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Communication

Activation of C−C Bonds via σ-Bond Metathesis: Hydroborenium-Catalyzed Hydrogenolysis of Cyclopropanes

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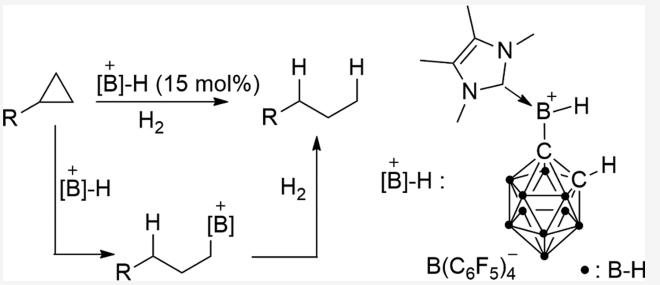
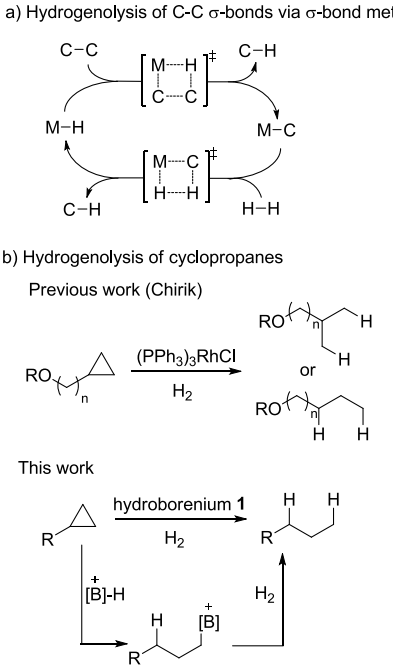
ABSTRACT: High-valent transition metal or main group complex mediated σ-bond metathesis plays an important role in the activation of covalent H−E bonds. However, its involvement in the activation of C−C bonds has remained elusive. Here we describe direct hydroboration of the C−C bonds of cyclopropanes by a hydroborenium complex. Our mechanism study suggests this reaction operates through a σ-bond metathesis pathway. With this hydroborenium complex as a catalyst, hydrogenolysis of unfunctionalized cyclopropanes was achieved, which is unprecedented for homogeneous catalysts and provides an unconventional approach for C−C bond functionalization in the absence of metals.



In recent decades, catalytic functionalization of carbon−carbon σ bonds has witnessed substantial advancements, which provide a variety of strategies to replace the carbon−carbon bonds with carbon−heteroatom[1−6] or carbon−hydrogen bonds.[7] The latter, directly related to the highly important hydrocracking process in the petroleum industry, can be achieved through catalytic hydrogenolysis with catalysts based on late transition metals, such as Rh,[8] Pd,[9] Ru,[10] etc. In these hydrogenolysis systems, the key step is believed to be the insertion of the transition-metal centers into C−C σ bonds via oxidative addition. Another potential approach for catalytic hydrogenolysis of C−C σ bonds, which requires no change in oxidation state of the catalysts, involves the activation of C−C bonds via σ-bond metathesis followed by hydrogenolysis of the newly formed metal−carbon bonds (Scheme 1a). Such a process would extend the hydrogenolysis catalysts to high-valent transition metal or main group complexes, therefore circumventing the use of expensive precious metals. However, despite the fact that σ-bond metathesis is well established in E−H (E = H, B, C, Si, etc.) bond activation,[11] to the best of our knowledge, activation of C−C bonds via σ-bond metathesis has remained unknown to date.

Cyclopropane derivatives are among the most studied substrates for C−C bond activation, as the ring strain relief allows their C−C bonds to be activated under relatively mild conditions.[5] While heterogeneous catalysts based on PtO_2 or Rh nanoparticles can efficiently catalyze the hydrogenolysis of cyclopropanes,[12] there is only one example of a homogeneous catalyst for such a reaction. In 2003, Chirik et al. discovered that the Wilkinson catalyst $(PPh_3)_3RhCl$ is capable of catalyzing the hydrogenolysis of a series of cyclopropanes containing oxygen functionalities, such as alcohol, ether, carbonyl, and phosphinite (Scheme 1b).[8c] The oxygen moiety

Scheme 1. (a) Working Hypothesis for the Hydrogenolysis of C−C Bonds via σ-Bond Metathesis and (b) Advances in the Hydrogenolysis of Cyclopropanes



