

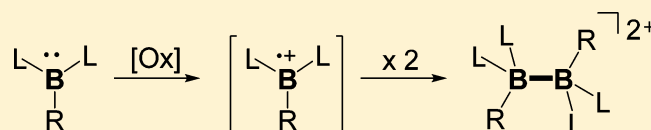
Isolation of a Diborane(6) Dication: Formation and Cleavage of an Electron-Precise B(sp³)–B(sp³) Bond

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Supporting Information

ABSTRACT: One-electron oxidation of organoboron L₂PhB: **1** (L = oxazol-2-ylidene) afforded a dicationic diborane(6) species [L₂PhB–BPhL₂]₂X₂ (X = OTf, BF₄, AlCl₄) **3**, representing a new strategy to construct a B(sp³)–B(sp³) covalent bond. Each boron atom in **3** is in the formal oxidation



state +II, and tetracoordinate with a Ph group and two oxazol-2-ylidenes. The cyclic voltammetry of **3** shows irreversible reduction and oxidation. Indeed, two-electron reduction of **3** with potassium graphite (KC₈) afforded **1**, making a fully reversible **1** ↔ **3** redox system, whereas two-electron oxidation with AuCl produced a boronium [L₂PhBCl]OTf **4**. Moreover, the reactions of **3** with isonitrile derivatives RNC: under heating conditions gave a cyano-substituted boronium [L₂PhBCN]BF₄ **5** and a 2-boranyl-indole derivative **6**, depending on the substituent R. The proposed reaction mechanism involves a borinylium radical **1**^{•+} which is generated via a homolytic cleavage of the B–B bond of **3**.

INTRODUCTION

The construction of B–B bonds has been of significant importance due to the extensive utility of diborane derivatives for various applications, particularly in organic synthesis.^{1,2} In contrast to the plethora of studies describing selective and precise formation of C–C bonds, however, the number of well-controlled protocols to form B–B bonds is confined. For the construction of electron-precise B–B single bonds, several strategies have been developed, which involve (i) classical haloborane reduction,³ (ii) the reaction between boryl anion and haloborane,⁴ (iii) borylene coupling,⁵ (iv) catalytic hydrocoupling,⁶ and (v) hydroboration of B=B bonds.⁷ The synthesis of diboranes(6) **I**–**III** bearing classical 2c–2e B(sp³)–B(sp³) bonds, that are isoelectronic with ethane, is limited to only a handful of reports, and still remains highly challenging (Scheme 1).⁸ Robinson and co-workers prepared the neutral, N-heterocyclic carbene-stabilized tetrahydridoborane **Ia** by the reductive coupling reaction of IPr–BBr₃ adduct with KC₈ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).⁹ Himmel et al. illustrated the metal-catalyzed or metal-free dehydrogenative coupling of the preorganized diboron derivatives to afford B–B bonded compound **Ib**.^{6f–i} Braunschweig et al. first demonstrated the direct *syn*-addition of catecholborane toward diborenes affording bis-carbene-stabilized triborane **Ic**.⁷ Power et al. reported the isolation of the dimeric 9H-9-borafluorene dianion **IIa**.¹⁰ Tamao and Matsuo et al.¹¹ showed the formation of B–B bond (**IIb**) through the reduction of the corresponding diborane(6). Wagner et al. reported the formation of **IIc** via a radical coupling of two linked triorganylboranes in the presence of lithium.¹² Significantly, Finze, Bernhardt, and co-workers demonstrated that hexacyanodiborane(6) dianion **IIId** can be accessible by (i) the reduction of [FB(CN)₃][–] with ^tBuLi or KC₈, (ii) the

