

# Reaction of B<sub>2</sub>(*o*-tol)<sub>4</sub> with CO and Isocyanides: Cleavage of the C≡O Triple Bond and Direct C-H Borylations

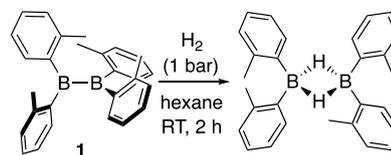
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**Abstract:** The reaction of highly Lewis-acidic tetra(*o*-tolyl)diborane(4) with CO afforded a mixture of boraindane and boroxine via the cleavage of the C≡O triple bond. <sup>13</sup>C-labeling experiments confirmed that the carbon atom in the boraindane stems from CO. Simultaneously, formation of boroxine **3** could be considered as "borylene transfer" to capture oxygen atom from CO. The reaction of diborane(4) with <sup>t</sup>Bu-NC afforded an azaallene, while the reaction with Xyl-NC furnished cyclic compounds via a direct C-H borylations.

Carbon monoxide (CO) strongly coordinates to low-valent and electron-rich transition metals to form the corresponding carbonyl complexes, whereby bonding occurs predominantly via  $\pi$ -backdonation to CO  $\pi^*$ -orbitals.<sup>[1]</sup> Carbonyl ligands in the coordination sphere of transition metal complexes exhibit diverse reactivity, which includes simple or oxidative dissociations, migratory insertions into covalent metal-ligand bonds, and electrophilic reactions toward nucleophiles. In comparison, the reactivity of CO towards main-group elements has been studied less intensively until recently.<sup>[2]</sup> However, during the last few decades a growing number of main-group-element compounds that react with CO has emerged.<sup>[3]</sup> Among these, only very few compounds are able to completely cleave the C≡O triple bond in CO without having to rely on transition metals.<sup>[4]</sup> Organic isocyanides are also often used as ligands for transition metals and as substrates in transition-metal-catalyzed transformations, given that they are isoelectronic to CO.<sup>[5]</sup> Similar to CO, organic isocyanides exhibit a formally divalent character, which renders them ideal partners for reactions with main-group elements.<sup>[3p, 6]</sup>

Bis(pinacolato)diborane (B<sub>2</sub>pin<sub>2</sub>), which is stabilized by  $p\pi-p\pi$  interactions from four adjacent oxygen atoms, has been widely used for transition-metal-catalyzed borylations of organic molecules.<sup>[7]</sup> We have recently reported a modification of B<sub>2</sub>pin<sub>2</sub>

with two 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (Mes) groups to form the unsymmetric diborane(4), pinB-BMes<sub>2</sub>, which exhibits a pinacolato and two mesityl groups.<sup>[8]</sup> The absence of heteroatoms at one of the two boron atoms renders this molecule highly electrophilic. In fact, pinB-BMes<sub>2</sub> reacts with *tert*-butylisocyanide leading to cleavage of the N=C triple bond,<sup>[8]</sup> with CO to provide a CO-coordinated boraalkene,<sup>[8]</sup> with alkynes to form diborylalkenes,<sup>[9]</sup> with 2,6-dimethylphenylisocyanide to furnish a 1,2-oxaboretane ring,<sup>[10]</sup> with pyridine to give C-H functionalized pyridines,<sup>[11]</sup> and with electrons to afford the corresponding radical anion.<sup>[12]</sup> Even though one can expect that diborane(4)s without the stabilization from heteroatoms should exhibit higher reactivity than heteroatom-stabilized diborane(4)s, examples for the reactivity of such diborane(4)s remain limited.<sup>[13]</sup> We have recently reported one such example, i.e., tetra(*o*-tolyl)diborane(4) (**1**), which exhibits high electron affinity and reactivity toward H<sub>2</sub> (Scheme 1).<sup>[14]</sup> Herein, we report that the reaction between **1** and CO affords 2-boraindane and boroxine leading to concomitant complete cleavage of the C≡O triple bond and a C(sp<sup>3</sup>)-H bond, while the reaction with isocyanides furnishes isocyanide-coordinated boraalkenes or the C(sp<sup>2</sup>)-H bond cleaved products.



