Formation of BCBH/BCBCl Four-Membered Rings by Complexation of Boron- and Nitrogen-Substituted Acetylene with Hydro-/Chloro-Boranes

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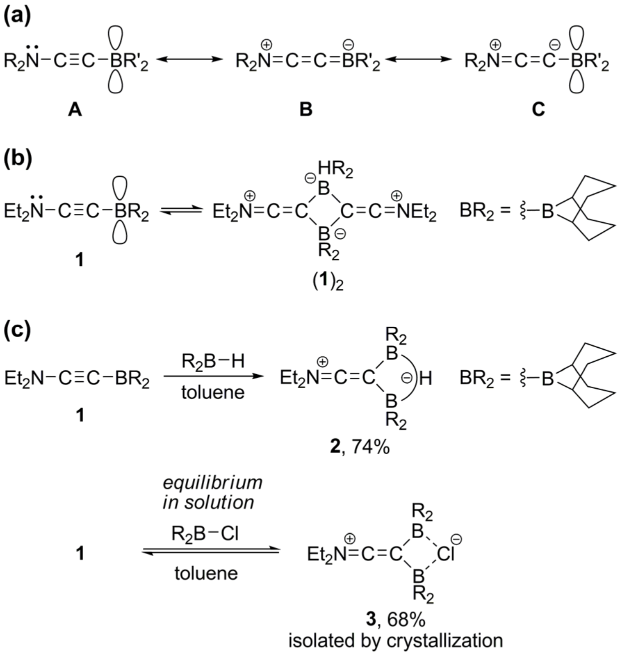
ABSTRACT: Reactions of boron- and nitrogen-substituted acetylene toward hydro-/chloro-boranes are described. The X-ray crystallography revealed the formation of BCBH/BCBCl four-membered rings in the solid state. By NMR and IR spectroscopic analysis, the BCBH four-membered ring was retained even in the solution. In contrast, the BCBCl four-membered ring exists as an association/dissociation equilibrium mixture in solution. The B−H−B moiety forms a three-center-two-electron bond through a spherical 1s orbital of hydrogen atom, therefore, the four-membered ring does not have significant strain. On the other hand, due to the weak coordination bond from Cl to B, the BCBCl four-membered ring was labile. In addition, the rearrangement of the BCBH ring under heating condition is described.

Nitrogen-substituted acetylenes (ynamine, ynamide) are known as a useful building block for nitrogen-containing organic molecules.[1] The β-carbon atom of ynamine possesses a nucleophilicity due to the electron donation from the lone pair electrons of nitrogen. Introduction of boryl group into ynamine gives boryl- and amino-substituted acetylene (BN-acetylene), which would have both nucleophilic and electrophilic characters because of the electron donating and withdrawing nature of amino- and boryl-groups (Scheme 1a, **A**). However, experimental research on the BN-acetylenes has been limited.[2,3] There have been only two examples of BN-acetylenes,[2] and no structural characterization by X-ray diffraction analysis has been reported, until our recent contribution.[3] Previously, we reported synthesis of dimesitylboryl- and diethylamino-substituted acetylene as the first example of crystallographically characterized BN-acetylene.[3b] It was revealed that the substituted boron and nitrogen atoms could conjugate through the C≡C triple bond to have butatriene-type resonance contribution with N=B, C=C, and B=C double bond character (Scheme 1a, **B**). On the other hand, due to the resonance contribution **C**, the boron moiety can act as electrophilic Lewis acidic site with an adjacent carbanion. In fact, BN-acetylene **1** bearing relatively small and Lewis acidic boryl group, such as 9-borabicyclo[3.3.1]nonyl (BBN) group, forms a head-to-head dimer bearing B_2C_2 four-membered ring through an intermolecular nucleophilic attack of the carbanion to boron atom (Scheme 1b).[3c] It should be noted that an anionic boraalkene (borataalkene) having a B=C bond, being similar to **1**, reacted with hydroborane derivatives to form a BCBH four-membered rings.[4,5] Herein, we report the formation of BCBH /BCBCl four-membered rings by the reaction of BN-acetylene **1** with hydro-/chloro-boranes **2** and **3** (Scheme 1c). The latter compound is the first organoborane compounds bearing the BCBCl four-membered ring. The structures and bonding natures of **2** and **3** are discussed on the basis of X-ray crystallographic and spectroscopic analysis as well as theoretical studies. In addition, the thermal isomerization of **2** into 1,1-diborylalkene is also described.

