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Dimerization of Boryl- and Amino-Substituted Acetylenes by B₂C₂ Four-Membered Ring Formation

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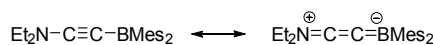
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Boryl- and amino-substituted acetylenes bearing diphenylboryl or 9-borabicyclononyl groups were synthesized. X-ray diffraction analyses revealed the dimerized structures of these acetylenes via the formation of B₂C₂ four-membered rings. Spectroscopic studies and DFT calculations indicated that these dimers can dissociate to afford monomeric acetylenes, and that the equilibrium constant for the dissociation depends on the structure of the boryl substituents.

Boryl-substituted acetylenes are useful synthons for organic transformations¹ such as the Suzuki-Miyaura coupling² and the alkynylation of carbonyl compounds.³ On the other hand, amino-substituted acetylenes (ynamines) are unique building blocks for organic molecules.³ As a result of the electron-donating ability of the amino substituent, the β-carbon atom of amino-acetylenes is highly nucleophilic.⁴ In addition to their utility in organic synthesis, diaminoacetylenes have recently been used as precursors for a variety of main-group-element-containing compounds and transition-metal complexes.⁵ In this context, boryl- and amino-substituted acetylenes could be considered as unique push-pull precursors given the electron-withdrawing boryl and the electron-donating amino groups. However, previously reported examples of boryl- and amino-substituted acetylenes remain limited, probably due to the high reactivity of the amino-acetylene moiety in addition to the Lewis acidity of the boryl group.^{6,7} We have already reported the solid-state structure of dimesitylboryl- and diethylamino-substituted acetylene **1a** as the first example for a structurally characterized boryl- and amino-substituted acetylene (Scheme 1).⁷ Importantly, **1a** exhibits a butatriene-type resonance contribution due to the interactions between the boryl and amino groups via the acetylene moiety. To get further insight

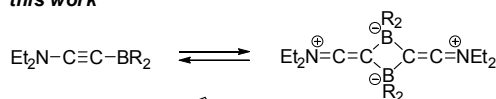
previous work



1a

Mes = 2,4,6-trimethylphenyl

this work



R₂ = Ph₂ (**1b**), (**1c**)

Scheme 1 Resonance contributions and dimerization of boryl- and amino-substituted acetylenes.

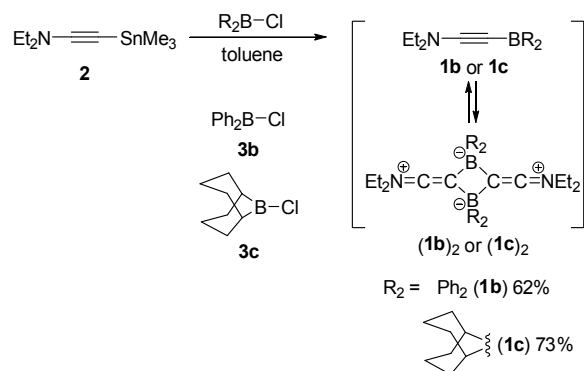
into the properties of boryl- and amino-substituted acetylenes, we focused on the introduction of a boryl group that bears sterically less demanding substituents. In the present study, we synthesized novel boryl- and amino-substituted acetylenes that bear diphenylboryl or 9-borabicyclononyl and diethylamino groups. X-ray crystallographic analyses revealed the dimerization of these acetylenes via the formation of a B₂C₂ four-membered ring. The resulting B₂C₂ core can be distinguished from the recently disclosed example of a three-centre-two-electron (3c-2e) B-C-B bond,⁸ as it arises from the interactions between the nucleophilic β-carbon atom relative to the amino group and the electrophilic boryl moiety. In addition, the formation of the B₂C₂ ring is reversible. In solution, the constituent acetylenes dissociate to afford the monomeric acetylenes via a reversible formation/cleavage of the B-C bonds.⁹

Diphenylboryl- and 9-borabicyclononyl-substituted diethylaminoacetylenes **1b** and **1c** were obtained from the reaction between stannyl-substituted aminoacetylene **2**¹⁰ and Ph₂BCl **3b**¹¹ or 9-borabicyclononyl chloride **3c**¹² (Scheme 1). An X-ray crystallographic analysis revealed that single crystals obtained from the crude mixture of the resulting acetylenes exhibited dimeric structures, henceforth described as (**1b**)₂ and (**1c**)₂. In the crystals, the two boryl-groups bridge two boron-bonded carbon atoms to form a planar B₂C₂ four-membered ring (Fig. 1), in which the boron atoms adopt a tetrahedral geometry. The

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† Electronic Supplementary Information (ESI) available: Experimental procedures, X-ray crystallographic analyses, and theoretical calculations. See DOI: 10.1039/x0xx00000x



Scheme 2 Synthesis of boryl- and amino-substituted acetylenes **1b** and **1c**, and their subsequent dimerization to afford (1b)₂ and (1c)₂.

