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Facile scission of isonitrile carbon–nitrogen triple bond using a diborane(4) reagent

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Transition metal reagents and catalysts are generally effective to cleave all three bonds (one σ and two π) in a triple bond despite its high bonding energy. Recently, chemistry of single-bond cleavage by using main-group element compounds is rapidly being developed in the absence of transition metals. However, the cleavage of a triple bond using non-transition-metal compounds is less explored. Here we report that an unsymmetrical diborane(4) compound could react with carbon monoxide and *tert*-butyl isonitrile at room temperature. In the latter case, the carbon–nitrogen triple bond was completely cleaved in the absence of transition metal as confirmed by X-ray crystallographic analysis, ^{13}C NMR spectroscopy with ^{13}C labelling and DFT calculations. The DFT calculations also revealed the detailed reaction mechanism and indicated that the key for the carbon–nitrogen triple-bond cleavage could be attributed to the presence of nucleophilic nitrogen atom in one of the intermediates.

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A triple bond having three shared electron pairs between two atoms is known as one of the strongest chemical bonds. In spite of the large bonding energy, complete cleavage of the three (one σ and two π) bonds in a C≡C triple bond of an alkyne molecule or in a C≡N triple bond of a nitrile molecule under oxidative or acidic condition is common in general organic chemistry. In addition to the well-established chemistry of alkyne metathesis[1], some stoichiometric[2–4] and catalytic[5–11] reactions for complete cleavage of a C≡C triple bond are also known with transition metal (TM) reagents and catalysts. However, only two examples about the cleavage of a C≡C triple bond without TMs have been reported using tandem- and multi-step reactions under harsh condition[12,13]. Moreover, cleavage of the C≡O triple bond in carbon monoxide (CO) is widely known as the Fischer–Tropsch process in the presence of a TM catalyst[14]. Recent development of TM catalysts enabled us to cleave the N≡N triple bond in dinitrogen for the formation of ammonia[15–17]. Several catalytic[18] and stoichiometric[19,20] cleavage reactions of a C≡N triple bond were also reported with use of TM catalyst and reagent[21–23]. Although some p-block element compounds could also react with CO[24–38] or isonitriles[28,39,40], the strongest σ-bond among the three bonds in a triple bond remained intact in all cases.

On the other hand, chemistry containing Lewis-base adduct of sp^2–sp^3 diborane(4) compounds has been quickly developed recently. After the isolation of the first example of base adduct of bis(catecholato)diborane(4)[41–45], a series of the sp^2–sp^3 diborane(4) compounds were applied as a boron source for copper-catalysed β-borylation of α,β-unsaturated carbonyl compounds in the absence of additional base[46–48], as a hydrogen donor for radical reduction[49] and as reactive compounds to undergo rearrangement reactions[50–53]. Some Lewis-base-catalysed β-borylation reactions of α,β-unsaturated carbonyl compounds were also considered to involve such sp^2–sp^3 diborane(4) intermediates[54–61]. Herein, we report a complete cleavage reaction of C≡N triple bond in isonitrile by using unsymmetrical diborane(4) compound, involving sp^2–sp^3 diborane(4) intermediates supported by density functional theory (DFT) calculations.
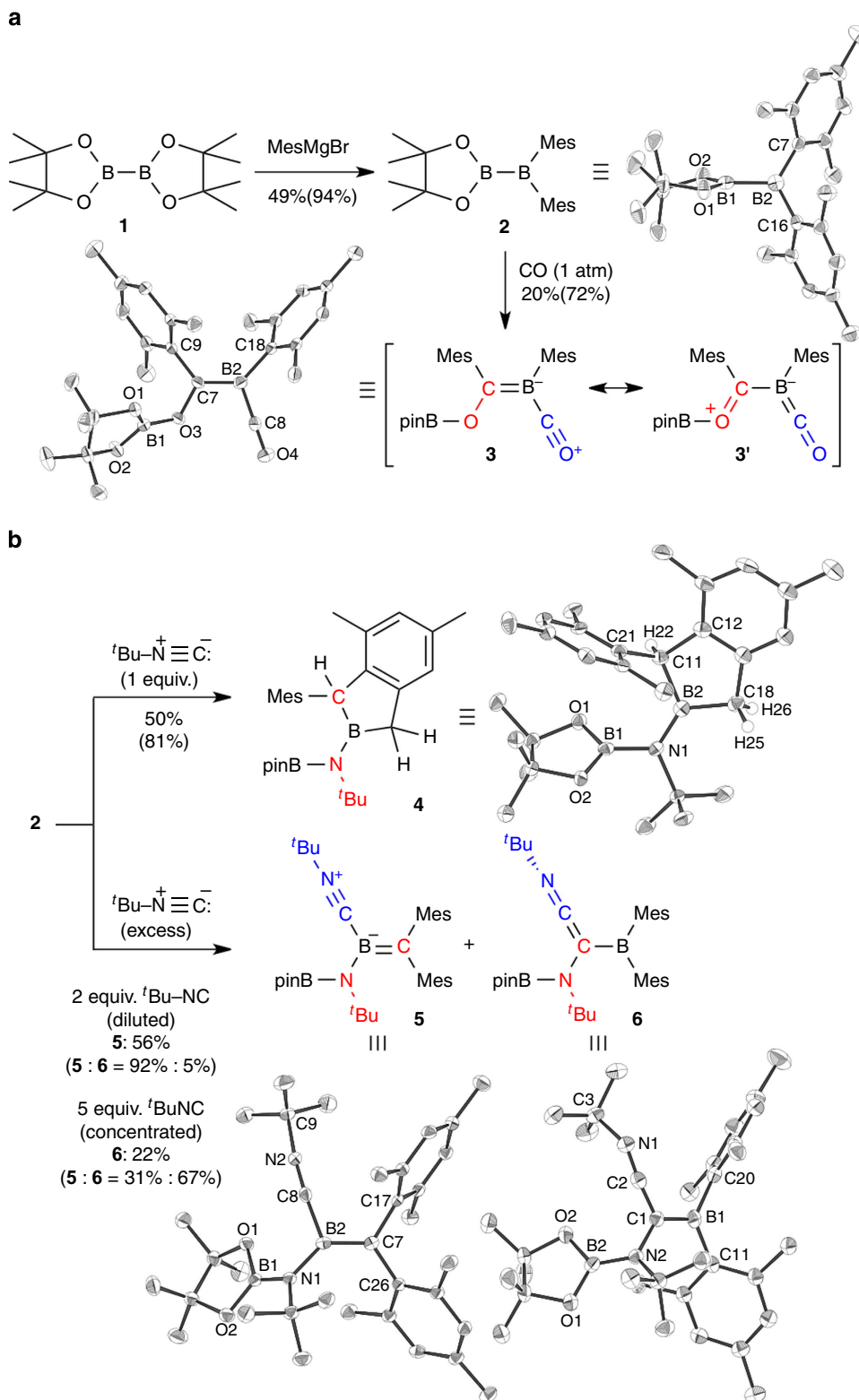
Results