Scheme 1. (a) Resonance structures of BN-acetylene. (b) Previously reported dimerization of 1. (c) This work: Reactions of BN-acetylene with hydro-/chloro-boranes.



Crystals of **2** were obtained from a mixture of BN-acetylene **1** with BBN-H dimer in toluene. The ^{1}H NMR spectrum of **2** in CDCl$_3$ showed a broad signal at −0.11 ppm, which was assignable to the hydride bridging two boron atoms. In the ^{11}B NMR spectrum of **2**, two magnetically equivalent boron nuclei resonated at 1.3 ppm, being similar region to that of previously reported dimer (**1**)$_2$ (−2.6 ppm).[3c] The ^{1}H and ^{13}C NMR spectra of **2** exhibited one set of signals of borabicyclo[3.3.1]nonyl groups, being in agreement with the C_{2v} symmetric structure of **2** in solution. On the other hand, chloroborane, BBN-Cl, also reacted with **1** to form crystals of **3**. Although the ^{1}H and ^{13}C NMR spectra of **3** showed two magnetically equivalent BBN groups, their chemical shifts changed depending on the concentration and temperature (Figure S14 and S15), suggesting the association/dissociation equilibrium in solution.

The formation of BCBH/BCBCl four-membered rings in **2** and **3** was unambiguously confirmed by X-ray crystallography (Figure 1). The hydrogen atom bridging two boron atoms in **2** was assigned from a peak in the differential Fourier map. In **3**, the two B−Cl distances were 2.081(2) and 2.120(2) Å, being similar to each other. These values are longer than the sum of the covalent radii (1.75 Å),[6] but in a standard range of those in the previously reported B−Cl−B bridged compounds [1.81(1)~2.555(2) Å].[7] The C−C−N moieties of **2** and **3** would have a keteneiminium-type structure, being similar to the previously reported dimer (**1**)$_2$.[3c] In fact, the distances of C−C bond which originates from acetylenic moiety [**2**: 1.2346(15) Å, **3**: 1.258(3) Å] are intermediate between typical carbon-carbon double (1.33 Å) and triple (1.20 Å) bond lengths.[6] The C−N bond lengths [**2**: 1.2939(14) Å, **3**: 1.280(3) Å] are comparable to those of imines (1.279 Å).[8] This structural features of **2** and **3** are similar to those of (**1**)$_2$ (C−C: 1.253(2) Å; C−N: 1.300(2) Å).[3c] In addition, the amino group in **2** and **3** are orthogonal to the BCBH/BCBCl rings, being in agreement with the keteneiminium type structure. On the other hand, structures of BCBH and BCBCl four-membered rings in **2** and **3** were different from each other. The diagonal B···B distance and B−C−B angle in the BCBH ring of **2** [B1···B2: 1.9422(19) Å, B1−C1−B2: 73.97(7)°] were shorter and smaller than those in the BCBCl ring of **3** [B1···B2: 2.525(3) Å, B1−C1−B2: 101.75(15)°].

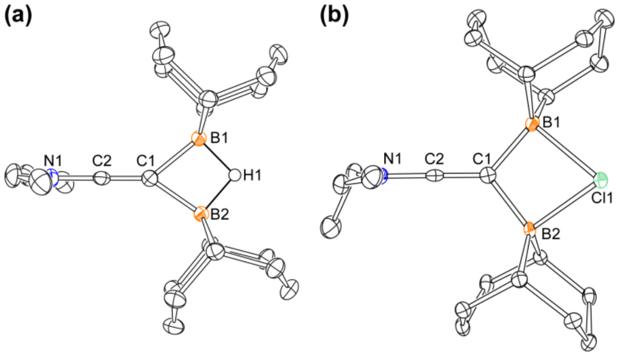
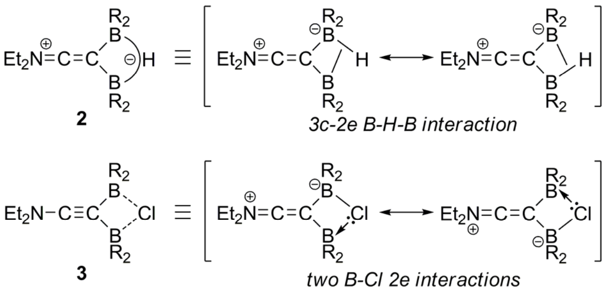


Figure 1. Molecular Structures of (a) **2** and (b) **3** (thermal ellipsoids set at 50% probability). Hydrogen atoms except for H1 of **2** were omitted for clarity.

