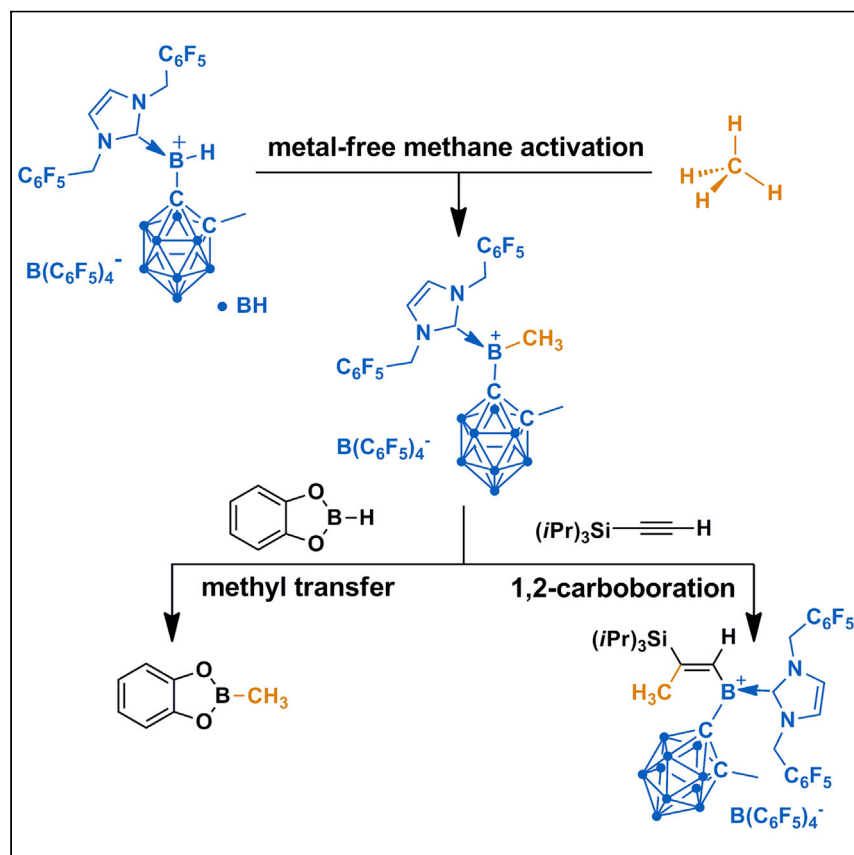


Article

Methane activation by a borenium complex



Methane, the most abundant hydrocarbon in the world, is also the hardest to transform, due to its particularly strong C–H bonds. Breaking these bonds generally requires the involvement of reactive transition metal complexes. This work describes a route to functionalize methane in the absence of metals by employing a cationic boron species. This result could potentially lead to the development of more sustainable and less environmentally impactful catalyst systems for methane conversion.

Yizhen Liu, Weishi Dong, Zhen Hua Li, Huadong Wang

huadongwang@fudan.edu.cn

Highlights

Isolable-borenium-mediated methane activation under relatively mild conditions

Involvement of σ -bond metathesis in methane activation supported by mechanism studies

A synthetic cycle for methylcatecholborane synthesis using methane and catecholborane



Article

Methane activation by a borenium complex

Yizhen Liu,¹ Weishi Dong,¹ Zhen Hua Li,¹ and Huadong Wang^{1,2,*}

SUMMARY

The selective functionalization of methane under ambient conditions remains a formidable challenge for chemists. While most studies have focused on transition metal complexes, much less attention has been devoted to molecular complexes based on non-metal elements, despite them being more sustainable and less environmentally impactful. Here, we report that an N-heterocyclic carbene-stabilized borenium complex can activate methane under relatively mild conditions. The resulting methylborenium complex can readily transfer the methyl group to catecholborane (HBcat), which can lead to a synthetic cycle for the conversion of methane to MeBcat. Both experimental and theoretical mechanistic studies suggest that the C–H bonds of methane are activated via a σ -bond metathesis pathway. Such direct aliphatic C–H borylation can be extended to other alkanes, such as ethane and octane. The formed alkylborenium complexes can react with terminal alkynes via 1,2-alkylboration to install both the alkyl and boryl functionalities onto organic scaffolds.

