

Characteristic Reactivity of an All-Carbon-Substituted Diborane (4), B₂(o-tol)₄

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Abstract- B₂(o-tol)₄ (1) was synthesized as a diborane (4) having four carbon substituents, and its extremely highly electron-accepting properties and the origin of the electron affinity have been clarified. According to its own electron affinity, 1 shows a variety of unique reactivities. For example, 1 reacted with H–H, C≡O, and N=N bonds, with which ordinary organic molecules do not react at all. In addition, the two-electron reduction of 1 resulted in the formation of a dianionic B=B species which can be an equivalent of a Ar₂B anion and a ligand of transition metal complexes. Furthermore, it was revealed that a diarylborylgold complex can be obtained by the metathesis of 1, which also shows characteristic reactivity.

Keywords: diborane (4), rearrangement, bond cleavage.



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Introduction

Organic molecules containing heteroatoms (= p-block elements other than carbon) have a wide variety of characteristics depending on the type of heteroatom. For example, boron, which is the lightest group 13 element, has a slightly larger atomic radius than that of carbon located to its right in the periodic table (B: 0.83 Å; C: 0.77 Å). Therefore, chemical bonds involving boron atom(s) are slightly longer than those in ordinary organic compounds, which leads to their high reactivity. The Nobel Prize-winning SuzukiMiyaura cross-coupling reaction is a C-C bondforming reaction based on the reactivity of a B-C bond contained in a boronic acid derivative and has an extremely wide tolerance for functional groups.

Borane (BH₃) exists as a dimer, diborane (B₂H₆), by forming a three-center-two-electron bond, but in the IUPAC nomenclature, B₂H₆ with six hydrogen atoms should be called diborane(6) (Figure 1).¹ On the other hand, B₂H₄ with a B–B single bond is named diborane(4) because it has four hydrogen atoms. Due to the long B–B single bond (1.75 Å) and two vacant p-orbitals on the two boron atoms, diborane(4) exhibits characteristic reactivity. Bis(pinacolato) diborane(4) (B₂pin₂), the most widely used diborane(4) in synthetic organic chemistry (TCI Product Code: B1964, CAS RN: 73183-34-3), is a water- and air-stable reagent and is known to be useful for the borylation of organic molecules catalyzed by transition metal complexes. In contrast, diborane(4) without substitution of heteroatoms such as oxygen and nitrogen, being able to interact with the vacant p-orbital of the boron atom, exhibits higher reactivity. Recently, we have revealed that pinB–BMe₂, a diborane(4) substituted with pinacol and Mes (2,4,6-Me₃C₆H₂) groups, is significantly more reactive than B₂pin₂. Furthermore, we have found that this pinB–BMe₂ causes multiple bond cleavage reactions via multi-step rearrangements, and that the origin of their high reactivity lies in the overlapping of two vacant 2p orbitals on two boron atoms. In this account, I briefly describe the characteristic reactivity of B₂(o-tol)₄ (1), which was newly synthesized as an all-carbon-substituted diborane(4) showing much higher Lewis acidity than that of pinB–BMe₂. Although compounds A to D have been reported as similar allcarbon-substituted diboranes, study on their reactivity is limited.²