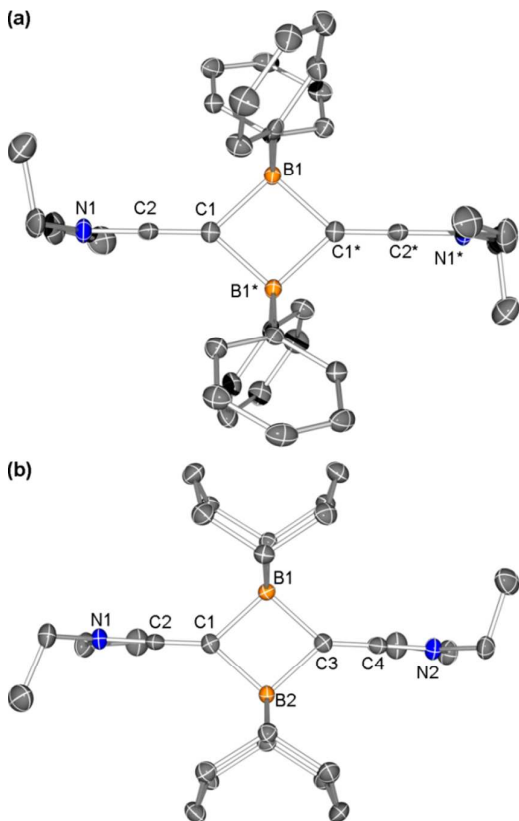


Fig. 1 Molecular structures of (a) (1b)₂ and (b) (1c)₂ (thermal ellipsoids set at 50% probability, hydrogen atoms omitted for clarity).

carbon-carbon bond distance of the CC unit that originates from the acetylenic moiety [(1b)₂: 1.2430(16) Å; (1c)₂: 1.243(2) Å] is longer than i) that of the previously reported boryl- and amino-substituted acetylene **1a** [1.227(3) Å] and ii) typical carbon-carbon triple bond distances [1.183 Å].¹³ The C-N bond distance [(1b)₂: 1.2949(16) Å; (1c)₂: 1.300(2)/1.298(2) Å] is shorter than that of **1a** [1.312(2) Å]. The observed lengthening of the C-C triple bond and the shortening of the C-N bond should be attributed to the allene-type (keteneiminium) structure of the C-C-N moiety in (1b)₂ and (1c)₂. The B-C bond distances in (1b)₂ and (1c)₂ are almost identical and fall in the range 1.6747(18)-1.680(2) Å, which is shorter than the bridged B-C-B 3c-2e bond [1.786(3) Å and 1.736(3) Å] recently

reported by Wagner.⁸ Thus, the B₂C₂ core in (1b)₂ and (1c)₂ should consist of four B-C single bonds.