INTRODUCTION

As the main component of natural gas, methane is the most abundant hydrocarbon in the world. While most globally produced methane (>90%) are used as an energy source, the use of methane as a raw material for chemical production constitutes only about 5% of methane consumption.¹ Current industrial methane conversion process relies on an indirect route, which initially converts methane into syngas, the mixture of CO and H₂, under high temperature and high pressure and subsequently turns syngas into methanol and other hydrocarbons. Besides being energy intensive, this indirect route is only economically feasible at a very large scale, excluding much desired local, on-site applications. Compared with the indirect route, direct functionalization of methane could be more advantageous from both economic and environmental points of view.^{2,3} Of particular interest is the development of well-defined complexes capable of activating methane in homogeneous solutions, which enable facile steric and electronic modification and are amenable to experimental mechanism investigation.⁴ In order to overcome the low reactivity of methane, molecular methane activation systems generally require the involvement of reactive transition metal complexes. Recently, a groundbreaking report by Periana and co-workers showed that main group complexes could outperform transition metal complexes in methane activation.^{5–8} They demonstrated that high-valent d⁰ main group salts Ti(O₂CCF₃)₃ and Pb(O₂CCF₃)₄ can activate methane in the solution of CF₃COOH at 180°C via electrophilic C–H activation, affording Ti(O₂CCF₃) or Pb(O₂CCF₃)₂ and CF₃COOMe after reductive functionalization. While highly efficient and selective, this method has a number of limitations, such as the usage of highly toxic metal complexes as well as harsh and corrosive conditions. The lack of straightforward ways to oxidize Ti(O₂CCF₃) or Pb(O₂CCF₃)₂ to their high-valent

The bigger picture

Methane is the most abundant hydrocarbon in the world. The direct transformation of methane into value-added chemicals under ambient conditions is a highly attractive but challenging endeavor. While most studies have focused on reactive transition metal complexes, much less attention has been devoted to non-metal molecular complexes, despite them being more sustainable and less environmentally impactful. In this work, we show that a highly electrophilic borenium complex can activate methane under relatively mild conditions. The resulting methylborenium complex can readily transfer the methyl group to catecholborane (HBcat), which can lead to a synthetic cycle for the conversion of methane to MeBcat. Furthermore, such direct aliphatic C–H borylation can be extended to other alkanes, such as ethane and octane.

counterparts could also hinder efforts to turn this stoichiometric reaction into a catalytic one.

Besides electrophilic C–H activation, σ -bond metathesis represents another attractive pathway for the activation of the C–H bonds of methane.^{9,10} This reactivity is primarily associated with rare earth complexes. Since the landmark discovery by Watson in 1983,^{11,12} a number of rare earth metallocene complexes with a general formula of Cp*₂MR (M = Sc, Y, Lu; R = alkyl or silyl) are known to react with methane in a degenerate or non-degenerate way via σ -bond metathesis.^{11–16} However, the Cp* ligand appears indispensable for such reactivity, thus significantly limiting the room for further optimization of their electronic and structural properties. While similar reactivity with methane has been extended to coordinatively unsaturated Ir(III) complexes,^{17,18} well-defined main group complexes capable of activating methane via σ -bond metathesis still remain elusive.¹⁹ Recently our group^{20,21} and others^{22–25} have reported that organoboranes or borenium complexes²⁶ are capable of activating H₂ via σ -bond metathesis. Particularly, we have shown that an N-heterocyclic carbene (NHC) stabilized *o*-carboranyl-substituted hydroborenium complex [IMe₄B(H)Cb][B(C₆F₅)₄] (IMe₄ = 1,3,4,5-tetramethylimidazol-2-ylidene, Cb = *o*-carboran-1-yl, **1**) can activate the C–C bonds of cyclopropanes via σ -bond metathesis.²⁷ As the easily modified NHC ligand²⁸ and *o*-carboranyl substituent²⁹ of the borenium complex enable judicious tuning of its electronic and steric properties, we questioned if such borenium complex could be applied in the activation of C–H bonds of methane. The resulting borylation will extend the scope of catalyst-free aliphatic C–H borylation reactions, which so far are limited to intramolecular processes,^{30–35} and provide an alternative to the recently reported noble-metal catalyzed methane borylation reactions.^{36,37} Herein we describe the borylation of methane and other alkanes with a borenium complex under relatively mild conditions. Our experimental and theoretical mechanistic studies suggest that the C–H bond of methane is activated via a σ -bond metathesis pathway.