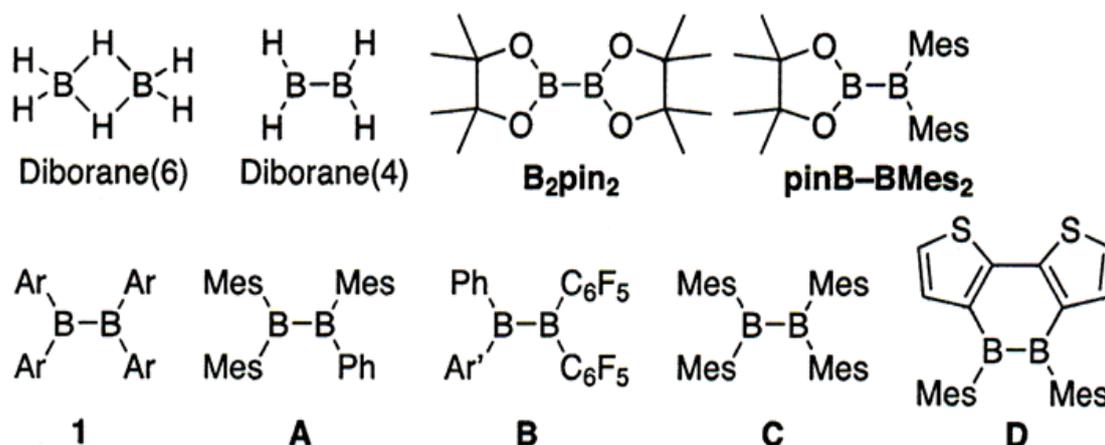
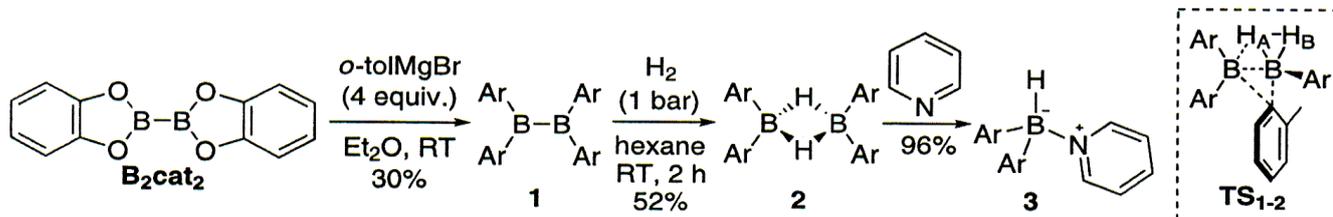


Figure 1. Structural formula of diboranes ($Ar = o\text{-tol}$, $Ar' = 2,5\text{-}(Me_3Si)2\text{-}4\text{-Ph-}6\text{-}C_6F_5C_6H$)

$B_2(o\text{-tol})_4$ (**1**) was synthesized by the reaction of *o*-tolylmagnesium bromide with commercially available B2cat2 (TCI Product Code: B3757, CAS RN: 13826-27-2) (Scheme 1).³ A single-crystal X-ray diffraction analysis of **1** revealed a twisted structure with a torsion angle of -96.6° formed by the two sp^2 boron planes. According to electrochemical measurements in solution, the reduction potential of **1** was found to be -2.1 V (in THF, vs. Fc/Fc^+), which was significantly less negative than that of pinB-BMes₂ (-2.5 V), due to the high electrophilicity of **1**. By DFT calculations, we estimated the dependency of the LUMO energy level (eV) and the electronic energy (kcal/mol) of conformational isomers of **1** in which the torsion angle of the C(ipso)-B-B-C(ipso) moiety was changed in increments of 10° . It was found that the electronic energy increases and the stability decreases as the torsion angle decreases, but the electrophilicity increases as the LUMO level decreases (Figure 2). In particular, when the two sp^2 boron planes are coplanar with a torsion angle of 0° , the LUMO level is the lowest due to the overlapping of the vacant 2p orbitals of the two boron atoms, much lower than those of Mes₃B and pinB-BMes₂. Exposure of the hexane solution of **1** to H₂ afforded diarylborane dimer **2**. It was later reported that a similar reaction of **D** also proceeded. The structure of **2** was revealed by single-crystal X-ray diffraction analysis, and the existence of bridged hydrogen atoms adopting three-center-two-electron bonds was confirmed by IR spectrophotometry. Since **2** was found to exist in equilibrium with a monomer or a trimer in the solution, it was difficult to assign by NMR spectroscopy. To fully identify the structure of **2**, it was converted to the corresponding pyridine adduct **3** and isolated, and then completely characterized by NMR spectroscopy. Using DFT calculations to evaluate the reaction mechanism of **1** with a hydrogen molecule, it was found that the reaction proceeded via the transition state TS1-2. NBO analysis of TS1-2 revealed the existence of interactions between a pair of electrons in the B-B bond and the HA atom, and between a pair of electrons in the B-HB bond and the HA atom. The reaction is thought to be initiated by coordination of the H-H bond to one of the vacant p-orbitals of the boron atom in the Ar₂B moiety (right side), and subsequently, deprotonation by the other Ar₂B moiety (left side) proceeded. As a conclusion from this finding, the Ar₂B moiety on the left side can be considered to act as a diarylboryl anion (Ar₂B⁻) equivalent by utilizing the electron pair of the B-B bond.