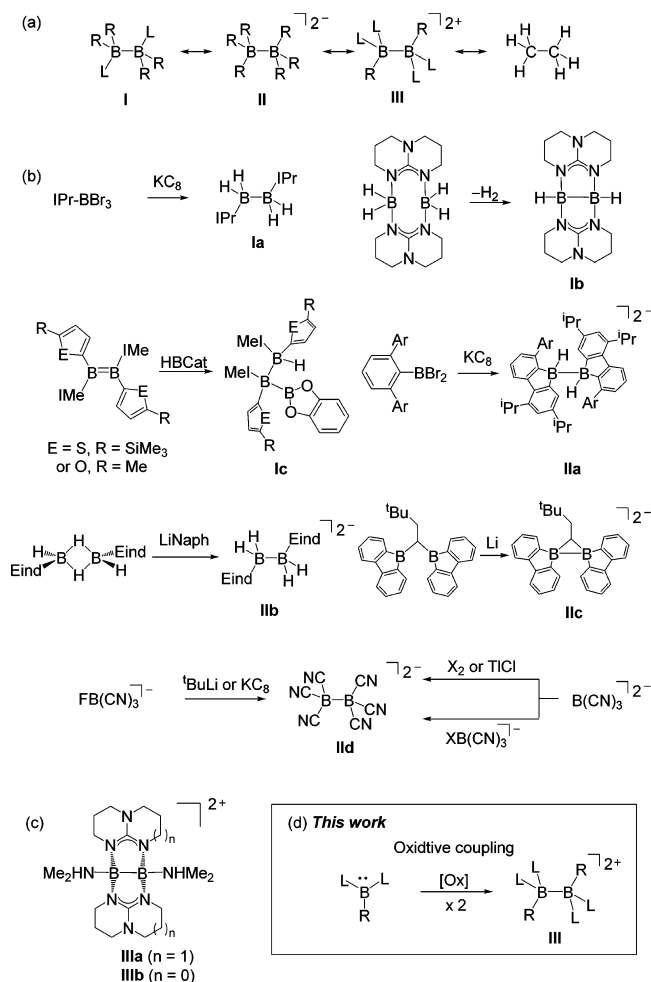
oxidation of [B(CN)₃]^{2–} with halogen or TlCl, or (iii) the reaction between [B(CN)₃]^{2–} and [XB(CN)₃][–].¹³ Isolable dimeric boron(+II) dication **III** is extremely rare, and only [{(Me₂HN)B(hpp)}₂]²⁺ **IIIa** and [{(Me₂HN)B(μ-tbn)}₂]²⁺ **IIIb** (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-*a*]-pyrimidate, tbn = 1,2,3,5,6,7-hexahydroimidazo[1,2-*a*]-pyrimidate) have been structurally characterized thus far by Himmel and co-workers.¹⁴ Note that **IIIa** and **IIIb** were prepared by the reaction of the diborane precursor B₂Cl₂(NMe₂)₂ with hppH and tbnH respectively, and to the best of our knowledge, the synthesis of diborane(6) dication **III** via an electron-precise B–B bond formation has never been achieved before.¹⁵

Recently, Bertrand,¹⁶ Braunschweig,¹⁷ and our groups¹⁸ have individually developed neutral nucleophilic organoboron compounds **IVa,b** and **1** that are isoelectronic with amines (Figure 1). It has been shown that one-electron oxidation of **IVa** affords the corresponding borinylium radical **IVa**^{•+} as an isolable species, which is kinetically stabilized by bulky CAAC ligands.^{16b} Compound **IVa** is reluctant to react with Lewis acids due to the excessive steric hindrance around the boron center, while the boron centers in **IVb** and **1** readily react with electrophiles such as trihalogallanes GaX₃ and transition metals (Cr, Au), to afford the Lewis acid–base adducts and the metal borylene complexes **2** [**2a** (L₂PhB)Cr(CO)₅, **2b** (L₂PhB)–AuCl], respectively.^{17a,18b} We envisaged that one-electron oxidation of **1** would undergo a radical coupling reaction as reported in the oxidation of NR₃ and PR₃,¹⁵ because the boron center in **1** is sterically much less shielded with respect to that in **IVa**. Indeed, the percent buried volume of **1** (2.00 Å, 40.0;

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Scheme 1. (a) Diborane(6) Compounds I–III Isoelectronic with Ethane, (b) Reported Examples of the Classical 2c–2e B(sp³)–B(sp³) Bond Construction, (c) IIIa,b, and (d) Present Work^a



^aIPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IMe = 1,3-dimethylimidazole-2-ylidene, Ar = 2,4-diisopropylphenyl, Eind = 1,1,3,3,5,5,7,7-octaethyl-1,2,3,5,6,7-hexahydro-*s*-indacen-4-yl.