The IR spectrum of **2** in solid state showed the absorption band derived from C−C unsaturated moiety at 2031 cm^{-1}, being slightly larger than that of the BN-acetylene dimer (**1**)$_2$ (1980 cm^{-1}).[3c] This value was identical even in CH$_2$Cl$_2$ solution (2032 cm^{-1}), indicating that the BCBH cyclic structure of **2** retained in solution. A characteristic vibration at 1609 cm^{-1} is assignable to B−H−B moiety in comparison with that of the BBN-H dimer (1580 cm^{-1}).[9] In the case of **3**, the absorption of C−C unsaturated moiety was observed at 1985 cm^{-1} in solid state, while two absorption bands appeared at 1978 cm^{-1} and 2100 cm^{-1} in CH$_2$Cl$_2$ solution. The former is comparable to that observed in the solid state, the latter is identical to the previously reported vibration (2099 cm^{-1}) of monomeric **1**.[3c] These results indicate the dissociation of **3** into the monomeric BN-acetylene **1** and BBN-Cl in solution, being similar to the association/dissociation equilibrium between **1** and dimer (**1**)$_2$.[3c]

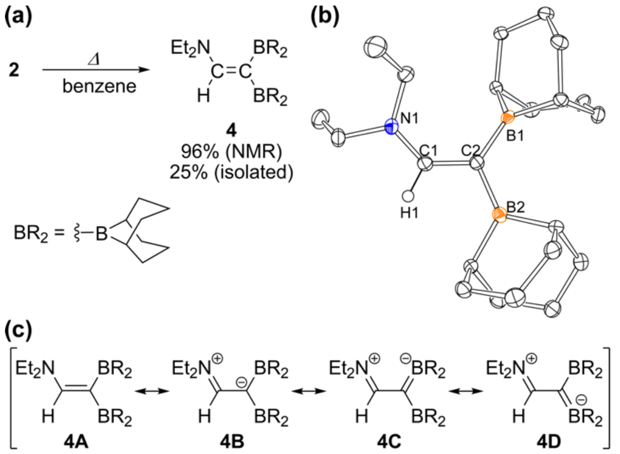
Next, we performed DFT calculations to gain insight into the structures of BCBH/BCBCl rings. The structure of **2** was optimized as a C_2 symmetric structure. The optimized structure of **3** was also planar ring structure with two identical B-Cl bonds, while the X-ray crystallography showed slightly bent BCBCl four-membered ring. This result suggests that the slightly bent BCBCl ring observed by X-ray crystallographic analysis would be attributed to the crystal packing force. The calculated vibrational frequencies of C−C unsaturated moieties scaled by a factor of 0.9636[10] were 2014 cm^{-1} for **2** and 1947 cm^{-1} for **3**, being comparable to experimentally observed wavelengths in solid state. To gain insight into the bonding nature of **2** and **3**, the bond orders were estimated on the basis of Wiberg bond index (WBI) (Figure S22 and S23).[11] The WBI values of C−C bond (2.20 for **2** and 2.09 for **3**) which originates from acetylenic moiety were intermediate between those of double (2.04) and triple (3.00) bonds.[12] The C−N bonds also have unsaturated character (WBI values, **2**: 1.37, **3**: 1.44). These values would be attributed to the keteneiminium-type structures of C−C−N moieties in **2** and **3**, being similar to (**1**)$_2$ (C−C: 2.22, C−N: 1.34).[3c] In **2**, the WBI values around B−H−B moiety in BCBH ring were 0.47 for B−H and 0.36 for diagonal B···B, being similar to those of B$_2$H$_2$ four-membered ring consisting of two sets of B−H−B three-center-two-electron (3c-2e) bond in BBN-H dimer (B−H: 0.47, B···B: 0.63).[13] This result suggests that the bonding nature of B−H−B moiety in **2** can be considered as 3c-2e bond. In the case of **3**, the WBI value of B−Cl bond was 0.63, while the WBI value of the diagonal B···B was negligible (B···B: 0.05), suggesting B–Cl–B moiety should be considered as two sets of two-center-two-electron (2c-2e) bond. Thus, the bonding nature of BCBH and BCBCl four-membered ring would be described as shown in Scheme 2. Because the B−H−B moiety in **2** forms a 3c-2e bond through a spherical 1s orbital of hydrogen atom, the four-membered ring does not have significant strain. On the other hand, B−Cl−B moiety consists of one covalent B–Cl bond and one coordination bond from Cl to B, which was reported to be labile,[14] inducing dissociation of BCBCl ring.