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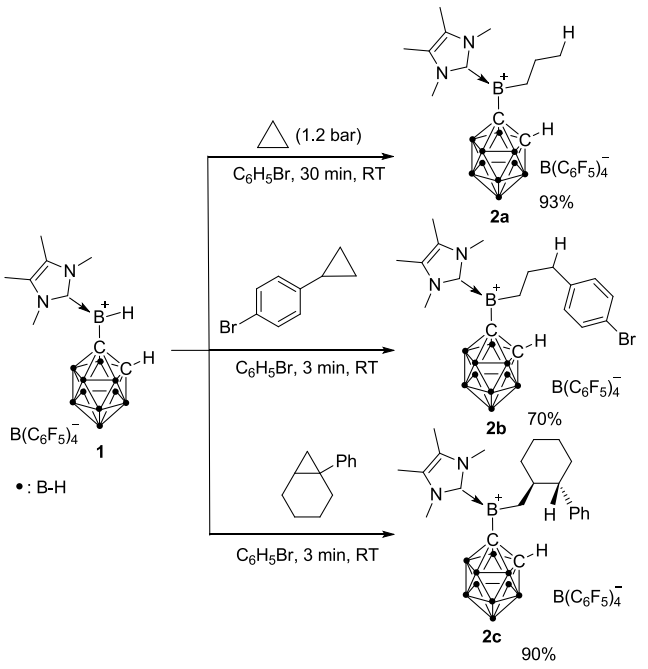
appears to be crucial for this hydrogenolysis reaction, as alkyl-substituted cyclopropanes without an oxygen moiety undergo isomerization to afford a mixture of olefins instead. A Rh(III) metallacycle complex formed via oxidative addition was proposed to be the intermediate. To complement this redox-based approach, we set out to examine the σ-bond metathesis strategy with a hydroborane species as a catalyst to realize the hydrogenolysis of unfunctionalized cyclopropanes without the involvement of transition metals. As hydrogenolysis of B−C bonds via σ-bond metathesis has been reported by our group[13] and others,[14] achieving catalytic hydrogenolysis of cyclopropanes would require a hydroborane species which can activate the C−C bonds of cyclopropanes. While there are a few examples of organoboranes activating cyclopropanes in the presence of Lewis bases, reported by Stephan[15] and others,[16−18] direct hydroboration of cyclopropanes is limited to one report by Rickborn et al. in 1971, who described that diborane B_2H_6 can react with cyclopropanes to afford alkylboranes at 100 °C.[19,20] Since the reaction temperature was above the decomposition temperature of diborane, the identity of the active species was unknown and a concerted B−H addition to the C−C bond of cyclopropanes was ruled out, as the reaction between diborane and 1-methylnorcarane yields a mixture of trans and cis products. Due to the difficulties in handling flammable and toxic diborane gas, a nonvolatile hydroborane reagent with a well-defined structure would be preferred as the cyclopropane hydrogenolysis catalyst. We recently reported the synthesis of an N-heterocyclic carbene stabilized hydroborenium complex with *o*-carboranyl[21] as a substituent ($[IMe_4B(H)Cb][B(_6F_5)_4]$ (**1**), IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene, Cb = *o*-carboran-1-yl), which can form a stable η^2(Si−H)-σ complex in the presence of $HSiEt_3$.[22] We decided to explore if **1** could activate cyclopropanes via σ-bond metathesis to yield an alkylborenium complex. Herein, we describe the reactivity of **1** with cyclopropanes as well as its application in the catalytic hydrogenolysis of unfunctionalized cyclopropanes.

When a solution of **1** in C_6D_5Br was treated with cyclopropane gas (1.2 bar) at room temperature, clean formation of the new species **2a** was observed after 30 min (Scheme 2). When this reaction was carried out on a preparative scale, complex **2a** was isolated in 93% yield after purification. In the ^{1}H NMR of **2a**, two triplet signals and one multiplet signal at 1.85, 0.94, and 1.34 ppm with an integration ratio of 2:3:2 were observed, which agrees with the presence of a *n*-propyl group. The ^{11}B NMR of **2a** shows a broad singlet at 79.9 ppm, indicating that the boron center remains tricoordinated. The identity of **2a** was further confirmed by single-crystal X-ray analysis (Figure S38). For comparison, we also treated Piers' borane $HB(C_6F_5)_2$[23] with cyclopropane gas (1.2 bar) and no reaction was observed even after 3 h at 100 °C. To examine the regioselectivity of this hydroboration reaction, we reacted **1** with 1 equiv of 1-bromo-4-cyclopropylbenzene in C_6H_5Br. This reaction was complete within 3 min, affording complex **2b** as the sole hydroboration product in 70% isolation yield. Complex **2b** was fully characterized by multinuclear NMR analysis as well as single-crystal X-ray analysis, revealing that the borenium center was added to the least steric CH_2 moiety and the hydrogen atom was selectively added to the carbon atom with the phenyl substituent (Figure 1a). Similar regioselectivity was also observed when Rickborn et al. treated substituted cyclopropanes with diborane.[19] To understand the stereoselectivity of this hydroboration reaction,