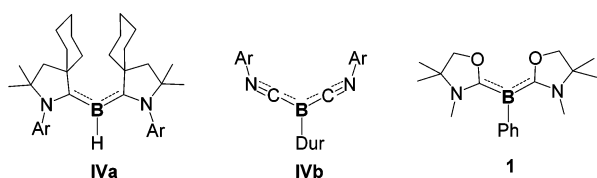


Figure 1. Tricoordinate monovalent organoboron compounds (Ar = 2,6-diisopropylphenyl, Dur = 2,3,5,6-tetramethylphenyl).

2.28 Å, 34.6) is similar to those of PPh₃ (2.00 Å, 34.8; 2.28 Å, 29.9), but significantly smaller than those (2.00 Å, 67.9; 2.28 Å, 63.8) of IVa.¹⁹ Herein, we report the synthesis, single crystal X-ray diffraction, and computational studies of a diborane(6) dication 3 featuring an electron-precise B(sp³)–B(sp³) bond via oxidative coupling of 1. We also describe its redox property and reactivity toward isonitriles.

RESULTS AND DISCUSSION

Synthesis of Diborane(6) Dication 3 via Oxidation of

1. Our previous study showed that reactions of 1 with excess

coinage metal chlorides MCl (M = Cu, Ag, Au) immediately afforded metal(0) as a black precipitate via an electron transfer from 1 to the metals, suggesting the electron-richness of 1.^{18b–d} This was supported by the cyclic voltammogram (CV) of 1 in an acetonitrile solution (0.1 M ⁿBu₄NPF₆ as electrolyte), in which a one-electron oxidation was observed at –1.108 V (Figure 2). In marked contrast to the reversible oxidation

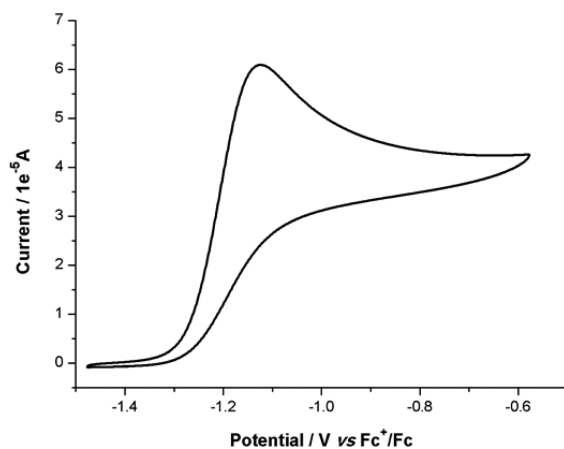
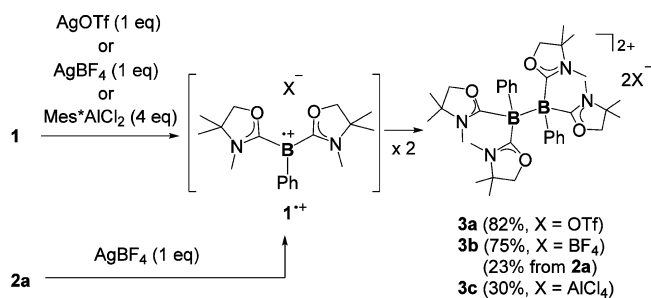


Figure 2. Cyclic voltammogram of 1 in acetonitrile (0.1 M ⁿBu₄NPF₆ as electrolyte, potential versus Fc⁺/Fc, scan rate 50 mV·s⁻¹) (see also the Supporting Information).

observed for IVa,^{16b} the one-electron oxidation process of 1 is found to be irreversible, indicating that the corresponding borinylium radical 1^{•+} *in situ* generated would undergo further reaction. To examine this hypothesis, we carried out one-electron chemical oxidation of 1.