Scheme 2. The resonance structures of 2 and 3.



The BCBH four-membered ring structure of **2** was labile to induce a migration of the bridging hydrogen atom (Scheme 3a). Heating complex **2** in benzene at 80 °C resulted in the quantitative formation of 1,1-diboryl-2-aminoalkene **4**, which is the first example of amino-substituted alkene bearing two boryl-groups. The molecular structure of **4** determined by X-ray crystallography is shown in Scheme 3b. The C−C double bond [1.3909(18) Å] of **4** was elongated, while the C-N bond (C1−N1: 1.3457(18) Å) was shortened, in comparison with those of typical bond lengths of enamines (C-C: 1.358 Å, N-C: 1.392 Å).[15] These structural features are similar to those of enamine bearing two electron withdrawing ester groups, $(Me_2N)HC{=}C(COOMe)_2$, (**5**, C=C: 1.380(5) Å, C−N: 1.337(4) Å).[16] Two C-B bond lengths of **4** were almost equal (C2−B1: 1.5456(19) Å, C2−B2: 1.540(2) Å), and in a range of C−B bond lengths of previously reported 1,1-diborylalkenes bearing alkyl-/aryl-substituted boryl groups (1.540(2)~1.572(2) Å).[17] The C=C double bond of **4** was slightly twisted [torsion angle N1−C1−C2−B1: 25.6(2)°], probably due to the steric repulsion between NEt_2 and BBN groups. These structural features would be explained by a resonance hybrid being composed of four resonance contributions **4A**-**4D** (Scheme 3c), which is also supported by spectroscopic analysis. The IR spectrum of **4** showed an absorption assignable to alkene moiety at 1533 cm^{-1}, being lower then the typical value of C=C double bonds (1670 cm^{-1}).[18] The NMR spectra of **4** showed one-set of signals assignable to two 9-BBN groups, indicating the facile rotation around C=C double bond, as was observed for **5**.[16,19] The results of DFT calculations of **4** are in agreement with experimental observations. The WBI bond orders of C-N (1.25) and C=C (1.51) bonds suggest an unsaturated character of the C-N bond and a decreased double bond character of the C=C bond. The calculated WBI values of two B-C bonds (0.97/0.98) suggest the absence of strong interaction between empty p-orbital of boron and C=C double bond. Thus, the resonance contributions **4C** and **4D** might be negligible.

Scheme 3. (a) Formation of 4 *via* isomerization of 2. (b) Molecular Structure of 4 (thermal ellipsoids set at 50% probability). Hydrogen atoms except for H1 were omitted for clarity. (c) Proposed resonance structures of 4.



In summary, we found the formation of BCBH/BCBCl four-membered ring by the complexation of BN-acetylene **1** with hydro-/chloro-boranes. The B-H-B moiety of BCBH ring in **2** is composed of 3c-2e bond. The BCBCl ring in **3** is labile in solution because of the weak coordination character of B-Cl-B moiety. Furthermore, heating of **2** induced the migration of the bridging hydride to afford 1-amino-2,2-diborylalkene.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Details of experiments, X-ray crystallography, NMR, and IR spectra, and DFT calculations (PDF)
Crystallographic information files (CIF)
Cartesian coordination of optimized structures (XYZ)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) For reviews see; (a) Zificsak, C. A.; Mulder, J. A.; Hsung, R. P.; Rameshkumar, C.; Wei, L.-L. Recent advances in the chemistry of ynamines and ynamides. *Tetrahedron* **2001,** *57,* 7575-7606. (b) Ficini, J. Ynamine: A versatile tool in organic synthesis. *Tetrahedron* **1976,** *32,* 1449-1486. (c) Evano, G.; Coste, A.; Jouvin, K. Ynamides: Versatile Tools in Organic Synthesis. *Angew. Chem., Int. Ed.* **2010,** *49,* 2840-2859.