**Scheme 1.** Reaction of tetra(*o*-tolyl)diborane(4) (**1**) with H<sub>2</sub>

Exposure of a benzene solution of **1** to CO (1 bar) resulted in the formation of 2-boraindane **2** via insertion of the carbon atom of the CO molecule and cleavage of a C(sp<sup>3</sup>)-H bond of a methyl group of an *o*-tolyl substituent (Scheme 2). The oxygen atom of CO is incorporated into *o*-tolylboroxine **3** as evident from NMR and mass spectra, as well as a comparison with previously reported spectra.<sup>[15]</sup> In order to facilitate the characterization, <sup>13</sup>CO was used to generate <sup>13</sup>C-labeled **2-<sup>13</sup>C**. The structure of **2** was unambiguously determined by single-crystal X-ray diffraction analysis (Figure 1). In the solid state, the boron-containing five-membered ring is almost planar, whereby the B1 atom is sp<sup>2</sup>-hybridized (angle sum around the boron atom: 359.9°). The captured carbon atom (C8) can be considered as sp<sup>3</sup>-hybridized, as the three C-C bonds are non-planar and one hydrogen atom (H8) was found in the differential Fourier map. The presence of H8 in **2** was also confirmed by a singlet at  $\delta_{\text{H}}$  4.17 ppm in the <sup>1</sup>H NMR spectrum. In the case of **2-<sup>13</sup>C**, H8 was observed as a doublet due to coupling with the introduced <sup>13</sup>C nucleus (<sup>1</sup>J<sub>CH</sub> = 111 Hz; Figures 2a,b).<sup>[16]</sup> In the <sup>13</sup>C NMR spectrum of **2-<sup>13</sup>C**, three doublets for aromatic quaternary carbons were found at  $\delta_{\text{C}}$  144.10

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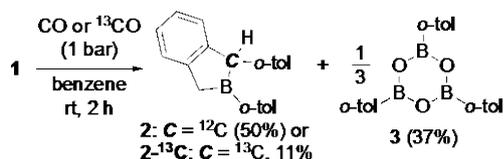
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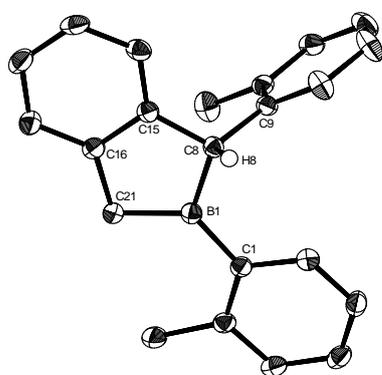
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## COMMUNICATION

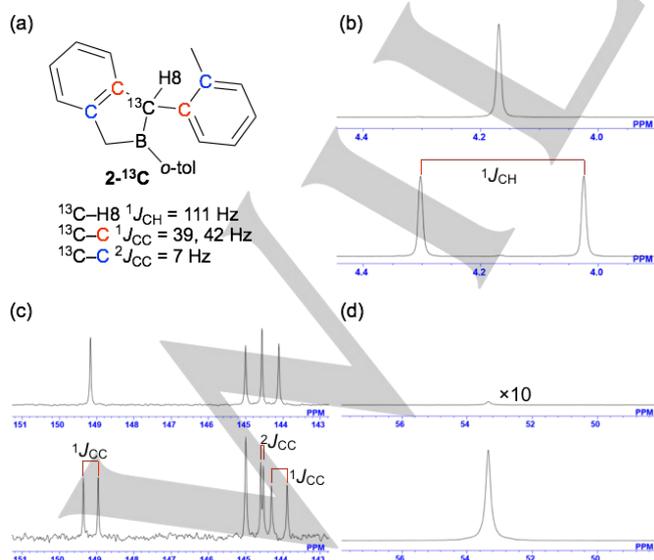
( $^1J_{CC} = 42$  Hz), 144.56 ( $^1J_{CC} = 7$  Hz), and 149.16 ( $^1J_{CC} = 39$  Hz) ppm [Figure 2c; cf.  $^1J_{CC} = 43$  Hz for the C(sp<sup>2</sup>)-C(sp<sup>3</sup>) linkage in strychnine,<sup>[17]</sup> and  $^2J_{CC} = 3-8$  Hz for allylic  $^{13}\text{C}-\text{C}=\text{C}^{13}\text{C}$ ].<sup>[18]</sup> In the aliphatic region, a methine signal was observed at  $\delta_{\text{C}} 53.34$  ppm, which was strongly enhanced in comparison to that of **2**. This result proves that the methine carbon atom stems from CO via cleavage of the C=O triple bond in the absence of a transition-metal complex. Simultaneously, this reaction can be considered as "borylene transfer" to capture oxygen atom of CO.



**Scheme 2.** Reaction of **1** with CO or  $^{13}\text{CO}$  (Yield in parentheses estimated by  $^1\text{H}$  NMR spectroscopy.)