A mixture of 1 and a stoichiometric amount of AgOTf in acetonitrile was stirred at –78 °C for 10 min and allowed to warm slowly to ambient temperature (Scheme 2). After

Scheme 2. Synthesis of 3a–c^a



^aMes* = 2,4,6-tri-*tert*-butylphenyl.

workup, a product 3a was obtained as a white powder. In the ¹H NMR spectrum, a singlet for the Me group on the N atom appears at 2.19 ppm. The ¹¹B NMR spectrum in a CD₃CN solution displays a sharp singlet at –16.7 ppm, indicating the presence of the tetracoordinate boron atom while the ¹⁹F NMR spectrum shows a peak at –79.2 ppm corresponding to triflate [OTf][–]. The ¹H and ¹¹B NMR spectra similar to those of 3a were obtained after the reactions of 1 with AgBF₄ and Mes*AlCl₂ (Mes* = 2,4,6-tri-*tert*-butylphenyl). The former product 3b showed a ¹⁹F NMR chemical shift at –151.8 ppm for [BF₄][–] whereas the latter 3c showed a peak at 103.8 ppm for [AlCl₄][–] in the ²⁷Al NMR spectrum, respectively.

Interestingly, we found that the reaction of chromium complex **2a** and AgBF_4 also yielded **3b** (23%). The NMR spectral data of these products indicate the ionic nature of **3**, which was decisively confirmed by X-ray diffraction studies of **3b** and **3c**. As the cationic fragments of **3b** and **3c** are essentially identical, only that in **3b** is shown in Figure 3.

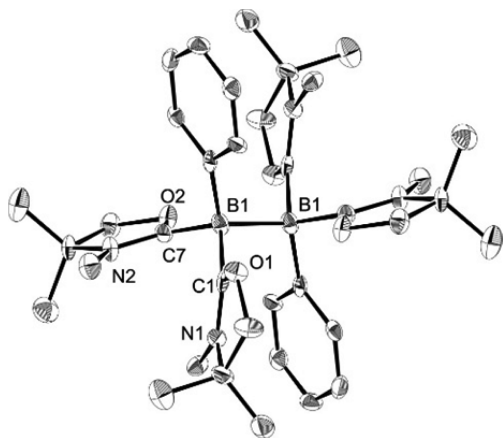


Figure 3. Solid-state structure of the cationic fragment of **3b**. (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms and counteranions are omitted for clarity.)

The solid-state structures of **3b** and **3c** involve the dicationic fragment featuring a B–B bond, which is fully separated from the counteranions (**3b** $[\text{BF}_4]^-$, **3c** $[\text{AlCl}_4]^-$).²⁰ Each boron atom is tetracoordinate with a phenyl group and two oxazol-2-ylidenes. Thus, the boron atoms are in the formal oxidation state of +II. Compounds **3** are termed also as bis-boronium dication. **3b,c** comprise the first structural authentication of diboron(+II) dication without chelating ligands. The B–B distances [**3b** 1.841(8) Å, **3c** 1.876(15) Å] are longer than those (1.746(2) and 1.801(5) Å) of **IIIa** and **IIIb**^{14a,b} and those [1.682(16) to 1.762(11) Å] in three-coordinate diboron compounds.²¹ All six B–C bond lengths are similar [1.620(5) to 1.654(5) Å] and in the range reported of typical B–C single bonds.²²

We confirmed no reaction between **1** and boronium $[\text{L}_2\text{PhBCl}]\text{OTf}$ **4** at ambient temperature, and thus the reaction mechanism involving the boronium can be ruled out for the formation of **3**. Hence, it is reasonable to infer that the mechanism involves a radical coupling between the boron centers of the borinylium intermediates **1**^{•+} generated in situ by an electron transfer. During electrochemical and chemical oxidation reactions, only decoloration of the red solution of **1** was observed. We attempted to detect the radical species by EPR spectroscopy;^{16a,b} however, no signal was observed even right after those reactions, indicating the rapid coupling process and no dissociation of the B–B bond of **3** in the solution. The result thus suggests the relatively strong B–B bond in **3**. Indeed, compound **3** is highly thermally stable and does not decompose even after heating at 100 °C for 2 days in an

acetonitrile solution. In this process, no color change of the solution was observed (see the Supporting Information).