Scheme 2. Reactivity of 1 with Cyclopropanes



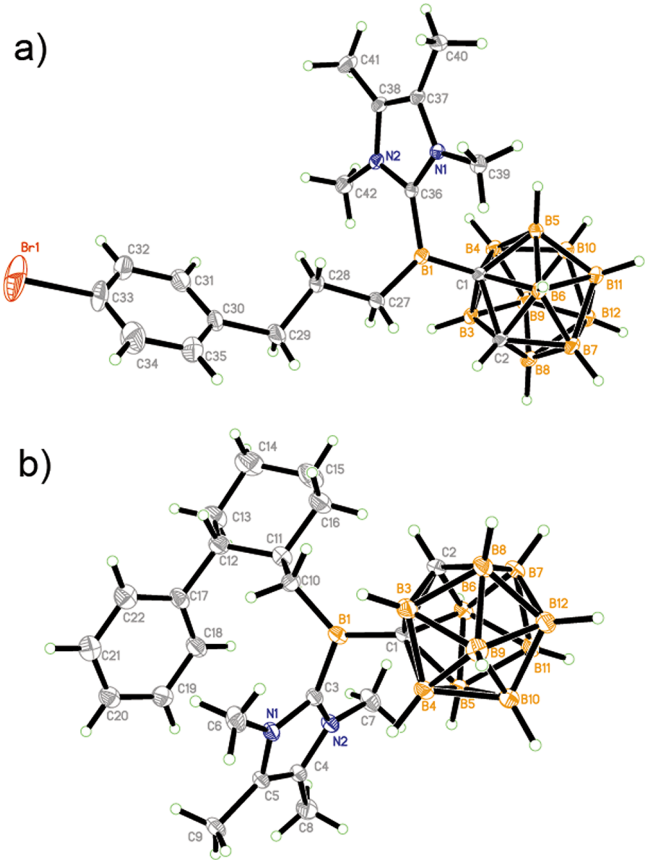


Figure 1. (a) Molecular structure of complex **2b**. (b) Molecular structure of complex **2c**. The counteranion $B(C_6F_5)_4^-$ is omitted for clarity.

we treated **1** with 1-phenylbicyclo[4.1.0]heptane in C_6H_5Br and discovered that only cis-addition product **2c** was observed, which can be isolated in 90% yield. The structure of **2c** was elucidated with single-crystal X-ray analysis (Figure 1b). Such

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stereospecific addition is in contrast to the reaction between cyclopropanes and diborane[19] but resembles the well-studied hydroboration of alkenes and alkynes.[24]

Intrigued by the concerted activation of C−C bonds with the hydroborenium complex **1**, we investigated the mechanism of hydroboration of cyclopropane with **1** by density functional theory (DFT (M06-2X)) calculations.[25,26] Our studies suggest that the thermodynamic driving force for this reaction is substantial with ΔG° = −27.7 kcal mol^{-1} at 298 K. The hydroboration takes place via a four-centered transition state without prior coordination of cyclopropane with **1**. The calculated free energy barrier is 27.4 kcal mol^{-1}, consistent with our observation that this reaction takes place under ambient conditions. In the transition state (**TS**; Figure 2),