Scheme 1. Synthesis of $B_2(o\text{-tol})_4$ (**1**) and reaction with molecular hydrogen and its transition state ($Ar = o\text{-tol}$)

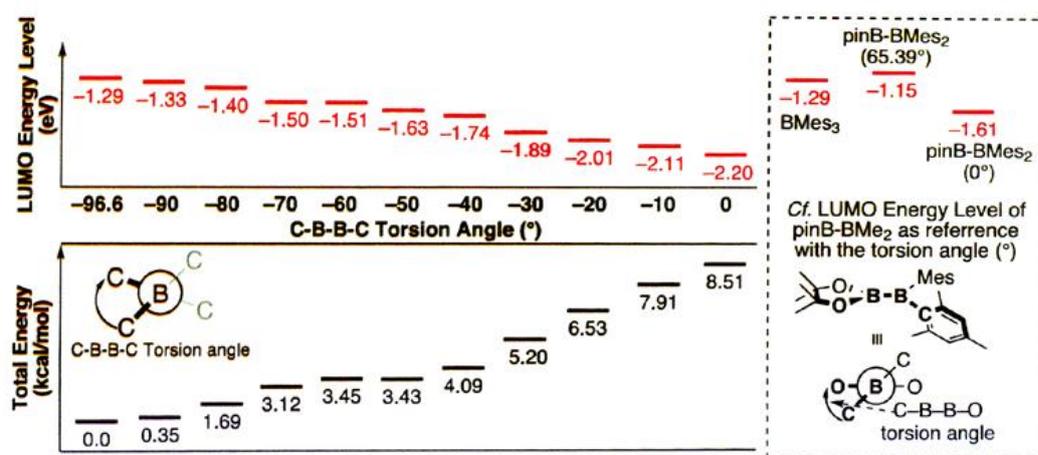
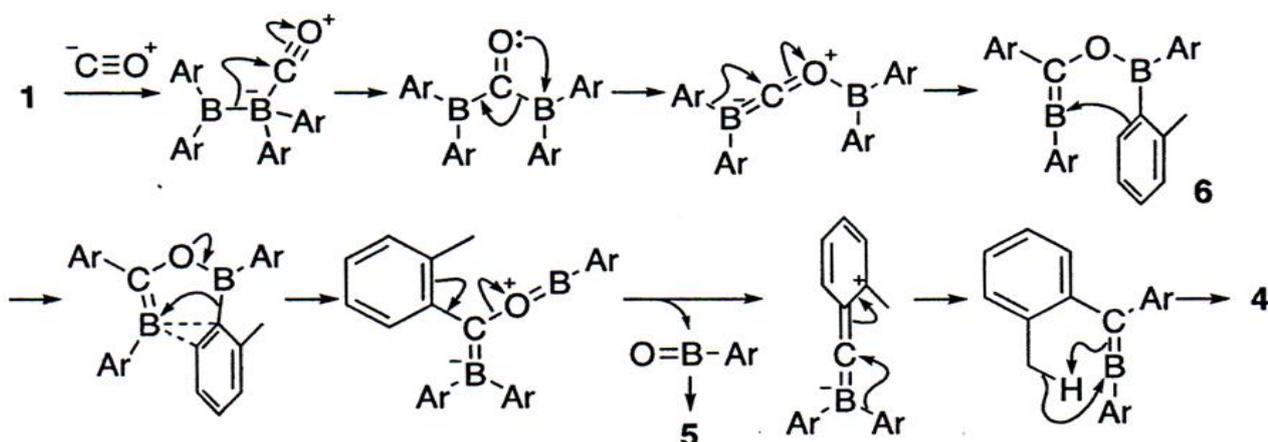