Spectroscopic studies on **1b** and **1c** revealed the existence of equilibria in solution (Figs. 2 and 3). The solid-state ¹¹B CP-MAS NMR spectrum of (1b)₂ showed a signal at δ_B -10.4 ppm, which is significantly shifted to higher field relative to that of **1a** (57.4 ppm)⁷ (Fig. 2a), indicating an sp³-hybridized boron atom in (1b)₂. In contrast, the ¹¹B NMR spectrum of **1b** in C₆D₆ showed a resonance at δ_B 50.8 ppm, which was assigned to the sp²-hybridized BPh₂ moiety of the monomer. The IR spectra showed similar trends (Fig. 2b), i.e., in the solid-state IR spectrum of (1b)₂, the vibration of the unsaturated C-C bond was observed at 1980 cm⁻¹, which is significantly shifted to lower wavenumbers than that of **1a** (2097 cm⁻¹).⁷ This value is not comparable to those of typical alkynes (2260-2100 cm⁻¹),¹⁴ but comparable to those of allenes (2000-1900 cm⁻¹),¹⁴ supporting the allene-type (keteneiminium) character of the C-C-N moiety of (1b)₂ as described in Scheme 2. The IR spectrum of **1b** in benzene showed a vibration band at 2106 cm⁻¹, which was assignable to the triple bond in the monomeric structure of **1b**.⁷ In the case of **1c**, the solid-state ¹¹B NMR spectrum showed a signal at δ_B -10.0 ppm, reflecting the dimeric structure of (1c)₂. The ¹¹B NMR spectrum in solution exhibited two signals at δ_B 66.1 and -2.7 ppm with a 12:88 ratio, indicating that the dimeric structure is dominant in solution (Fig. 3a). The IR spectra of **1c** in the solid state (1980 cm⁻¹) and in solution (1979 and 2099 cm⁻¹) corroborate the results obtained from the NMR spectra (Fig. 3b). Thus, the results of the NMR and IR spectroscopic studies for **1b** and **1c** indicate dimeric structures in the solid state and their

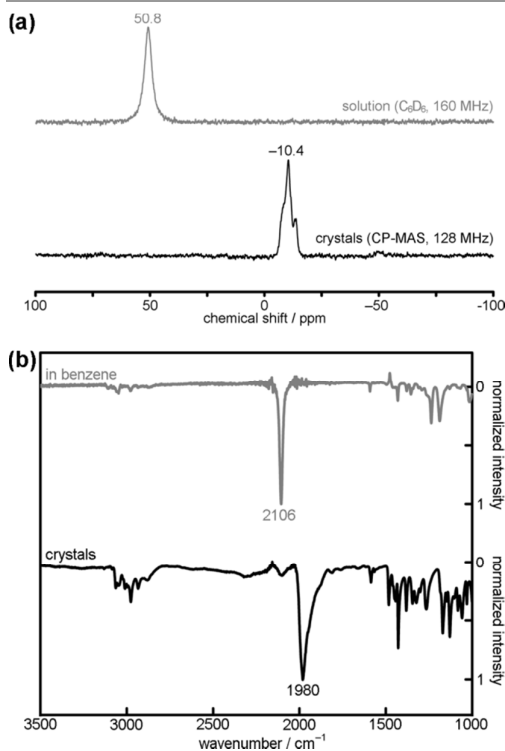


Fig. 2 (a) ¹¹B NMR and (b) IR spectra of (1b)₂ in solution and the solid state.

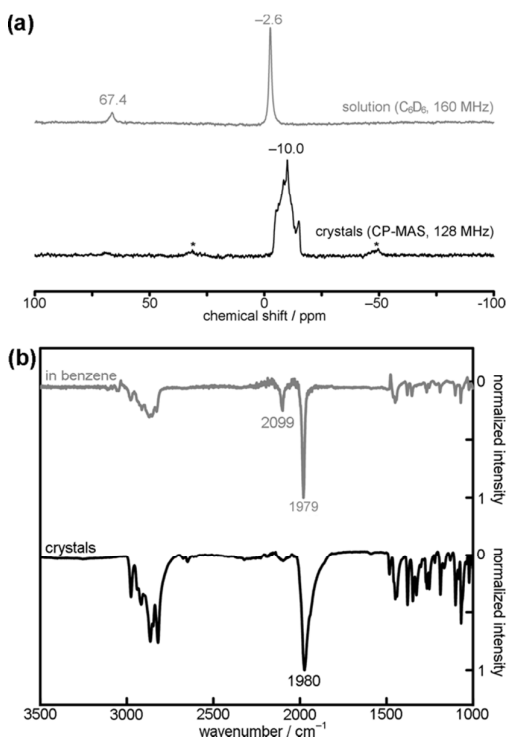


Fig. 3 (a) ^{11}B NMR and (b) IR spectra of $(\mathbf{1c})_2$ in solution and the solid state (*: spinning sideband).

dissociation into the monomers in solution. The thermal [2+2] cycloaddition of boryl- and amino-substituted acetylenes with butatriene-type resonance character is symmetry-forbidden, therefore, the dimerization of acetylenes $\mathbf{1b}$ and $\mathbf{1c}$ should proceed *via* two consecutive nucleophilic additions of the β -carbon atoms relative to the amino groups onto the electrophilic boryl moieties.