(2) (a) Goswami, A.; Maier, C.-J.; Pritzkow, H.; Siebert, W. Cobalt-Mediated Cyclooligomerization Reactions of Borylacetylenes. *Eur. J. Inorg. Chem.* **2004,** *2004,* 2635-2645. (b) Ponomarev, S. V.; Gromova, E. M.; Nikolaeva, S. N.; Zolotaereva, A. S. Boron-substituted alkoxy- and aminoacetylenes. *Zh. Obshch. Khim.* **1989,** *59,* 2277-2282. (c) Berger, H.-O.; Nöth, H.; Wrackmeyer, B. Beiträge zur chemie des bors : XCII. Darstellung und charakterisierung eines C-borylierten diethylaminoethins. *J. Organomet. Chem.* **1978,** *145,* 17-20.

(3) (a) Onuma, K.; Suzuki, K.; Yamashita, M. Rhombic Cyclobutadiene with a Boryl/Amino-Substitution Pattern: Boryl Group Migration Induced by Reaction with Water. *Org. Lett.* **2015,** *17,* 1212-1215. (b) Onuma, K.; Suzuki, K.; Yamashita, M. Dimesitylboryl- and Amino-substituted Acetylene Having Butatriene-type Resonance Contribution. *Chem. Lett.* **2015,** *44,* 405-407. (c) Kitamura, R.; Suzuki, K.; Yamashita, M. Dimerization of boryl- and amino-substituted acetylenes by B_2C_2 four-membered ring formation. *Chem. Commun.* **2018,** *54,* 5819-5822.

(4) (a) Kohrt, S.; Dachwitz, S.; Daniliuc, C. G.; Kehr, G.; Erker, G. Stabilized borata-alkene formation: structural features, reactions and the role of the counter cation. *Dalton Trans.* **2015,** *44,* 21032-21040. (b) Moquist, P.; Chen, G.-Q.; Mück-Lichtenfeld, C.; Bussmann, K.; Daniliuc, C. G.; Kehr, G.; Erker, G. α-CH acidity of alkyl–$B(C_6F_5)_2$ compounds – the role of stabilized borata-alkene formation in frustrated Lewis pair chemistry. *Chem. Sci.* **2015,** *6,* 816-825. (c) Lafage, M.; Pujol, A.; Saffon-Merceron, N.; Mézailles, N. BH_3 Activation by Phosphorus-Stabilized Geminal Dianions: Synthesis of Ambiphilic Organoborane, DFT Studies, and Catalytic CO_2 Reduction into Methanol Derivatives. *ACS Catal.* **2016,** *6,* 3030-3035. (d) Wang, T.; Kohrt,

S.; Daniliuc, C. G.; Kehr, G.; Erker, G. Borata-Wittig olefination reactions of ketones, carboxylic esters and amides with bis(pentafluorophenyl)borata-alkene reagents. *Org. Biomol. Chem.* **2017,** *15,* 6223-6232. (e) Wang, T.; Kehr, G.; Liu, L.; Grimme, S.; Daniliuc, C. G.; Erker, G. Selective Oxidation of an Active Intramolecular Amine/Borane Frustrated Lewis Pair with Dioxygen. *J. Am. Chem. Soc.* **2016,** *138,* 4302-4305. (f) Wang, T.; Daniliuc, C. G.; Mück-Lichtenfeld, C.; Kehr, G.; Erker, G. Formation of Reactive π-Conjugated Frustrated N/B Pairs by Borane-Induced Propargyl Amine Rearrangement. *J. Am. Chem. Soc.* **2018,** *140,* 3635-3643.