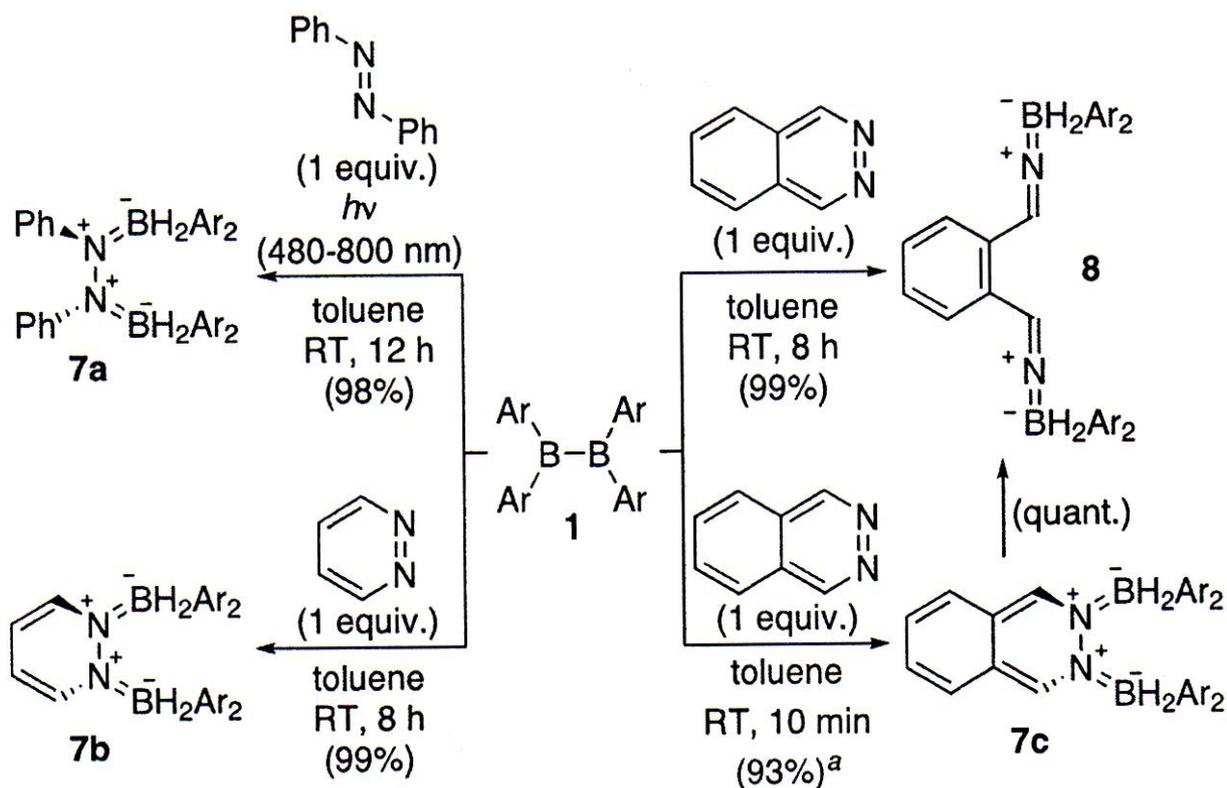
Figure 2. Dependence of LUMO energy level and total energy of **1** on torsion angle

Highly reactive **1** also reacts directly with CO molecules (Scheme 2). Exposure of a benzene solution of **1** to a CO atmosphere (1 bar) resulted in the formation of boraindane **4** and boroxine **5**. In this reaction, the $C\equiv O$ triple bond of the CO molecule was cleaved in one step. The formation of **4** was confirmed by NMR spectroscopy and single-crystal X-ray structure analysis, and **5** was identified by comparing the NMR and MS data with the data from the literature. Since the benzylic carbon of **4** was presumed to be derived from the CO molecule, $4\text{-}^{13}\text{C}$ was synthesized using ^{13}C -labeled carbon monoxide gas. It was confirmed that the benzylic carbon of **4** was derived from CO based on the splitting pattern and increased intensity of the ^1H and ^{13}C NMR signals of $4\text{-}^{13}\text{C}$. In addition, the reaction mechanism was estimated based on the DFT calculations (Scheme 3). Coordination of CO to **1**, nucleophilic migration of the Ar_2B moiety, C–B bond cleavage to form a thermodynamically stable B–O bond, followed by the migration of the Ar group produces boraalkene intermediate **6**. After that, the Ar group migrates to the highly electrophilic boraalkene moiety to form a borataalkene intermediate, which spontaneously dissociates into oxoborane $Ar\text{-B=O}$ and betaine-type borataallene, leading to the cleavage of the CO-derived C–O bond. The produced oxoborane is immediately trimerized to form **5**, and the borataallene forms **4** through the transfer of the Ar group and hydrogen atom.



