forbidden by the Laporte selection rule to give the small oscillator strength.

The contribution of a stabilized carbanion resonance form in **1** is also reflected in its reactivity. Reaction of **1** with H₂O proceeded smoothly to give **4** in quantitative yield through the double protonation of a ring carbon atom, migration of a boryl group, and subsequent formation of a bridging oxygen atom between two boron atoms (Scheme 2). Similar to a previously reported push–pull CBD,⁸ the reaction should be initiated via the protonation of the boryl-substituted carbon atom to form possible intermediate **5**. A nucleophilic attack of the resulting hydroxide toward the boron atom would then result in the formation of a hydroxyborane and **6** under concomitant

Scheme 2. Reaction of CBDs **1** and **7**



regeneration of the CBD skeleton. Further protonation of **6** together with the formation of a B–O bond should subsequently afford **4**. Ester/amino-substituted CBD **7** was reported to react with H₂O to form ring-opened enone **10**. The formation of the observed reaction product was explained by an initial protonation of an ester-substituted carbon atom, followed by a nucleophilic attack of the resulting hydroxide toward **8**, resulting in an ensuing ring opening of cyclobutene **9**.^{8c} In the case of boryl-substituted CBD **1**, the hydroxide in **5** preferentially attacks the boron atom rather than the CBD ring carbon to form the 1,2-adduct. The different reactivity of **1** relative to **7** may arise from the higher Lewis acidity of the boryl group in **5** compared to that of the ester group in **8**, which is probably due to the electropositive nature of the boron atoms, facilitating both incorporation of the hydroxide nucleophile and release of the hydroxyborane intermediate. As a result, the four-membered ring of the CBD skeleton remains intact even after reaction with H₂O. This result promises the possibility for utilization of water as two protons and one oxygen atom separate by using the chemistry of CBD without transition metal catalyst.

We have successfully synthesized boryl/amino-substituted CBD **1**. X-ray crystallography, theoretical investigations, and spectroscopic analyses suggest that **1** should be stabilized by contributions from a charge-separated [4]radialene and a stabilized carbanion structure. Reaction of **1** with H₂O afforded the doubly protonated product **4**, which was generated via protonation of the CBD skeleton, followed by cleavage of the C–Bpin bond. This behavior should most likely be attributed to the strong Lewis acidity of the boron atoms. The reactivity of **1** toward other organic reagents is currently under investigation, and results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

Details of experiments, crystallographic data, and 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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