(5) related examples of BCBH four-membered rings, see: (a) Hübner, A.; Diefenbach, M.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M., Confirmation of an Early Postulate: B-C-B Two-Electron–Three-Center Bonding in Organo(hydro)boranes. *Angew. Chem. Int. Ed.* **2012,** *51,* 12514-12518. (b) Hübner, A.; Kaese, T.; Diefenbach, M.; Endeward, B.; Bolte, M.; Lerner, H.-W.; Holthausen, M. C.; Wagner, M., A Preorganized Ditopic Borane as Highly Efficient One- or Two-Electron Trap. *J. Am. Chem. Soc.* **2015,** *137,* 3705-3714. (c) Kaese, T.; Trageser, T.; Budy, H.; Bolte, M.; Lerner, H.-W.; Wagner, M., A redox-active diborane platform performs C(sp3)–H activation and nucleophilic substitution reactions. *Chem. Sci.* **2018,** *9,* 3881-3891. (d) Bamford, K. L.; Qu, Z.-W.; Stephan, D. W., Activation of H_2 and Et_3SiH by the Borinium Cation $[Mes_2B]^+$: Avenues to Cations $[MesB(\mu\text{-}H)_2(\mu\text{-}Mes)BMes]^+$ and $[H_2B(\mu\text{-}H)(\mu\text{-}Mes)B(\mu\text{-}Mes)(\mu\text{-}H)BH_2]^+$. *J. Am. Chem. Soc.* **2019,** *141,* 6180-6184. (e) Hering-Junghans, C.; Watson, I. C.; Ferguson, M. J.; McDonald, R.; Rivard, E., Organocatalytic hydroborylation promoted by N-heterocyclic olefins. *Dalton Trans.* **2017,** *46,* 7150-7153. (f) Kaese, T.; Budy, H.; Bolte, M.; Lerner, H. W.; Wagner, M., Deprotonation of a Seemingly Hydridic Diborane(6) To Build a B−B Bond. *Angew. Chem. Int. Ed.* **2017,** *56,* 7546-7550. (g) Liu, Y.-L.; Kehr, G.; Daniliuc, C. G.; Erker, G., Geminal bis-borane formation by borane Lewis acid induced cyclopropyl rearrangement and its frustrated Lewis pair reaction with carbon dioxide. *Chem. Sci.* **2017,** *8,* 1097-1104.

(6) Emsley, J. *The Elements,* 3rd ed.; Oxford University Press: New York, 1998.

(7) (a) Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Kramer, T.; Kupfer, T.; Radacki, K.; Siedler, E.; Trumpp, A.; Wagner, K.; Werner, C. Quaternizing Diboranes(4): Highly Divergent Outcomes and an Inorganic Wagner–Meerwein Rearrangement. *J. Am. Chem. Soc.* **2013,** *135,* 8702-8707. (b) Barnett, B. R.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. Cooperative Transition Metal/Lewis Acid Bond-Activation Reactions by a Bidentate (Boryl)iminomethane Complex: A Significant Metal–Borane Interaction Promoted by a Small Bite-Angle LZ Chelate. *J. Am. Chem. Soc.* **2014,** *136,* 10262-10265. (c) Samigullin, K.; Georg, I.; Bolte, M.; Lerner, H.-W.; Wagner, M. A Highly Reactive Geminal P/B Frustrated Lewis Pair: Expanding the Scope to C−X (X=Cl, Br) Bond Activation. *Chem.–Eur. J.* **2016,** *22,* 3478-3484. (d) Arnold, N.; Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Radacki, K.; Trumpp, A. Desymmetrizing Electron-Deficient Diboranes(4): Diverse Products and Their Reactivity. *Chem.–Eur. J.* **2016,** *22,* 13927-13934. (e) Deissenberger, A.; Welz, E.; Drescher, R.; Krummenacher, I.; Dewhurst, R. D.; Engels, B.; Braunschweig, H. A New Class of Neutral Boron-Based Diradicals Spanned by a Two-Carbon-Atom Bridge. *Angew. Chem., Int. Ed.* **2019,** *58,* 1842-1846. (f) Katz, H. E. 1,8-Naphthalenediylbis(dichloroborane) chloride: the first bis boron chloride chelate. *Organometallics* **1987,** *6,* 1134-1136. (g) Lewis, S. P.; Taylor, N. J.; Piers, W. E.; Collins, S. Isobutene Polymerization Using a Chelating Diborane Co-Initiator. *J. Am. Chem. Soc.* **2003,** *125,* 14686-14687. (h) Sgro, M. J.; Dömer, J.; Stephan, D. W. Stoichiometric CO2 reductions using a bis-borane-based frustrated Lewis pair. *Chem. Commun.* **2012,** *48,* 7253-7255.