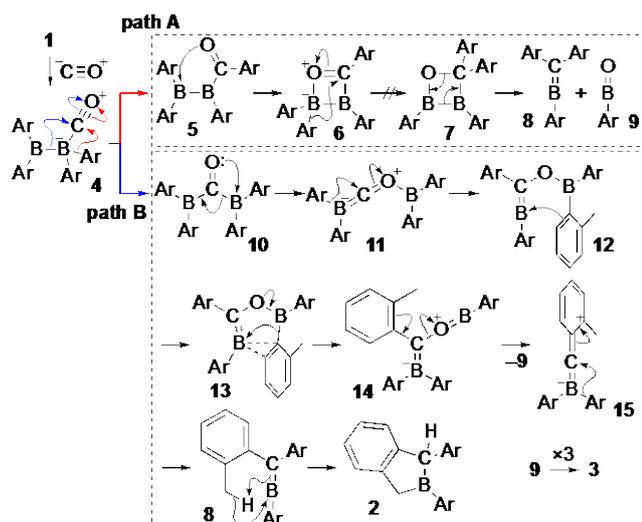


**Figure 1.** Molecular structure of **2** (thermal ellipsoids set at 50% probability, hydrogen atoms except H8 omitted for clarity). Selected bond lengths (Å) and angles (°): B1-C1 1.558(2), B1-C8 1.613(2), B1-C21 1.582(2), C21-C16 1.507(2), C16-C15 1.395(2), C15-C8 1.524(2); C1-B1-C8 123.65(13), C1-B1-C21 129.39(13), C8-B1-C21 106.88(12), B1-C8-C15 102.92(11), C8-C15-C16 112.82(13), C15-C16-C21 112.67(13), B1-C21-C16 104.51(12).



**Figure 2.** NMR spectra of **2** and **2- $^{13}\text{C}$**  (red solid lines denote coupling with  $^{13}\text{C}$ , top: **2**; bottom: **2- $^{13}\text{C}$** ). (a) Schematic summary of the coupling in **2- $^{13}\text{C}$** ; (b) the  $^1\text{H}$  NMR signal for the methine proton; (c)  $^{13}\text{C}$  NMR signal for the  $^{13}\text{C}$ -bonded quaternary carbon atom; (d)  $^{13}\text{C}$  NMR signal for the methine carbon (the signal of **2** was increased by one order of magnitude for clarity).

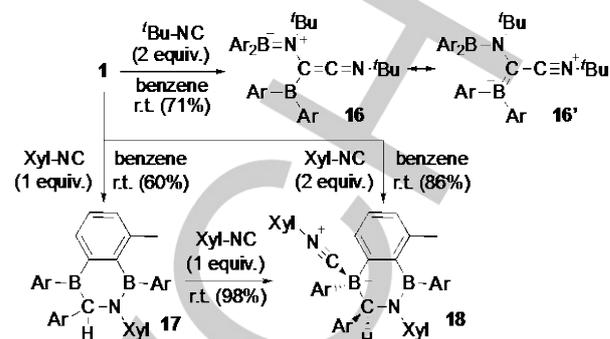
A feasible mechanism for the formation of **2** and **3** based on the DFT calculations is proposed in Scheme 3 (cf. SI for details and energy profiles). In the first step, a lone pair on the carbon atom of CO coordinates to one boron atom of **1** to form sp<sup>2</sup>-sp<sup>3</sup> species **4**. Based on our previous work on the reaction of unsymmetric pinB-BMes<sub>2</sub> with CO,<sup>[8]</sup> we considered two possible pathways, i.e., migration of one *o*-tolyl group or the boryl group in **4** to afford **5** (red arrows: path A) or **10** (blue arrows: path B). The cyclization of diboranyl ketone **5** results in the formation of a four-membered ring in **6**. However, DFT calculations suggested a higher activation energy for the formation of **5** and a very high activation energy (47.3 kcal/mol) for the subsequent migration of the *o*-tolyl group in **6** to furnish **7**, which would be able to dissociate into boraalkene **8** and oxoborane **9**.<sup>[19]</sup> Instead, path B was calculated as an appropriate mechanism for the formation of **8** and **9**. Diborylketone **10** undergoes further migration of a BAr<sub>2</sub> group to afford **11** via the formation of a thermally stable B-O bond. It should be noted that **11** can be considered as a carbene that is stabilized by a  $\pi$ -donating oxygen atom and a  $\pi$ -accepting boron atom. This carbene character could induce the subsequent nucleophilic migration of one *o*-tolyl group on the negatively charged boron atom in **11** to furnish **12**. Coordination of adjacent *o*-tol group to the resulting boraalkene moiety in **12** affords boraalkene-arene complex **13**.<sup>[20]</sup> The B-Ar bond in **12**, which is more reactive than B-O bond of the similar boraalkene intermediate in the reaction of pinB-BMes<sub>2</sub> with CO,<sup>[8]</sup> would induce the rapid intramolecular migration of aryl group. The coordinating aryl group in **13** migrates to the boraalkene moiety with an assistance of the lone pair on the oxygen atom to furnish oxonium borate **14**. The subsequent dissociation of **9** from **14** spontaneously takes place to give an allenic betaine **15**. To cancel positive and negative charges in **15**, the aryl group on borate moiety migrates to the carbon atom to furnish boraalkene **8**. A simultaneous intramolecular proton transfer and a cyclization at the benzylic position finally give boraindane **2**. Simultaneously, oxoborane **9** trimerizes to form boroxine **3**.