Computational Study of 3. To gain insight into the property of the B–B bond in **3**, quantum chemical density functional theory (DFT) calculation involving geometry optimization, natural bond orbital (NBO) analysis, and natural population analysis (NPA) were performed at the M05-2X/6-311G(d,p) level of theory. The optimized geometry of the cationic fragment in **3** is in good agreement with the X-ray results of **3b,c**. Wiberg bond index (WBI) value of the B–B bond (0.75) indicates the single bond character. To evaluate the strength of the B–B bond, we estimated the bond dissociation energies (BDEs) for homolytic cleavage of the B–B bond in **3** and other related compounds for comparison (Table 1). The computed B–B bond dissociation enthalpy (11.9 kcal·mol⁻¹) of **3** is similar to that (6.8 kcal·mol⁻¹) of $[(\text{L})_2\text{HB}-\text{BH}(\text{L})_2]^{2+}$, but significantly smaller than that (110.4 kcal·mol⁻¹) of $\text{H}_2\text{B}-\text{BH}_2$. When oxazol-2-ylidene ligand and CO are installed on each B atom of $\text{H}_2\text{B}-\text{BH}_2$, the BDE values decrease to 38.4 kcal·mol⁻¹ and 46.2 kcal·mol⁻¹, respectively, indicating that coordination of a neutral ligand to the boron center may weaken the B–B bond strength. Interestingly, the B–B bond breaking process for $[(\text{OC})_2\text{HB}-\text{BH}(\text{CO})_2]^{2+}$ is exergonic (BDE = -26.3 kcal·mol⁻¹). Thus, the corresponding borinylium radical $[(\text{OC})_2\text{BH}]^{\bullet+}$ is thermodynamically stable, which is probably due to the high π -acceptor property of carbonyl ligands, which allows for the delocalization of the unpaired electron over the entire molecule.²³ Meanwhile, the greater computed thermodynamic stability of **3** than **1**^{•+} is consistent with the fact that a silent spectrum was observed for **3** in our EPR study. The HOMO of **3** is mainly the B–B σ -bonding with participation of the π -orbitals on two phenyl groups whereas the LUMO exhibits significant contribution from π -type orbitals of the two oxazol-2-ylidene ligands (Figure 4). NPA shows that each B atom carries a small positive charge of +0.1e. The major positive charges (sum +2.4e) are distributed over the four oxazol-2-ylidenes, which may minimize the charge repulsion between the two boron centers.

Electrochemical Study and Redox Reactions of 3. The CV of **3a** shows a positive oxidation potential of 1.190 V and a negative reduction potential of -2.401 V (Figure 5). Both the oxidation and reduction waves are found to be irreversible, suggesting that both species generated by one-electron oxidation and reduction are unstable, and would undergo further transformations. This prompted us to investigate chemical redox reactions of **3**. Note that although the first dimeric boron(II) dication **IIIa** was reported almost ten years ago,^{14a} as far as we are aware, its chemical reactivity has never been described to date.

To a mixture of **3a** and two equivalents of potassium graphite (KC_8) in a J-Young NMR tube, THF-*d*₈ was added at ambient temperature. The ¹H and ¹¹B NMR spectra were measured immediately, which showed the quantitative reproduction of **1**, presenting the first example of synthesis of low-valent mononuclear boron species from a diboron compound (Scheme 3). Next, we examined oxidation of **3a**. According

Table 1. Bond Dissociation Energies of the B–B Bonds (kcal·mol⁻¹)^a

3	11.9	$(\text{L})\text{H}_2\text{B}-\text{BH}_2(\text{L})$	38.4	$[(\text{L})_2\text{HB}-\text{BH}(\text{L})_2]^{2+}$	6.8
$\text{H}_2\text{B}-\text{BH}_2$	110.4	$(\text{OC})\text{H}_2\text{B}-\text{BH}_2(\text{CO})$	46.2	$[(\text{OC})_2\text{HB}-\text{BH}(\text{CO})_2]^{2+}$	-26.3

^aL = oxazol-2-ylidene.