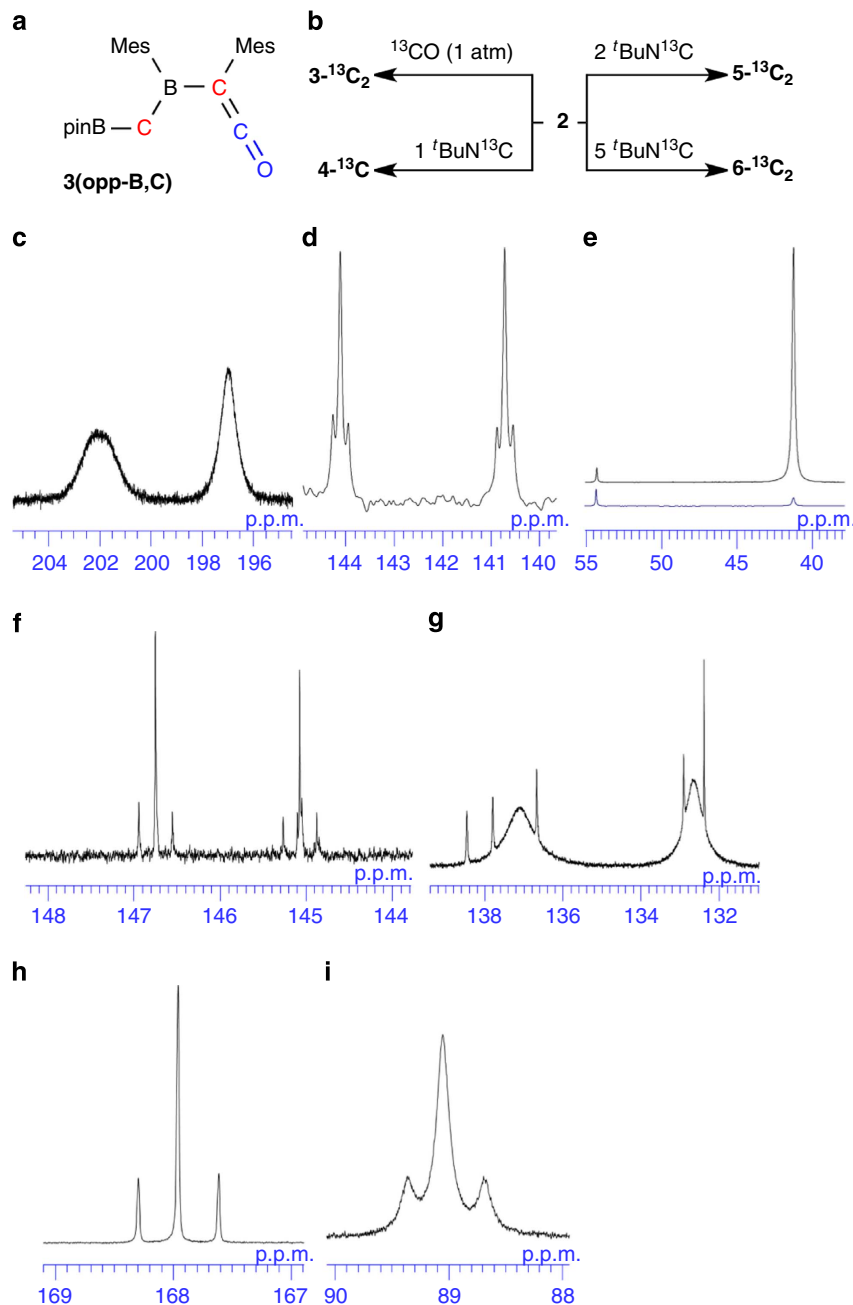**Synthesis and reactivity of diborane(4) with CO and ^{t}BuNC.** Synthesis of the unsymmetrical diborane(4) **2**, its reactions and characterization of the resulting products are summarized in Fig. 1 (see also, Supplementary Figs 1–15, Supplementary Tables 1 and 2, and Supplementary Methods). Reaction of **1** with mesitylmagnesium bromide gave **2** in 49% yield. The ^{1}H NMR spectrum of **2** showed C_{2v} symmetrical pattern of signals. Two broad ^{11}B NMR signals were observed at δ_B 34 and 89 p.p.m., indicating the selective conversion of one (pinacolato)boryl group to a dimesitylboryl group. Broadening of a ^{13}C NMR signal at δ_C 144.2 p.p.m. also confirmed the connection between the mesityl groups and a quadrupolar boron nucleus. X-ray crystallographic analysis of **2** revealed twisted orientation described by the dihedral angle of O1–B1–B2–C16 in contrast to the case of **1** (Supplementary Fig. 16)[62]. DFT calculation showed that the vacant *p*-orbital of the boron atom in the Bpin moiety slightly contribute to the LUMO of **2** (Supplementary Figs 17–18), which mainly consisted of the vacant p-orbital of the boron atom in the BMes₂ moiety, in spite of the twisted structure.