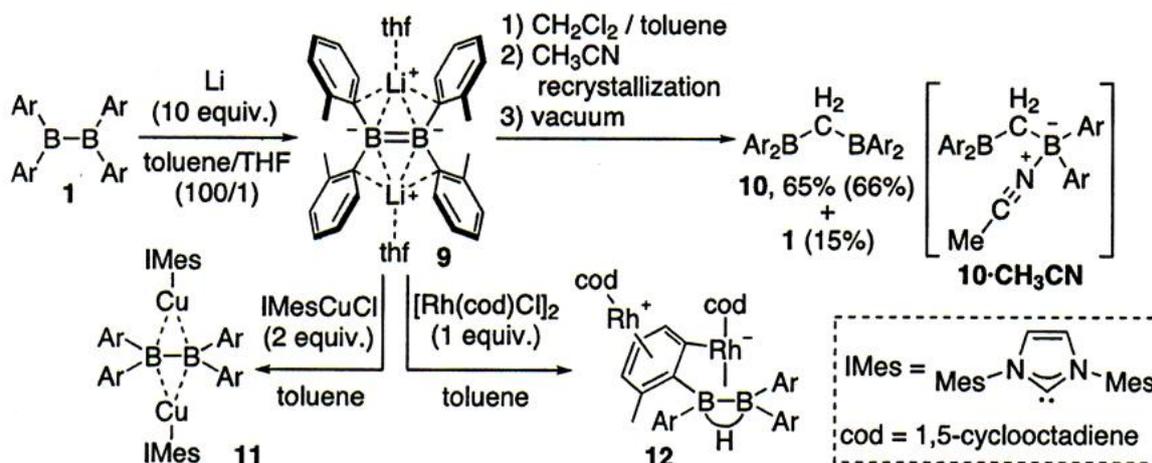
Scheme 3. Possible reaction mechanism of 1 with CO estimated by DFT calculations (Ar = *o*-tol)

The reactivity of 1 toward N=N double-bond species was also investigated.⁵ The reaction of 1 with azobenzene afforded the N–N single bond species 7a by the diboration of the N=N double bond. The reaction was carried out under light irradiation since it was found that only the *cis* form of azobenzene reacted with 1. The reaction with pyridazine, in which the geometry of the N=N double bond was fixed as *cis*, proceeded immediately to afford the corresponding N–N single bond species 7b, also by diboration. On the other hand, when the reaction of 1 with bicyclic phthalazine was examined, quantitative formation of 8 through N=N double bond cleavage was confirmed by singlecrystal X-ray diffraction analysis. Such N=N double bond cleavage reactions are rare and limited to severe reaction conditions using strong oxidants, reductants, or a chromium-carbene complex. When this reaction was stopped after a short time, the intermediate 7c could be isolated. 7c is a product with an N–N single bond formed via diboration, similar to the case for 7a and 7b. It was found that when a solution of 7c was left at room temperature, isomerization proceeded quantitatively to give 8 regardless of the presence or absence of room light. This isomerization involves the rearomatization of the six-membered ring of 7c, which is considered to have driven the reaction thermodynamically. DFT calculations revealed that the formation of 7a-7c can be understood by a common reaction mechanism which starts with coordination of a nitrogen to the boron atom in one Ar₂B group followed by migration of the other Ar₂B group.



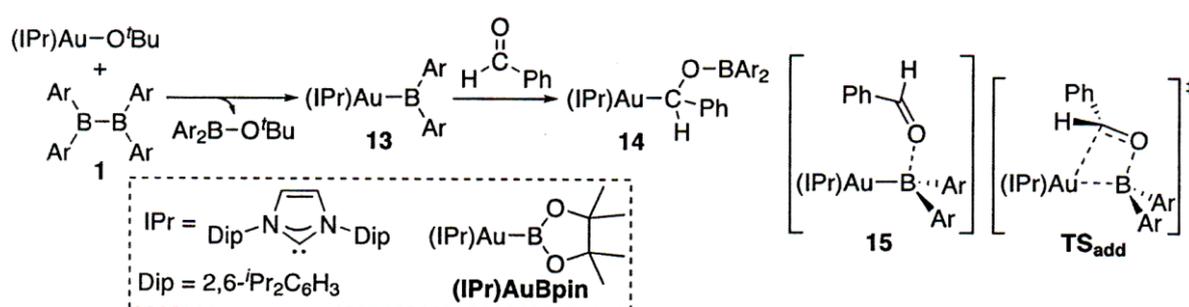
Scheme 4. Reactions of 1 with N=N double bond species (Ar = o-tol)