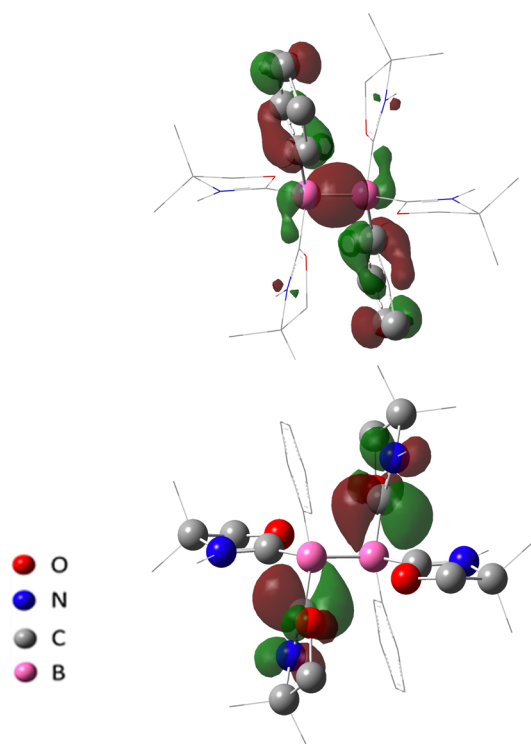


Figure 4. Plots of the HOMO (−12.01 eV) (top) and LUMO (−5.24 eV) (bottom) of the cationic fragment in **3** calculated at the M05-2X/6-311G(d,p) level of theory (hydrogen atoms are omitted for clarity). The isovalue of 0.05 was utilized for generating the images.

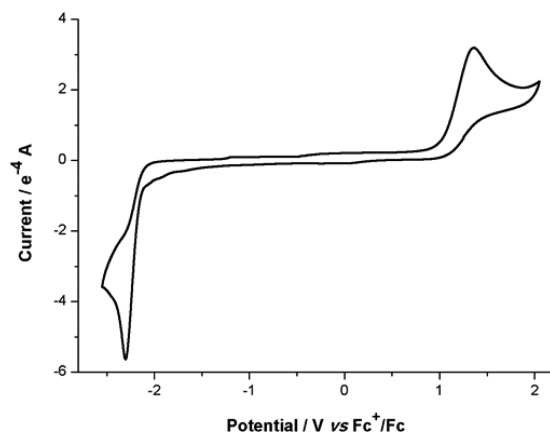
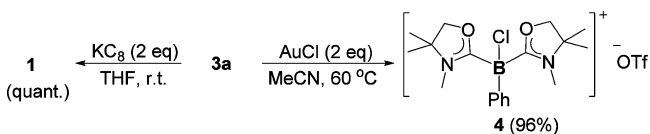


Figure 5. Cyclic voltammogram of **3a** in acetonitrile (0.1 M ${}^n\text{Bu}_4\text{NPF}_6$ as electrolyte, potential versus Fc^+/Fc , scan rate $50 \text{ mV}\cdot\text{s}^{-1}$).

Scheme 3. Redox reactions of **3a**



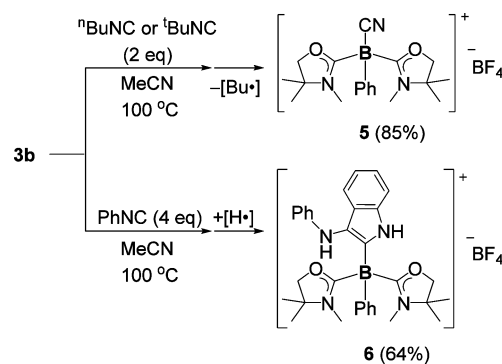
to the CV data of **3a**, it can be inferred that a strong oxidant is required to oxidize **3a**. Hence, we employed AuCl to test the reaction. **3a** and two equivalents of AuCl were mixed in acetonitrile, and the reaction mixture was heated at 60°C . After workup, the boronium **4** featuring the boron atom in the oxidation state +III was obtained in 96% yield.^{18c} These results thus demonstrate that the B–B bond in **3** can be cleaved by

both reduction and oxidation reactions. It is salient to mention that reactions involving a cleavage of a $\text{B}(\text{sp}^3)\text{--B}(\text{sp}^3)$ bond have rarely been reported¹² although studies on $\text{B}(\text{sp}^3)\text{--B}(\text{sp}^2)$ bond cleavage have been widely explored.^{1,4b,24} We also confirmed that CO_2 , N_2O , and P_4 do not oxidize **3a**, which is in line with the observed highly positive oxidation potential in the CV.

Reactivity of 3 toward Isonitriles. Activation of B–B bonds is of significant importance in synthetic chemistry because the cleavage process is widely involved in the various metal-catalyzed and metal-free borylation reactions ranging from diboration of C–C multiple bonds to C–H borylation.^{24,25} In this respect, insertion of isonitriles and CO into $\text{B}(\text{sp}^2)\text{--B}(\text{sp}^2)$ bonds has been well documented.²⁶ In contrast, the cleavage of $\text{B}(\text{sp}^3)\text{--B}(\text{sp}^3)$ bonds by isonitriles and CO has never been described thus far, which encouraged us to investigate the reactions of **3** with these molecules.