The unsymmetrical diborane(4) **2** reacted with CO or ^{t}BuNC to give a variety of products (Fig. 1). A benzene solution of **2** was exposed to CO at room temperature for 30 min to give pale yellow solids of **3** in 20% isolated yield. X-ray crystallography for **3** showed incorporation of two CO molecules (it should be noted

the complete assignment of atomic order in **3**, **5** and **6** would be difficult due to small difference in electron density of the second period elements; see below and Fig. 2). The O3–C7 [1.406(3) Å], C7–B2 [1.459(4) Å] and B2–C8 [1.492(4) Å] bonds are shorter than the conventional single bonds, and C8–O4 [1.144(3) Å] is slightly longer than the C≡O bond of free CO molecule (1.1283 Å)[63]. These data proposed resonance structures of **3** and **3'** with a characteristic conjugated O–C–B–C–O linkage giving a pale yellow colour (Supplementary Fig. 19 for ultraviolet–visible spectrum and Supplementary Tables 3 and 4 for time-dependent DFT calculation). Thus, compound **3** could be described as CO-coordinated alkoxyboraalkene. Reaction of **2** with one equivalent of ^{t}BuNC gave a colourless cyclized product **4** in 50% yield through scission of the isonitrile C≡N triple bond and of a C(sp^3)–H bond in one of the mesityl substituents, as the molecular structure of **4** was confirmed by X-ray crystallographic analysis. The assignment of the B2 atom in the 2-boraindane skeleton could also be supported by the relatively long B2–C11 [1.626(4) Å] and B2–C18 [1.591(4) Å] bonds. In contrast, the reaction of **2** with an excess amount of ^{t}BuNC gave a mixture of ^{t}BuNC-coordinated boraalkene **5** and borylethenylideneamine **6**. The reaction with two equivalents of ^{t}BuNC in a diluted solution gave **5** as the major product, while the reaction with a large excess amount of ^{t}BuNC in a concentrated solution afforded **6** as the major product. X-ray crystallographic analysis of **5** and **6** revealed that these two compounds have similar arrangement of all atoms, except the order of the two atoms in the central B=C or C–B bond and the terminal C–N–^{t}Bu angle (**5**, B2–C8–N2 = 173.6(2)°; **6**, C2–N1–C3 = 131.7(4)°). To form **5**, the C≡N triple bond in ^{t}BuNC, one B–B bond and two B–Mes bonds were cleaved from **2**, while the two mesityl groups are still attached to the boron atom in **6**. In the molecular structure of **5**, the boron centre has B=C double-bond character (B2–C7 = 1.456(3) Å) and the second equivalent of ^{t}BuNC coordinates to the boron atom in the B=C moiety. In the case of **6**, the ^{t}BuNC moiety has consecutive N=C and C=C double bonds (N1=C2 = 1.217(5) Å, C2=C1 = 1.353(6) Å) with a slightly short C–B single bond (C1–B1 = 1.516(7) Å). All the obtained crystal structures could be reproduced by DFT calculation to support the assignment of atomic order (see below).