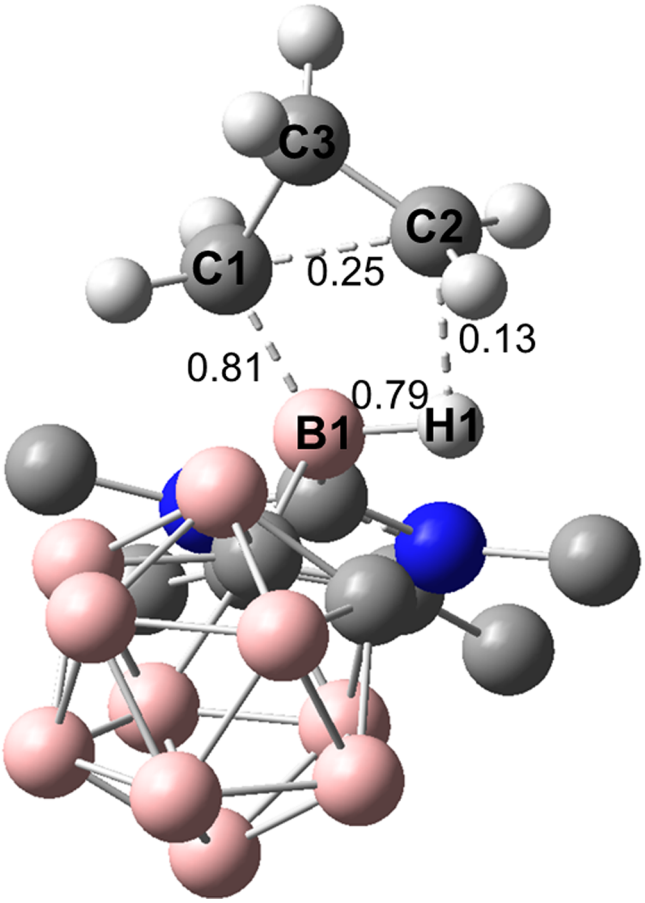

Figure 2. Geometry of **TS** with WBI values. Hydrogen atoms except H1 and those in cyclopropane are omitted for clarity.

while the B1 and H1 atoms remain closely bonded with a distance of 1.21 Å, the C1−C2 bond is substantially elongated from 1.51 Å in cyclopropane to 2.06 Å. Meanwhile, the C1 atom is bonded to the B1 atom with a distance of 1.67 Å, and a weak bonding interaction between C2 and H1 (1.828 Å) is also observed. Accordingly, the Wiberg bond indices (WBI) revealed fractional C1−C2 (0.25), B1−H1 (0.79), B1−C1 (0.81), and C2−H1 (0.13) interactions. Although the geometry of **TS** resembles a typical four-membered σ-bond metathesis transition state, the lack of interaction between B1 and C2 atoms (2.46 Å, WBI = 0.01) is in sharp contrast to σ-bond metathesis transition states of H−E bond activation, which have a strong interaction between the central element and the element at the β position.[27] It is likely that the release of ring strain in **TS** (the C1−C3−C2 angle increases from 60° in cyclopropane to 86° in **TS**) substantially stabilizes the transition state and does not require an additional interaction between B1 and C2, thus avoiding a six-coordinated carbon center in the transition state. Natural bond orbital (NBO) analysis of **TS** shows that 0.67 e$^-$ charge transfers from the σ-bonding orbital of C1−C2 to the empty p orbital of B1 and 0.29 e$^-$ charge transfers from the occupied σ-bonding orbital of B1−H1 to the σ^*-antibonding orbital of C1−C2 (Figure S39). This result indicates that the electrophilicity of the borenium center plays a paramount role in this hydroboration reaction, consistent with our observation that the weaker Lewis acid $HB(C_6F_5)_2$ does not react with cyclopropane. It is noteworthy that similar unequal electron charge transfers were also observed in the transition state of the reaction between alkylborane and H_2 via σ-bond metathesis.[13b] Further NBO analysis revealed that in **TS** the $(C1)H_2$ and $(C3)H_2$ fragments are almost neutral with charges of −0.08 and +0.05 e, respectively. On the other hand, the $(C2)H_2$ fragment bears a considerable positive charge of +0.51 e. This is likely the cause of the observed regioselectivity of this hydroboration, as substituents on the C2 atom can help to delocalize the positive charge, thus lowering the energy of the transition state and rendering the transfer of hydrogen to the most substituted carbon favorable. Analogous arguments were also applied in the explanation of anti-Markovnikov hydroboration of alkenes.[28] Indeed, the formation of $[IMe_4BCH(BrC_6H_4)(Me)]^+$, the isomer of **2b**, from **1** and 1-bromo-4-cyclopropylbenzene needs to overcome a free energy barrier of 37.0 kcal mol^{-1}. On the other hand, the free energy barrier for the formation of **2b** is found to be only 18.7 kcal mol^{-1} (Figure S40). Interestingly, after this transition state, we identified an intermediate, which is 15.7 kcal mol^{-1} above free **1** and 1-bromo-4-cyclopropylbenzene. Given that the free energy barrier from this intermediate to **2b** is only 2.1 kcal mol^{-1}, the existence of this intermediate is likely experimentally irrelevant.