Due to the presence of the 2p orbital of the two boron atoms, **1** is easily reduced to give a dianion species **9** with a B=B double bond character. **6** Compound **9** is the third dianionic B=B double-bond species reported so far. Reaction of **9** with CH₂Cl₂ afforded **10** as a geminal-diborated product. In this reaction, **9** can be regarded to behave as 2 equivalents of an anionic Ar₂B nucleophile equivalent. Since a small amount of **1** was recovered, it is considered that part of the reaction may proceed via an electron transfer reaction. The structure of **10** with a B-C-B bond was confirmed by single-crystal X-ray diffraction analysis of acetonitrile-coordinated **10**·CH₃CN, which was crystallized from an acetonitrile solution of **10**. The dianionic species **9** can also be used as a ligand for transition metal complexes.⁷ The reaction of **9** with 2 equivalents of IMesCuCl produced a dinuclear copper **11** in which both the top and bottom of the diborane moiety were coordinated to Cu. In the structure of **11**, it is considered that the π electron of the B=B double bond coordinated to the two Cu centers at the same time, which is presumed to be due to the negative charge of dianion **9**. Similarly, the reaction of **9** with [Rh(cod)Cl]₂ gave complex **12** in which the C-H bond of the o-tolyl group was cleaved after the B-B moiety coordinated to the Rh center. In this reaction, the hydrogen atom generated by bond cleavage transferred to the opposite side of the B-B moiety. Thus, it was clarified that the dianionic B=B double bond species **9** derived from **1** also shows a characteristic reaction.



Scheme 5. Formation and reactions of dianion **9** by reduction of **1** (Ar = *o*-tol)

It was also revealed that the highly electrophilic **1** affords a boryl complex by a metathesis reaction with a metal alkoxide (Scheme 6).⁸ When **1** reacted with a gold tert-butoxide complex having an IPr ligand, diarylborylgold complex **13** formed with the elimination of alkoxyborane. Complex **13** exhibits an orange color in contrast to the colorless oxygensubstituted boryl complex (IPr)AuBpin. As revealed by the DFT calculations, this is because the HOMOLUMO energy gap of **13** becomes smaller due to the higher π -accepting and σ -donating abilities of the diarylboryl ligand as compared with those of Bpin, so the absorption extended into the visible region. In addition, the reaction of complex **13** with the C=O double bond of benzaldehyde gave **14** as the main product by the formation of Au–C and O–B bonds. In a typical transition-metal boryl complex, the boryl ligand attacks the carbonyl as a nucleophile, whereas the product obtained by this reaction has the opposite selectivity. We performed DFT calculations to analyze the reaction mechanism. It was revealed that after forming an intermediate **15** in which the oxygen atom of the carbonyl group coordinated to the highly electrophilic boron atom in **13**, the reaction proceeded through the transition state TS_{add}, where the gold atom behaved as a nucleophile, leading to the opposite selectivity