The NMR spectroscopic characterization of the products. The nuclear magnetic resonance (NMR) spectra of **3**–**5** were consistent with the crystallographically determined structures. The ^{1}H NMR spectrum of **3** in C_6D_6 showed two distinct Mes groups and one pinacol moiety. Two boron nuclei resonated at δ_B −5 and 18 p.p.m., where the former signal could be assigned as the CO-coordinated boron atom due to the negatively charged boron atom in both the resonance structures **3** and **3'**. The calculated ^{11}B NMR chemical shift (δ_B −4.1, 20 p.p.m.) of **3** by the Gauge-independent atomic orbital (GIAO) method at B3LYP/6-311 + + G(2d,p)//B3LYP/6-31 + G(d,p) level was also in good agreement with the experimental data (Supplementary Table 5). Although the two Mes groups and the pinacol moiety could be assigned in the ^{13}C NMR spectrum of **3**, no signal corresponding to a B=C unit and a coordinating CO molecule was observed. The ^{1}H NMR spectrum of **4** showed one benzylic methine proton (δ_H 4.22) and two vicinally coupled methylene protons (δ_H 2.87 and 2.93, $^2J_{HH}$ = 21 Hz), supporting the scission of a C(sp^3)–H bond in one of the two mesityl groups to give a chiral centre on C11. Reflecting the asymmetry below and above the 2-boraindane plane in **4**, all the remaining five methyl groups on the mesityl substituents were separately observed and the four methyl groups on the pinacolato moiety resonated two singlet signals. Both the boron nuclei in **4** resonated at a typical region for an sp^2 boron

Figure 1 | Synthesis and reactions of unsymmetrical diborane(4) 2. (**a**) Synthesis and reaction of **2** with CO to form **3** and their crystal structures. (**b**) Reaction of **2** towards *tert*-butylisonitrile to form **4**–**6** and crystal structures of the products (isolated and ^{1}H NMR yield in parentheses, Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$, pinB = [(CH$_3$)$_2$CO]$_2$B): Selected bond lengths (Å), bond angles (°) and dihedral angles (°); **2**: B1–B2 = 1.722(4); **3**: B1–O1 = 1.366(3), B1–O2 = 1.356(3), B1–O3 = 1.374(3), O3–C7 = 1.406(3), C7–B2 = 1.459(4), B2–C8 = 1.492(4), C8–O4 = 1.144(3); **4**: B1–N1 = 1.455(3), N1–B2 = 1.415(3), B2–C11 = 1.626(4), B2–C18 = 1.591(4); **5**: B1–N1 = 1.413(3), N1–B2 = 1.495(3), B2–C7 = 1.456(3), B2–C8 = 1.569(3), C8–N2 = 1.152(3), B2–C8–N2 = 173.6(2); **6**: B1–C1 = 1.516(7), C1–C2 = 1.353(6), C2–N1 = 1.217(5), C1–N2 = 1.450(5), B2–N2 = 1.419(6), B1–C1–C2 = 114.8(4), C1–C2–N1 = 174.5(5), C2–N1–C3 = 131.7(4).

Figure 2 | Assignment of atomic order in 3–6 by ^{13}C NMR experiments with ^{13}C labelling. (**a**) Potential regioisomer **3(opp-B,C)** derived from exchange of the positions of boron and carbon atoms in **3**. (**b**) Reactions of **2** with ^{13}C-labelled ^{13}CO and $^tBuN^{13}C$ to form the corresponding ^{13}C-labelled **3-$^{13}C_2$**, **4-^{13}C**, **5-$^{13}C_2$** and **6-$^{13}C_2$**. (**c**) Newly appeared ^{13}C NMR signals of **3-$^{13}C_2$** on ^{13}C labelling. (**d**) The 4° aromatic signals of **4-^{13}C** with satellite on ^{13}C labelling (**e**) enhancement of ^{13}C NMR signal (top: **4-^{13}C**, bottom: **4**). (**f**) The 4° aromatic signals of **5-$^{13}C_2$** with satellite on ^{13}C labelling (**g**) newly appeared ^{13}C NMR signals of **5-$^{13}C_2$** on ^{13}C labelling (**h**). (**i**) Strengthened ^{13}C NMR signals of **6-$^{13}C_2$** with satellite on ^{13}C labelling.

atom (δ_B 27, 55 p.p.m.). The lower-field shifted signal could be assigned as the dicarbyl-substituted boron atom as supported by our GIAO calculations. Two relatively broadened ^{13}C NMR signals at δ_C 30.3 and 41.2 p.p.m., compared with other signals of **4**, supported their connection to quadrupolar boron nucleus. The ^1H NMR spectra of **5** and **6** similarly showed six methyl signals for the Mes groups, two methyl signals for the pinacol moiety, two ^tBu signals and four aromatic CH signals, because they are regioisomers with the same combination of the substituents and are close in symmetry of molecule. In the ^{13}C NMR spectrum of **5**, the number of observed signals was two short of the number of