(8) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. *J. Chem. Soc., Perkin Trans. 2* **1987,** S1-S19.

(9) Brown, H. C.; Kulkarni, S. U. Organoboranes: XXIV. Facile substitution and exchange reactions of 9-borabicyclo[3.3.1]nonane (9-BBN) and its B-substituted derivatives. Simple convenient preparations of B-halo derivatives. *J. Organomet. Chem.* **1979,** *168,* 281-293.

(10) Merrick, J. P.; Moran, D.; Radom, L. An Evaluation of Harmonic Vibrational Frequency Scale Factors. *J. Phys. Chem. A* **2007,** *111,* 11683-11700.

(11) Sizova, O. V.; Skripnikov, L. V.; Sokolov, A. Y. Symmetry decomposition of quantum chemical bond orders. *THEOCHEM* **2008,** *870,* 1-9.

(12) Values for carbon-carbon double and triple bonds of ethylene and acetylene calculated at the same level.

(13) Values for 9-borabicyclo[3.3.1]nonane dimer were calculated at the same level. Details were described in the Supporting Information.

(14) Edwards, H. G. M.; Fawcett, V.; Price, G. P. J. A quantitative spectroscopic study of molecular association in liquid boron(III) chloride. *J. Mol. Struct.* **1990,** *220,* 227-234.

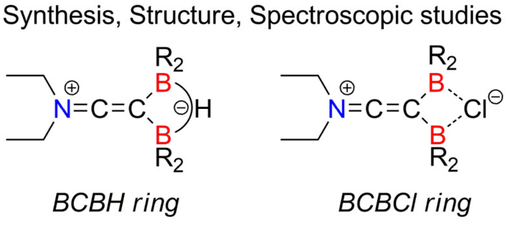
(15) Oleksyn, B. J.; Stadnicka, K.; Śliwiński, J. Structural Chemistry of Enamines: A Statistical Approach. In *The chemistry of enamines*, Patai, S.; Rappoport, Z., Eds. John Wiley & Sons, Ltd: 1994; pp 87-218.

(16) Shmueli, U.; Shanan-Atidi, H.; Horwitz, H.; Shvo, Y. Dimethyl (dimethylaminomethylene)malonate: crystal structure and dynamic behaviour in solution. *J. Chem. Soc., Perkin Trans. 2* **1973,** 657-662.

(17) (a) Febenbecker, A.; Schulz, H.; Pritzkow, H.; Siebert, W. Synthese, Reaktivität und Ligandeigenschaften von 1,4-Dihydro-1,4-diboranaphthalin- und 2,3-Benzo-1,4-dihydro-1,4-diborafulven-Derivaten. *Chem. Ber.* **1990,** *123,* 2273-2278. (b) Köhler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Feng, Y.; Bravakis, A. M.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. Bifunctional Lewis Acids. Synthesis and Olefin Polymerization Chemistry of the 1,1-Di[bis(perfluorophenyl)boryl]alkenes $RHC[B(C_6F_5)_2]_2$ (R = t-Bu, C_6H_5, C_6F_5). *Organometallics* **1998,** *17,* 3557-3566. (c) Ge, F.; Tao, X.; Daniliuc, C. G.; Kehr, G.; Erker, G. The Borole Route to Reactive Pentafluorophenyl-Substituted Diboranes(4). *Angew. Chem., Int. Ed.* **2018,** *57,* 14570-14574.

(18) *Spectrometric Identification of Organic Compounds*, 5th edition, ed. by R. M. Silverstein, G. C. Bassler, T. C. Morrill, Wiley-Interscience, New York, **1991**.

(19) Shvo, Y.; Shanan-Atidi, H. Internal rotation in olefins. I. Kinetic investigation by nuclear magnetic resonance. *J. Am. Chem. Soc.* **1969,** *91,* 6683-6689.



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