A mixture of **3b** and two equivalents of ${}^n\text{BuNC}$ in acetonitrile was heated at 100°C for 5 h (Scheme 4). After workup, a

Scheme 4. Reactions of **3b** with Isonitriles



product **5** was obtained, and the ${}^{11}\text{B}$ NMR spectrum displays a sharp singlet at -20.9 ppm in addition to a peak (-1.2 ppm) for $[\text{BF}_4]^-$, indicating the presence of a tetracoordinate boron center. Interestingly, when ${}^t\text{BuNC}$ was utilized, the same product **5** was formed, as confirmed by NMR spectroscopy. The solid-state molecular structure of **5** was unambiguously determined by an X-ray diffraction analysis, which revealed the boronium structure of **5** (Figure 6, top). Obviously, the butyl moiety of the isonitriles was eliminated during the reactions, presumably as a butyl radical. We reasoned that the employment of aryl isonitrile would impede the radical elimination process due to the $\text{N--C}(\text{sp}^2)$ single bond being stronger than the $\text{N--C}(\text{sp}^3)$ bond in ${}^n\text{BuNC}$ and ${}^t\text{BuNC}$. To bear out this hypothesis, we tested the reaction of **3b** with PhNC. Upon heating an acetonitrile solution of **3b** with four equivalents of PhNC to 100°C for 12 h, full conversion of **3b** into a new product was observed. By recrystallization from a mixed toluene/THF solution, compound **6** was isolated as colorless crystals in 64% yield. An X-ray analysis identified the product as a 2-boranyl-indole derivative, confirming that two PhNC units were involved for the formation of **6** (Figure 6, bottom). Note that conventional methods for the construction of indole frameworks from isonitriles require predesigned substrates and organometallic reagents.²⁷ The ${}^{11}\text{B}$ NMR chemical shift (-16.4 ppm) for the cationic part of **6** is nearly identical to that (-16.7 ppm) of **3b**. We also examined the similar reaction with CO, but no reaction was observed. It is noteworthy to highlight that reactions between the dicationic

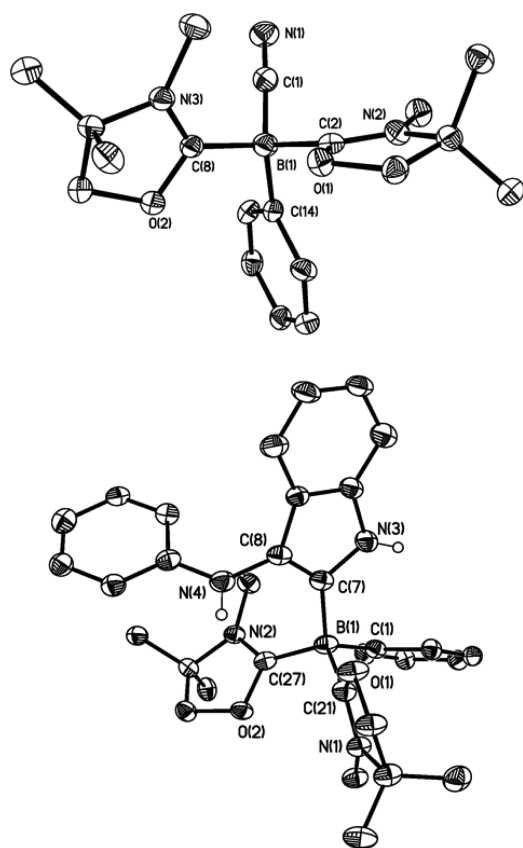
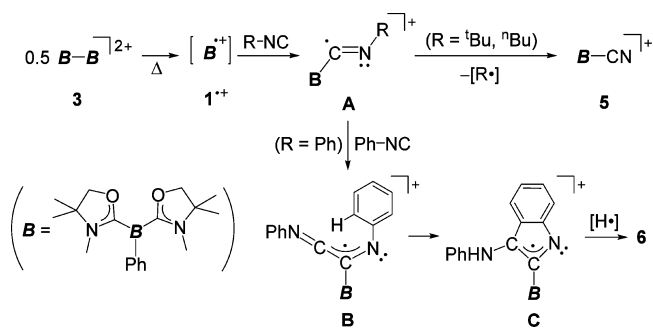