^{13}C nuclei expected from the symmetry of the ^1H NMR spectrum. Similarly, one carbon signal was missing in the ^{13}C NMR spectrum of **6**. The missing of the ^{13}C signals was probably due to broadening of quaternary carbon bonded to quadrupolar boron nucleus. The ^{11}B NMR signals of **5** (δ_B 13, 21 p.p.m.) and **6** (δ_B 21, 63 p.p.m.) could also be assigned by our GIAO calculations.

The ^{13}C-labelling study to determine the atomic order. In addition to the conventional NMR spectra of **3–5**, ^{13}C-labelling experiment could confirm the structures of **3–6** including

connectivity between boron and carbon atoms (Fig. 2). Complete structural characterization of **3**, **5** and **6** was difficult due to the following reasons: (1) in general, X-ray crystallographic analysis has difficulty to distinguish two adjacent atoms in the same row of the periodic table. This means that positions of carbon and boron atoms in **3** versus **3(opp-B,C)** (Fig. 2a) and **5** versus **6** could not be unambiguously determined by crystallography. (2) Both [10]B and [11]B nuclei are quadrupolar to induce significant broadening of the signal for boron-bonded nuclei, leading in difficulty for observation of quaternary carbon bonded to boron nucleus. In this context, we performed ^{13}C-labelling experiments for **3**–**6** to observe the [13]C–[13]C coupling and broadened ^{13}C NMR signals bonded to boron atom. The unsymmetrical diborane **2** reacted with ^{13}C-labelled [13]CO (99% [13]C) or ^{t}BuN[13]C (20%