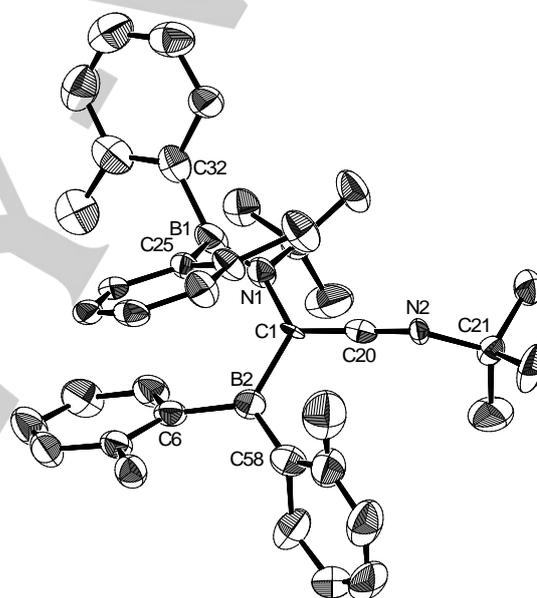
**Scheme 3.** Possible mechanism of for the cleavage of the C=O triple bond during the reaction between 1 and CO to afford 2 and 3 (Ar = o-tol).

Tetra(o-tolyl)diborane(4) **1** also reacted with isocyanides (Scheme 4). The reaction of **1** with 2 equiv. of <sup>t</sup>Bu-NC in benzene afforded 1-azaallene **16**. The solid-state structure of **16** was determined by a single-crystal X-ray diffraction analysis (Figure 3), albeit that the disorder of the structure due to the orientation of the o-tolyl groups and the <sup>t</sup>Bu group on the terminal nitrogen atom prevented us from estimating accurate structural parameters. Nevertheless, it is clear that **16** is resulted from a coupling of two isocyanide molecules at the carbon atom and the separation of the two boron atoms. The N-terminus of the <sup>t</sup>Bu-N=C moiety is slightly bent [139.4(6)°/133.3(9)°], indicating that N2 is sp<sup>2</sup>-hybridized. The <sup>1</sup>H NMR spectrum of isolated crystalline **16** indicated the presence of two conformers in solution, probably due to the restricted rotation around the N1–C1 bond and the relative orientation of the two <sup>t</sup>Bu groups on N1 and N2. The VT <sup>1</sup>H NMR spectra of **16** (RT and 70 °C) suggested interconversion of these isomers on the <sup>1</sup>H NMR timescale (*cf.* SI). The reaction between **1** and 1 equiv. of Xyl-NC (Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) afforded **17**, which contains a benzoannulated six-membered ring. The structure of **17** was determined by a single-crystal X-ray diffraction analysis (Figure 4). The annulated benzene ring in **17** is derived from one of the four o-tolyl groups in **1**, whereby the C–H bond at the 6-position of the annulated o-tolyl group is cleaved. In the solid state, the six-membered ring in **17** is slightly distorted from planarity, reflecting the contribution from sp<sup>3</sup>-hybridized C1 to the six-membered ring. Given the high number of possible rotamers of **17**, which arises from the orientation of three o-tolyl groups, a complete characterization of **17** by <sup>1</sup>H NMR spectroscopy was not possible, although the <sup>11</sup>B NMR spectrum, the X-ray diffraction analysis, and the elemental analysis all supported the formation of **17**. The reaction between **1** and 2 equiv. of Xyl-NC led to the formation of **18**, in which Xyl-NC coordinates to **17**. Based on the X-ray crystallographic analysis (Figure 5), coordination of Xyl-NC to **17** directly affords **18**, as confirmed by independent experiment for the formation of **18** by a reaction of **17** with 1 equiv. of Xyl-NC. The <sup>1</sup>H, <sup>11</sup>B, and <sup>13</sup>C NMR spectra of **18** suggested the presence