Figure 6. Solid-state structures of **5** (top) and **6** (bottom). (Thermal ellipsoids are set at the 30% probability level. Hydrogen atoms except for the N–H in **6** and counteranions are omitted for clarity.)

species $[R_3E-ER_3]^{2+}$ ($E = N, P$) and isonitriles or CO have never been reported to date.¹⁵

To gain information about the reaction pathways for the formation of **5** and **6** from **3**, we carried out a couple of control experiments. A CD_3CN solution of **1** in a sealed NMR tube was heated at 100 °C, and monitored by NMR spectroscopy. After 5 h, no signals for **5** but a partial decomposition of **1** were observed. We also examined the similar reaction in the presence of two equivalents of nBuNC . After 5 h with heating at 100 °C, nBuNC remained unchanged whereas thermal decomposition of **1** was confirmed, indicating that compound **1** is not involved in the reaction between **3** and isonitriles. These results suggest that the cleavage of the B–B bond would be homolytic rather than heterolytic since the heterolytic cleavage should yield **1**. Hence, we propose a plausible reaction mechanism involving the borinylium radical $1^{\bullet+}$ as illustrated in Scheme 5. The reactions may be initiated by the dissociation of the B–B bond under heating conditions to generate borinylium radical $1^{\bullet+}$. Subsequent addition of isonitrile to $1^{\bullet+}$ would afford imido radical **A**,²⁸ from which elimination of an alkyl radical, when R is butyl group, would produce **5**. Analogous fragmentation concomitant with the loss of *tert*-butyl radical has been proposed for the formation of cyano-substituted disilene and diborene from the corresponding disilyne- and diboryne-isonitrile adducts.^{29,30} With PhNC, second addition of PhNC molecule to **A** would occur to yield the intermediate **B**. Subsequent cyclization via an insertion of a C–H bond at the *ortho*-position in the phenyl ring into the C=N bond would form **C**, which was hydrogenated under the reaction conditions to afford **6**. To gain additional insight into the mechanism, we

Scheme 5. Proposed Reaction Pathway for the Formation of **5** and **6**



performed further analysis of the reaction of **3b** with PhNC in CD_3CN . After the reaction, the crude 1H NMR spectrum confirmed that the product **6** involves two singlets corresponding to the N–H (see the Supporting Information). This result suggests that the hydrogen source for both N–H in **6** is not acetonitrile solvent, and thus the intermediate **C** would undergo H-shift intramolecularly to generate another radical species which presumably abstracts a hydrogen atom from acetonitrile. Attempts to trap the borinylium $1^{\bullet+}$ or intermediates **A**–**C** using TEMPO gave a complex mixture.

CONCLUSION

Almost decade after the first isolation of dimeric boron(II) dication **IIIa** coordinated by the N,N' -chelating hpp ligands by Himmel and co-workers, this report has presented that an oxidative coupling of low-valent boron-containing species **1** and **2a** may produce dicationic diboron(II) **3**, which is supported only by monodentate oxazol-2-ylidene ligands. The result demonstrates a novel strategy for the construction of a $B(sp^3)-B(sp^3)$ single bond. We revealed that the B–B bond in **3** is redox active, and thus it can be cleaved by chemical reduction and oxidation. The former reproduced **1**, presenting a new synthetic method of borylene **1**, while the latter afforded a boronium **4**, respectively. The reactions of **3** with isonitriles produced cyano-substituted boronium **5** or a 2-boranyl-indole **6**, depending on the substitutes of isonitriles. Formations of **5** and **6** suggest that the homolytic cleavage of the B–B bond of **3** is involved in the initial step of these reactions, indicating the potential utility of **3** as a borinylium equivalent. Investigation on the reactivity of **3** toward other substrates is currently underway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04858.

Complete experimental data and computational details including Cartesian coordinates for stationary points (PDF)

Crystallographic data (CIF) of **3b**, **3c**, **5**, **6** (ZIP)

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Notes

The authors declare no competing financial interest.

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