DFT calculations on monomers $\mathbf{1b}$ and $\mathbf{1c}$, as well as dimers $(\mathbf{1b})_2$ and $(\mathbf{1c})_2$ were carried out at the B3LYP/6-31(d) level of theory.¹⁵ The optimized structures of the dimers exhibited D_2 symmetry and thus four equivalent B-C bonds in the B_2C_2 ring. The energy calculations revealed that monomer $\mathbf{1b}$ should be 4.8 kcal/mol more stable than dimer $(\mathbf{1b})_2$. On the other hand, dimer $(\mathbf{1c})_2$ should be slightly more stable (0.47 kcal/mol) than monomer $\mathbf{1c}$. These calculated energy differences may be consistent with the exclusive formation of monomeric $\mathbf{1b}$, while a mixture of monomeric $\mathbf{1c}$ and dimeric $(\mathbf{1c})_2$ was observed in solution. The preferable formation of dimers in the solid state for both compounds might be attributed to crystal packing forces. The experimentally observed vibrational frequencies of monomers and dimers was reproduced by DFT calculations. The vibrations of the triple bond in the monomeric structures were estimated to be 2124 cm^{-1} ($\mathbf{1b}$) and 2116 cm^{-1} ($\mathbf{1c}$).¹⁶ These frequencies shift to lower energies for the dimeric structures [$(\mathbf{1b})_2$: 1980 cm^{-1} ; $(\mathbf{1c})_2$: 1962 cm^{-1}].

To gain further insight into the electronic structure of acetylene monomers $\mathbf{1b}$ and $\mathbf{1c}$, as well as dimers $(\mathbf{1b})_2$ and $(\mathbf{1c})_2$, a bond-order analysis based on the Wiberg bond indexes (WBI) was carried out (Fig. 4). In the monomers, bond orders of 2.48, 1.11, and 1.24 ($\mathbf{1b}$), as well as 2.46, 1.12, and 1.24 ($\mathbf{1c}$)

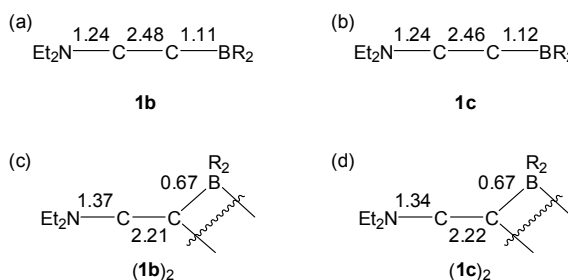


Fig. 4 WBI values for (a) $\mathbf{1b}$, (b) $\mathbf{1c}$, (c) $(\mathbf{1b})_2$, and (d) $(\mathbf{1c})_2$.

were calculated for the C-C triple, C-BR₂, and C-NEt₂ bonds, respectively. These values are similar to those of $\mathbf{1a}$, which exhibits a butatriene-type resonance contribution. In the case of the dimers, the C-C bond orders decreased [$(\mathbf{1b})_2$: 2.21; $(\mathbf{1c})_2$: 2.22], while the bond order for the C-NEt₂ bonds increased [$(\mathbf{1b})_2$: 1.37; $(\mathbf{1c})_2$: 1.34]. These results should be in agreement with the allene-type (keteneiminium) structure of the C-C-N moieties in the dimers.

In summary, we have synthesized novel boryl- and amino-substituted acetylenes that bear Ph₂B ($\mathbf{1b}$) or 9-borabicyclononyl groups ($\mathbf{1c}$) as Lewis-acidic boryl groups. On the basis of experimental structural characterization in solution and the solid state, as well as DFT calculations, the monomer/dimer interconversion of $\mathbf{1b}$ and $\mathbf{1c}$ was examined.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- For reviews, see: (a) J. Jiao, Y. Nishihara, *J. Organomet. Chem.* 2012, **721-722**, 3-16; (b) M. Sugimoto, *Chem. Rec.* 2010, **10**, 348-358.
- For reviews, see: (a) A. Suzuki, *J. Organomet. Chem.* 1999, **576**, 147-168; (b) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* 2002, **58**, 9633-9695.
- (a) H. C. Brown, G. A. Molander, S. M. Singh, U. S. Racherla, *J. Org. Chem.* 1985, **50**, 1578-1582. (b) M. L. Yao, A. B. Pippin, Z.-Z. Wu, M. P. Quinn, L. Yong, M. S. Reddy, G. W. Kabalka, *J. Organomet. Chem.* 2012, **721-722**, 164-166.