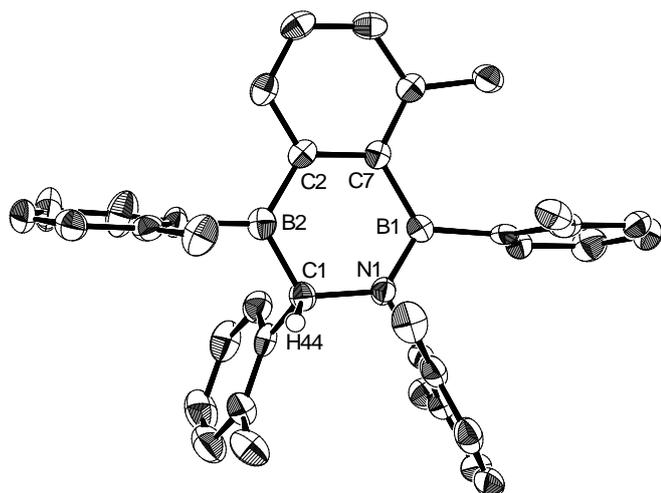
of a single diastereoisomer, which is most likely due to the steric repulsion between two o-tolyl groups.



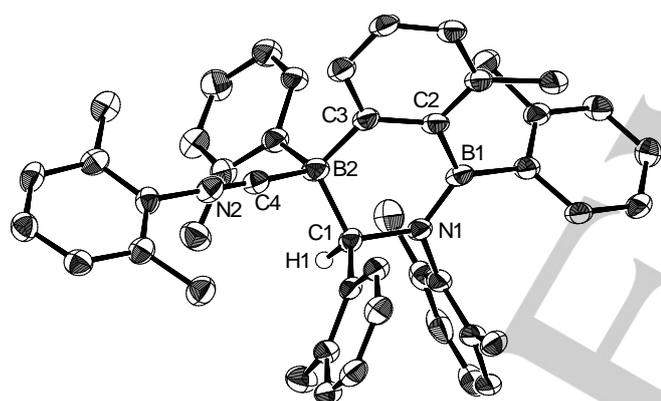
**Scheme 4.** Reaction of **1** with isocyanides (Ar = o-tol, Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Yield estimated by <sup>1</sup>H NMR spectroscopy.)



**Figure 3.** Molecular structure of **16** (thermal ellipsoids set at 50% probability, minor part of disordered moiety and hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): B1–N1 1.407(4), B1–C25 1.584(6), B1–C32 1.618(10), N1–C1 1.41(2), C1–B2 1.635(15), C1–C20 1.36(2), C20–N2 1.171(7); B2–C1–C20 1.36(2), C1–C20–N2 1.790(10), C20–N2–C21 139.4(6).



**Figure 4.** Molecular structure of **17** (thermal ellipsoids set at 50% probability, hydrogen atoms except H44 omitted for clarity). Selected bond lengths (Å) and angles (°): C1–N1 1.448(4), N1–B1 1.488(4), B1–C7 1.583(4), C7–C2 1.429(4), C2–B2 1.543(5); B2–C1–N2 115.0(2), C1–N1–B1 124.7(2), N1–B1–C7 119.9(3), B1–C7–C2 118.5(3), C7–C2–B2 120.7(3), C2–B2–C1 119.8(3).

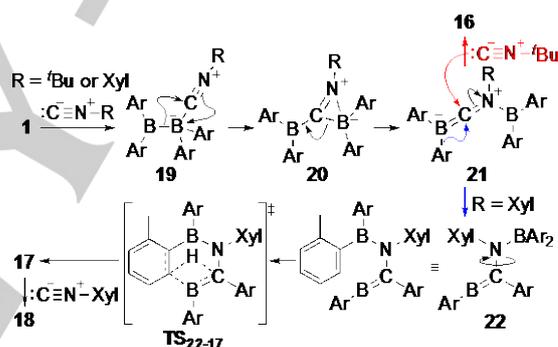


**Figure 5.** Molecular structure of **18** (thermal ellipsoids set at 50% probability, hydrogen atoms except H1 omitted for clarity). Selected bond lengths (Å) and angles (°): C1–N1 1.514(3), N1–B1 1.405(4), B1–C2 1.597(4), C2–C3 1.416(4), C3–B2 1.620(4), B2–C1 1.648(4), B2–C38 1.604(4), C38–N2 1.155(3); B2–C1–N1 109.75, C1–N1–B1 124.8(2), N1–B1–C2119.2(2), B1–C2–C3 117.5(2), C2–C3–B2 120.0(2), C3–B2–C1 130.0(2), C38–N2–C39 169.3(3).