After the establishment of direct hydroboration of cyclopropanes with **1**, we set out to examine the reactivity of the resulting alkylboreniums against H_2. **2b** was chosen as the substrate. While **2b** shows no reactivity at room temperature against H_2 (4 bar) in C_6D_5Br, under harsher conditions (80 °C, 80 bar of H_2) **2b** can be quantitatively converted to 1-bromo-4-*n*-propylbenzene after 12 h. However, the formed **1** appeared to be unstable under such conditions and decomposed to several unidentified species. A controlled experiment carried out with **1** afforded the same decomposition products after heating its C_6D_5Br solution to 80 °C for 12 h. Although the decomposition of **1** at elevated temperature seems to suggest the unsuitability of **1** as a hydrogenolysis catalyst, we found that alkylborenium **2b** is very stable in C_6D_5Br and shows no decomposition after 12 h at 80 °C. Therefore, the **1** formed upon hydrogenolysis of alkylboreniums can immediately react with cyclopropanes to regenerate the more stable alkylboreniums, which will be the resting state of the catalyst. Indeed, with 15 mol % of **1** as the catalyst, 1-bromo-4-cyclopropylbenzene can be converted to 1-bromo-4-*n*-propylbenzene in 82% NMR yield with C_6D_5Br as solvent at 80 °C under 80 bar of H_2. Since the rather high boiling point of bromobenzene rendered the isolation of pure 1-bromo-4-*n*-propylbenzene difficult, we switched the solvent to the more volatile benzene for preparative-scale reactions and

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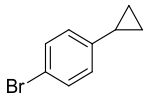
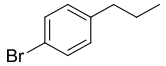
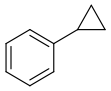
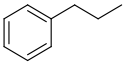
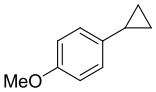
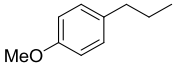
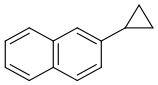
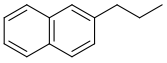
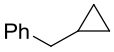
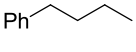
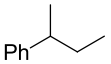
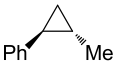
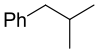
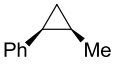
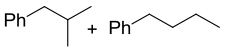
1-bromo-4-*n*-propylbenzene can be obtained in 76% isolated yield on a preparative scale (1.0 mmol). Replacing **1** with **2b** as the catalyst resulted in 90% NMR yield, confirming alkylborenium **2b** to be an on-cycle intermediate. A variety of substituted cyclopropanes can be effectively hydrogenated with **1** as catalyst with one hydrogen atom added to the least steric CH_2 moiety and the other to the most substituted carbon (Table 1). Interestingly, in the case of *cis*-1-methyl-2-

Table 1. Hydrogenolysis of Cyclopropanes Catalyzed by 1[a]

Entry	Substrate	Product	Yield[b]
1			76%
2			88%
3			69%
4			50%
5			76%
6			72%
7			70%[c]
8		 (13:1)	73%[c]
9			53%[d]

[a]Conditions unless specified otherwise: cyclopropane (1.0 mmol) and **1** (0.15 mmol) in 0.8 mL of benzene, H_2 (80 bar), 80 °C. [b]Isolated yield. [c]1,2-Difluorobenzene was used as the solvent. [d]A mixture of benzene and 1,2-difluorobenzene (1/1) was used as the solvent.

phenylcyclopropane (entry 8), a minor product, *n*-butylbenzene, resulting from addition of both hydrogen atoms to the substituted carbons was also observed. It is noteworthy that the stereoselective hydrogenolysis of norcarane derivatives (entry 9) is unprecedented.[8c,12]

In conclusion, direct hydroboration of cyclopropanes with hydroborenium complex **1** was observed. Such unprecedented reactivity led to the development of the first metal-free catalytic hydrogenolysis of unfunctionalized cyclopropanes, constituting a complementary approach to existing hydrogenolysis methods that require transition metal complexes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00099.

Experimental methods, NMR spectra, and computational details (PDF)

Cartesian coordinates for the optimized geometries (XYZ)

Accession Codes

CCDC 1960563−1960565 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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