- 4 For reviews, see: (a) G. Evano, A. Coste, K. Jouvin, *Angew. Chem., Int. Ed.* 2010, **49**, 2840-2859; (b) C. A. Zifcick, J. A. Mulder, R. P. Hsung, C. Rameshkumar, L.-L. Wei, *Tetrahedron* 2001, **57**, 7575-7606. (c) J. Ficini, *Tetrahedron* 1976, **32**, 1449-1486.
- 5 For recent examples, see: (a) H. Kelch, S. Kachel, M. A. Celik, M. Schäfer, B. Wennemann, K. Radacki, A. R. Petrov, M. Tamm and H. Braunschweig, *Chem.–Eur. J.* 2016, **22**, 13815-13818; (b) A. Hofmann, A. Lamprecht, O. F. Gonzalez-Belman, R. D. Dewhurst, J. O. C. Jimenez-Halla, S. Kachel and H. Braunschweig, *Chem. Commun.* 2018, **54**, 1639-1642. (c) J. Bohnke, H. Braunschweig, Dei, T. Dellermann, R. D. Dewhurst, J. O. C. Jimenez-Halla, S. Kachel, H. Kelch and D. Prieschl, *Chem. Commun.* 2017, **53**, 12132-12135; (d) R. Bertermann, H. Braunschweig, M. A. Celik, T. Dellermann and H. Kelch, *Chem. Commun.* 2016, **52**, 13249-13252. (e) O. Arias, K. Brandhorst, D. Baabe, M. Freytag, P. G. Jones and M. Tamm, *Dalton Trans.* 2017, **46**, 4737-4748. (f) Y. N. Lebedev, U. Das, O. Chernov, G. Schnakenburg and A. C. Filippou, *Chem.–Eur. J.* 2014, **20**, 9280-9289. (g) O. Arias, A. R. Petrov, T. Bannenberg, K. Altenburger, P. Arndt, P. G. Jones, U. Rosenthal and M. Tamm, *Organometallics*, 2014, **33**, 1774-1786. (h) A. R. Petrov, T. Bannenberg, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.* 2011, **40**, 10503-10512.
- 6 (a) K. Onuma, K. Suzuki, M. Yamashita, *Org. Lett.* 2015, **17**, 1212-1215; (b) A. Goswami, C.-J. Maier, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* 2004, 2635-2645; (c) S. V. Ponomarev, E. M. Gromova, S. N. Nikolaeva, A. S. Zolotareva, *Zh. Obshch. Khim.* 1989, **59**, 2277-2282. (d) H.-O. Berger, H. Nöth, B. Wrackmeyer, *J. Organomet. Chem.* 1978, **145**, 17-20.
- 7 K. Onuma, K. Suzuki, M. Yamashita, *Chem. Lett.* 2015, **44**, 405-407.
- 8 A. Hubner, M. Diefenbach, M. Bolte, H.-W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem., Int. Ed.* 2012, **51**, 12514-12518.
- 9 A. F. Eichhorn, S. Fuchs, M. Flock, T. B. Marder and U. Radius, *Angew. Chem., Int. Ed.* 2017, **56**, 10209-10213.
- 10 (a) G. Himbert, M. Regitz, *Chem. Ber.* 1972, **105**, 2963-2974. (b) G. Himbert, *Angew. Chem., Int. Ed.* 1979, **18**, 405-406.
- 11 J. C. Thomas, J. C. Peters, *Inorg. Chem.* 2003, **42**, 5055-5073.
- 12 H. C. Brown, S. U. Kulkarni, *J. Organomet. Chem.* 1979, **168**, 281-293.
- 13 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1987, S1-S19.
- 14 Spectroscopic Identification of Organic Compounds, ed. by R. M. Silverstein, G. C. Bassler, T. C. Morrill, Wiley-Interscience, New York, 1991.
- 15 For details on the DFT calculations, see: ESI.
- 16 Calculated vibrational frequencies were scaled by a factor of 0.9614; A. P. Scott, L. Radom, *J. Phys. Chem.* 1996, **100**, 16502-16513.