A plausible mechanism for the formation of **16–18** via the common intermediate **21** is proposed in Scheme 5, based on the DFT calculations (cf. SI for details and energy profiles). Similar to the formation of **2** and **3** (Scheme 3), coordination of isocyanide to the boron atom formed  $sp^2$ - $sp^3$  species **19**. A subsequent B–B bond cleavage of **19** should generate diborylimine **20** with an intramolecular coordination of nitrogen atom to the boron atom. The cleavage of B–C bond to release the ring strain of the BNC three-membered ring affords boryl-substituted azaboreallene **21**. Because of a carbenic character of **21**, similar to **11**, a nucleophilic attack on the central carbon atom of **21** by the second equivalent of  $t$ Bu-NC, under simultaneous elimination of the positive charge on the nitrogen atom would then result in the formation of azaallene **16**. The nucleophilic attack of the second  $t$ Bu-NC to **21**

could be differentiated from the reactivity of the intermediate **11** in Scheme 3, probably due to higher concentration of  $t$ Bu-NC in solution than that of gaseous CO. In the case of using less-hindered Xyl-NC, the common intermediate **21** engages in a migration of an *o*-tolyl group to the carbenic carbon atom, which generates boraalkene **22**.<sup>[21]</sup> After the rotation of the N–C bond in **22**, rotamer **22'** would have the appropriate orientation to induce an electrophilic attack of the boraalkene moiety on the *o*-tolyl ring. A subsequent deprotonation by the negatively charged boraalkene in **23** would furnish cyclized product **17**, followed by the coordination of Xyl-NC to afford **18**.

In summary, we found that the reaction between highly Lewis-acidic tetra(*o*-tolyl)diborane(4) **1** and CO afforded a mixture of boraindane **2** and boroxine **3** via complete cleavage of the C=O triple bond. The incorporation of the CO carbon atom in boraindane **2** was confirmed by <sup>13</sup>C-labeling experiments. Simultaneously, formation of boroxine **3** could be considered as "borylene transfer" to capture oxygen atom from CO. The reaction between **1** and  $t$ Bu-NC generated azaallene **13**, while the reaction between **1** and Xyl-NC resulted in the formation of cyclic compounds **14** and **15** through C–H borylations.



**Scheme 5.** Plausible mechanism for the incorporation of isocyanides in **1** and the C–H bond cleavage to generate **16–18** (Ar = *o*-tol, Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

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**Keywords:** diborane(4) • carbon monoxide • isocyanide • triple bond • bond cleavage

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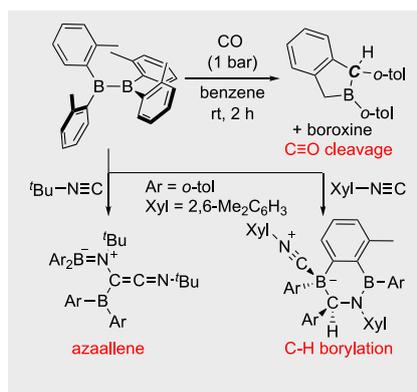
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Layout 1:

## COMMUNICATION

The reaction between highly Lewis-acidic  $(o\text{-tol})_2\text{B}-\text{B}(o\text{-tol})_2$  and CO afforded a mixture of boraindane and boroxine via a complete cleavage of the  $\text{C}\equiv\text{O}$  triple bond.  $^{13}\text{C}$ -labeling experiments demonstrated that the carbon atom in boraindane stems from CO. The reaction of diborane(4) with  ${}^t\text{Bu}-\text{NC}$  afforded an azaallene, while the reaction with  $\text{Xyl}-\text{NC}$  afforded cyclic borylations via direct C-H borylations.



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Reaction of  $\text{B}_2(o\text{-tol})_4$  with CO and Isocyanides: Cleavage of the  $\text{C}\equiv\text{O}$  Triple Bond and Direct C-H Borylations