[13]C) gave ^{13}C-labelled **3-[13]C₂**, **4-[13]C**, **5-[13]C₂** and **6-[13]C₂** (Fig. 2b). On ^{13}C-labelling of **3**, two broad signals at δ_C 197.1 and 201.8 p.p.m. appeared without apparent coupling in the ^{13}C NMR spectrum of **3-[13]C₂** (Fig. 2c), indicating that these two carbon atoms connected to a quadrupolar boron atom with the C–B=C skeleton in **3** (not C–C=B in **3(opp-B,C)**). As described above, two broadened signals δ_C 30.3 and 41.2 p.p.m. may be assigned to the boron nucleus in **4**. The lower-field shifted signal at δ_C 41.2 p.p.m. was strengthened on ^{13}C labelling to form **4-[13]C** (Fig. 2e), indicating this benzylic methine carbon came from ^{t}BuN[13]C. Concomitantly, two signals of aromatic quaternary carbons at δ_C 140.7 and 144.1 p.p.m. were accompanied with satellite signal with $^1J_{CC}$ of 40 Hz (Fig. 2d), similar to that (43 Hz) for the C(sp^2)–C(sp^3) linkage in strychnine[64], indicating that the
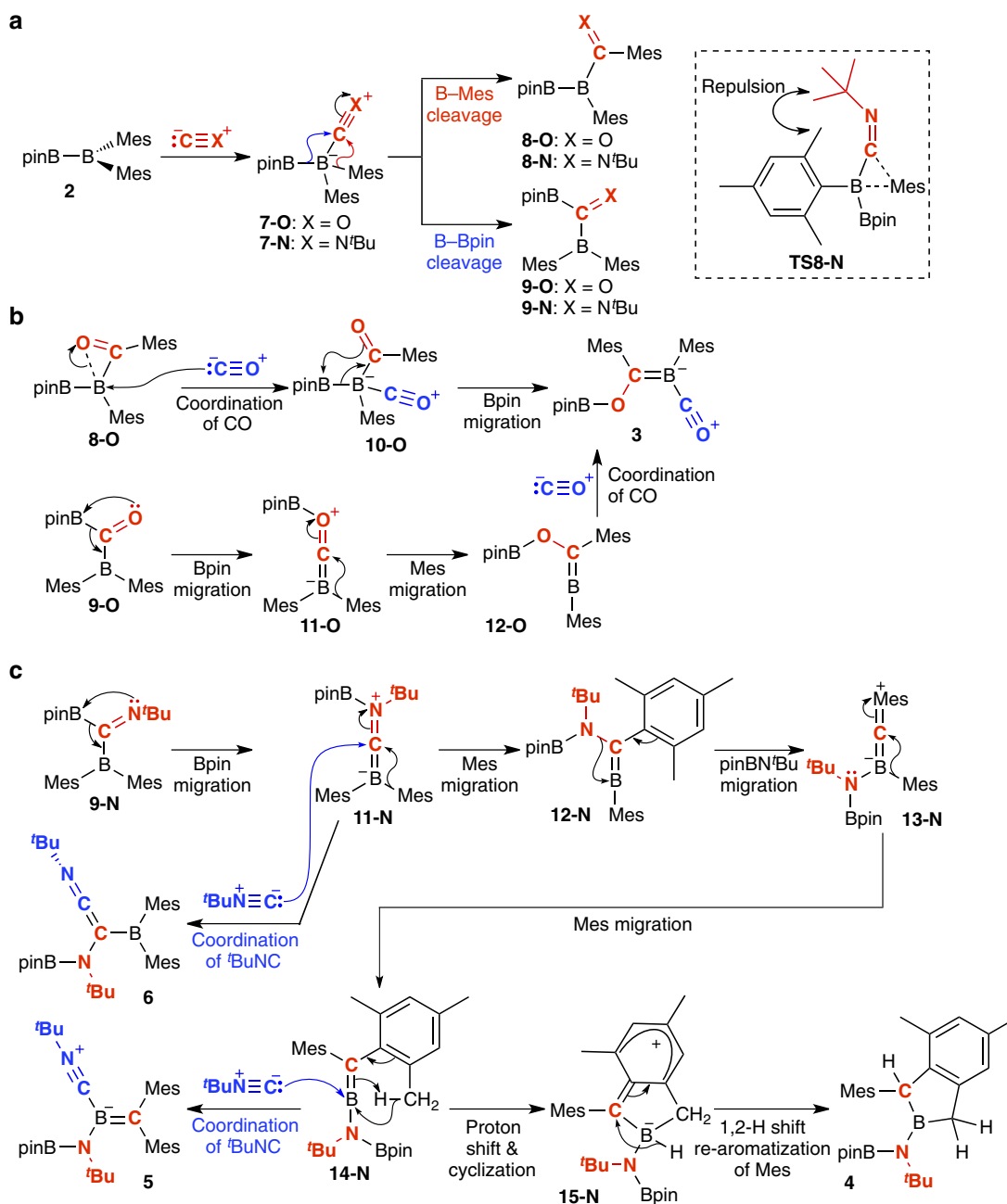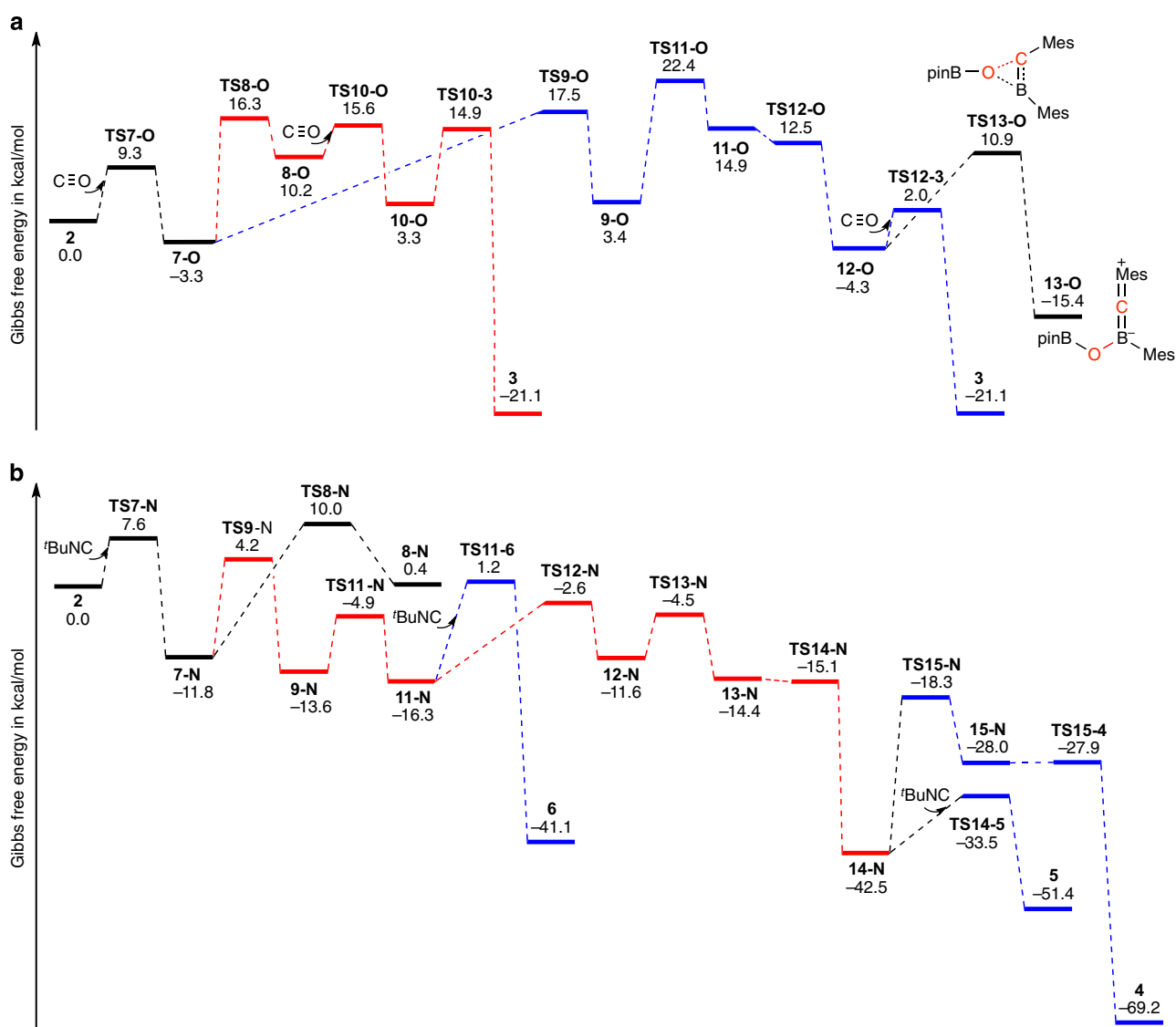