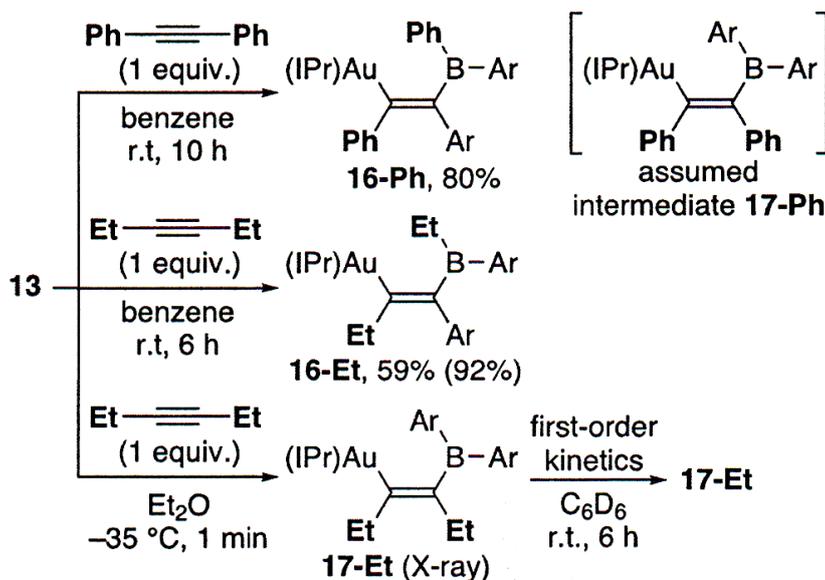


Scheme 6. Synthesis and reaction of diarylborylgold complex **13** by metathesis of **1** (Ar = *o*-tol)

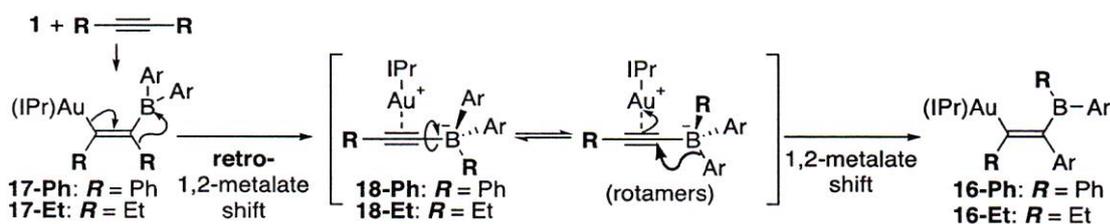
The diarylborylgold complex **13** also showed characteristic reactivity toward internal alkynes (Scheme 7).⁹ The reaction of **13** with diphenylacetylene gave **16**-Ph as an auroboration product with synselectivity. However, it should be noted that the positions of the Ph group that should be on the carbon atom of the alkenyl group and the *o*-tol group that should be on the boron atom were exchanged. The formation of **16**-Ph is considered to arise from a simple syn-addition intermediate **17**-Ph, which could not be isolated. Similar to the formation of **16**-Ph, the reaction using 3-hexyne afforded **16**-Et in which the substituents also became exchanged in the same manner. When the same reaction was performed at a lower temperature and stopped after a short time, the simple syn addition product **17**-Et without exchanging substituents could be isolated.

When the solution of 17-Et was allowed to stand at room temperature, isomerization to 16-Et proceeded gradually. The reaction obeyed first-order kinetics for the concentration of 17-Et, indicating an intramolecular pathway. The reaction mechanism was analyzed by DFT calculations and gold alkynylborate complexes 18-Ph and 18-Et were identified as intermediates connecting 16 and 17 (Scheme 8). Complexes 18 are expected to be formed by a 1,2-shift of carbon substituents attached to the alkenyl group on the highly Lewis acidic boron atom with the cooperation of the pair of bonding electrons in the highly polarized Au–C bond. In this context, we named the reaction forming 18 as a "retro-1,2-metalate shift" because it can be regarded as the reverse reaction of the 1,2-metalate shift, in which one of the substituents in the 4-coordinated borate migrates to a neighboring atom. These reactions proceeded due to the coexistence of polarized Au–C bonds and highly

Lewis acidic Ar₂B groups in the molecule of 17.



Scheme 7. Reactions of diarylborylgold complex 13 with internal alkynes (Ar = *o*-tol)



Scheme 8. Reaction mechanism for diarylborylgold complex 13 with internal alkynes estimated by DFT calculations (Ar = *o*-tol)

Summary

This account describes the synthesis, properties, and characteristic reactivities of the highly reactive diborane(4), B₂(*o*-tol)₄ (1), which we have recently reported. 1 exhibits highly electron-accepting accepting properties due to the two vacant overlapping p-orbitals of the two boron atoms. As a result, 1 showed high reactivity toward H–H, C≡O, and N=N bonds, with which ordinary organic molecules do not react. In addition, the two-electron reduction of 1 resulted in the formation of a dianionic B=B species, which can be used as an Ar₂B anion equivalent or a ligand for transition metal complexes. Furthermore, it was revealed that a diarylborylgold complex can be obtained by the metathesis of 1, which shows unusual reactivity toward C=O and C≡C bonds.

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