Figure 3 | Possible reaction mechanism for the formation of 3–6 from 2 estimated by DFT calculations. (**a**) Two types of possible products **8** and **9** formed by B–Mes or B–Bpin cleavage after the coordination of CO or ^{t}BuNC. (**b**) Two energetically comparable pathways to **3** from **8-O** and **9-O**. (**c**) Three pathways to **4**-**6** from **9-N**.

two ipso carbons of the two Mes groups bonded to the sp^3 methine ^{13}C are from ^{t}BuN^{13}C. In the case of **5**-^{13}C$_2$, two broad signals appeared at δ_C 132.7 and 137.1 p.p.m. on labelling (Fig. 2g), supporting the C–B=C skeleton of **5**. Two split 4° aromatic signals with $^1J_{CC}$ of 24 Hz in **5**-^{13}C$_2$ also showed that the two Mes groups bonds to a carbon atom (Fig. 2f). The ^{13}C NMR spectrum of **6**-^{13}C$_2$ showed two strengthened signals at δ_C 89.1 and 168.0 p.p.m. (Fig. 2h,i) with a satellite ($^1J_{CC}$ = 86 Hz), supporting the C(sp^2)–C(sp) coupling (107 Hz in diphenylketene-^{13}C$_2$)[65]. One can confirm that the carbon atom with the δ_C 89.1 p.p.m. signal is bonded to a quadrupolar boron atom in the structure of **6**, according to the broadening observed.

Proposed mechanism based on DFT calculation. The whole mechanisms for the formation of **3**–**6** from **2** were estimated by DFT calculations[66–69] with full geometry optimization of all the

available transition states (TSs) at the B3LYP/6-31G(d,p) level and single-point energy calculation at M06-2X/6-311+G(d,p) with solvent effect of benzene using conductor-like polarizable continuum model (Fig. 3: mechanism with curly arrows, Fig. 4: energy profiles with relative Gibbs free energies and Supplementary Table 6 for coordinates of all the structures). An initial coordination of CO or ^{t}BuNC to **2** gave the sp^2–sp^3 diborane(4) **7-O** and **7-N**, which would undergo two types of bond cleavage reactions (Fig. 3a): (1) B–Mes bond cleavage to give acyldiborane(4) **8-O** or imidoyldiborane(4) **8-N**, (2) B–Bpin bond cleavage to give diborylketone **9-O** or diborylimine **9-N**. In the reaction of **2** with CO, energy levels of **TS8-O** and **TS9-O** are comparable to each other and both TSs are higher than the **TS7-O** (Fig. 4a). The slightly lower **TS8-O** could be explained by the higher nucleophilicity of a Mes substituent than a Bpin substituent due to the electronegativity difference between carbon and boron atoms, as supported by natural bond orbital

Figure 4 | Energy profiles of possible mechanism. Energy profiles of possible mechanism for the formation of **3**–**6** from **2** with relative Gibbs free energies in kcal mol^{-1} (estimated by optimization at the B3LYP/6-31G(d,p) level and subsequent single-point energy calculation at M06-2X/6-311+G(d,p) level with consideration of entropy contribution and solvent effect of benzene (conductor-like polarizable continuum model (CPCM)), all the compound numbers are in conjunction with Fig. 3). (**a**) Two possible pathways for the formation of **3** by reaction of **2** with CO (red: pathway through **8-O**, blue: pathway through **9-O**) (**b**) pathway for the formation of **4**–**6** by reaction of **2** with ^{t}BuNC (red: main pathway to **4**–**6**, blue: branching to each of the compounds **4**–**6**). (Remark: before the solvation correction, **TS12-O** is slightly higher than **11-O** and **TS14-N** is slightly higher than **13-N** in energy.)

analysis (Supplementary Fig. 20). The subsequent reactions from **8-O** and **9-O** afforded the same product **3** (Fig. 3b). The former pathway through **8-O** included a coordination of a second CO molecule to give **10-O** and subsequent migration of the Bpin moiety by a nucleophilic attack of the acyl oxygen atom in **10-O** with B–B bond cleavage to give **3**. The large energy gain in this step may be attributed to the formation of B–O bond. The latter pathway through **9-O** was initiated by a Bpin migration to form the borataalkene **11-O**. **TS11-O** was the global TS, which lies 6.1 kcal mol^{-1} higher than **TS8-O**. Subsequently, one of the two Mes groups in **11-O** migrated to the carbon atom to afford the boraalkene **12-O**. Coordination of a second CO molecule to **12-O** could form the same product **3**. This step could be considered as a coordination of CO to electron-deficient boraalkene for a large energy gain. Formation of a possible C–O cleaved product **13-O** would be suppressed due to the higher **TS13-O** (Fig. 4a).

In the reaction of **2** with ^{t}BuNC, **TS8-N** was 5.8 kcal mol^{-1} higher than **TS9-N**, indicating that the pathway through **9-N** would be favourable (Fig. 4a). The high energy level of **TS8-N** may be explained by a steric repulsion between the spectator Mes group and the ^{t}Bu group (Fig. 3a and Supplementary Table 7). The intermediate **9-N** would undergo Bpin migration to give **11-N** followed by a Mes group migration to form the boraalkene **12-N** (Fig. 3c). Coordination of ^{t}BuNC to the central carbon atom in **11-N** could lead to formation of **6**, but the TS to **6** was calculated to be slightly higher (by 3.8 kcal mol^{-1}) than the TS to **12-N**. Requirement of higher concentration to prepare **6** was consistent with this result. Again, the simple coordination of ^{t}BuNC to boraalkene would give a large energy gain. As a nitrogen atom in **12-N** may have higher nucleophilicity than the oxygen atom in **12-O**, a migration of the amino substituent ($-$N^{t}BuBpin) to the Mes-bonded boron atom would take place with an assistance of electron donation from the carbon-bonded Mes group to form the amino-substituted borataalkene **13-N**. This step (from **12-N** to **13-N**) involves a cleavage of the C–N bond originated from the C≡N triple bond in ^{t}BuNC. Electron donation from the nitrogen atom to the boron atom in **13-N** induced the second Mes migration to the carbon atom to give the aminoboraalkene **14-N**. The neutralization of the positively charged Mes group may contribute a large energy gain. A simple coordination of a second ^{t}BuNC molecule to **14-N** affords the product **5**. This result is consistent with the experimental observation that when ^{t}BuNC is in excess the product **5** was obtained. In the absence of excess ^{t}BuNC, the boron centre of **14-N** would attack to one of the benzylic protons to give the cyclic hydroborate **15-N** having delocalized cationic charge on the cyclized Mes ring, as a boryl anion could undergo the same deprotonation cyclization[70]. The energy barrier of 24.2 kcal mol^{-1} from **14-N** to **TS15-N** is accessible at the room temperature (the reaction condition). Subsequent 1,2-hydride shift from **15-N** and re-aromatization would form the product **4**. The formation of B–N π-bond in the last step would contribute a large energy gain.

Discussion

Thus, the detailed spectroscopic and structural analysis of the obtained products and the DFT calculations revealed the complexity of the consecutive rearrangement reactions of **2**. The reason why the newly synthesized diborane(4) **2** showed a remarkable reactivity towards CO and ^{t}BuNC in comparison with the conventional boron-containing compounds may be attributed to the existence of two reactive B–C bonds and one reactive B–B bond. Throughout the reactions, the boron atoms in the intermediates undergo repetitive interconversion between sp^2 and sp^3 states to induce the subsequent reactions. In the case of ^{t}BuNC, the intermediate **12-N**, which is derived after the two

π-bonds of the isonitrile moiety have been cleaved, contains a single C–N σ-bond and has a highly nucleophilic nitrogen atom. The highly nucleophilic nitrogen atom facilitates further cleavage of the remaining σ-bond through migrating to the adjacent unsaturated boron centre. Coexistence of the reactive B–B and B–C bonds, steric crowdedness in **2** and the high nucleophilicity of N in **12-N** containing a single C–N σ-bond cooperatively achieved the complete cleavage of the C≡N triple bond. In conclusion, we demonstrated the first example of C≡N triple bond cleavage by using newly synthesized diborane(4) **2** in the absence of TM reagents and catalysts. The present results may inspire new idea to achieve multiple bond cleavage reactions using main group element compounds.

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Author contributions

M.Y. and Z.L. designed the study. H.A. conducted all the experiments and part of DFT calculations. H.A. and M.Y. analysed crystal structures. K.H.L. and Z.L. performed mechanistic study. Z.L. and M.Y. wrote the manuscript.

Additional information

Accession codes. The X-ray crystal structure information is available at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-985350 (**1**), CCDC-981112 (**2**), CCDC-981113 (**3**), CCDC-981114 (**4**), CCDC-981115 (**5**) and CCDC-985351 (**6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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