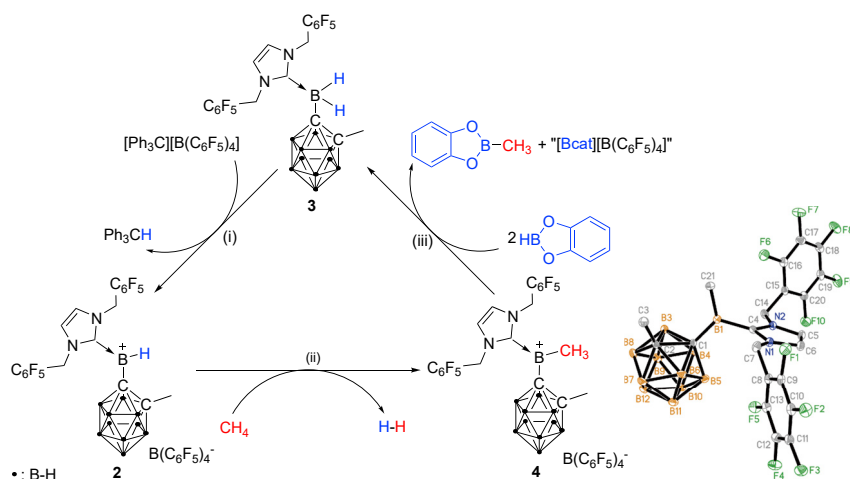
RESULTS AND DISCUSSION

We started our investigation by examining the reactivity of the known borenium **1** with methane. Heating the solution of **1** in C₆D₅Br or *o*-C₆H₄F₂ under 60 bar of CH₄ to 100°C for 10 h only resulted in complete decomposition of **1**. Reasoning that the low thermal stability of **1** could be due to the lack of kinetic protection around the borenium center, we replaced the *o*-carboran-1-yl substituent with bulkier 2-methyl-*o*-carboran-1-yl (Cb^{Me}) group. Additionally, 1,3-bis(2,3,4,5,6-pentafluorobenzyl)imidazol-2-ylidene (IBn^F)³⁸ was employed as the NHC ligand. Besides being bulkier compared with IMe₄, IBn^F is a relatively electron-poor ligand, which will likely increase the electrophilicity of the borenium center, thus promoting its activity in σ -bond metathesis.^{21,27} The target [IBn^FB(H)Cb^{Me}][B(C₆F₅)₄] (**2**) was prepared by treating IBn^FB(H)₂Cb^{Me} (**3**) with [Ph₃C][B(C₆F₅)₄] in the solution of *o*-C₆H₄F₂/hexane with a yield of 78% (Scheme 1). Borenium **2** was characterized by multinuclear NMR analysis and HR-MS. In the ¹H NMR spectrum of **2**, a broad singlet corresponding to the hydrogen substituent on the borenium center was observed at 4.38 ppm. The ¹¹B NMR spectrum of **2** consists of a broad singlet at 66.2 ppm, which is assigned to the tri-coordinated borenium center. This signal is substantially downfield shifted relative to the corresponding resonance in **1** (54.2 ppm),³⁹ indicating increased positive charge on the borenium center of **2** compared with **1**. The identity of **2** was further confirmed using derivatization. Treatment of **2** with 1 equiv of pyridine gave pyridine coordinated boronium complex **2-py**, which was characterized by X-ray diffraction (Figure S69). Borenium **2** shows higher thermal stability compared

¹Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Songhu Road 2005, Shanghai 200438, China

²Lead contact

*Correspondence: huadongwang@fudan.edu.cn
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Scheme 1. Synthetic cycle for the conversion of methane into MeBcat initiated by borenium 2 and the molecular structure of methylborenium 4 (for clarity, the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion and hydrogen atoms were removed)

- (i) $o\text{-C}_6\text{H}_4\text{F}_2/\text{hexane}$, 25°C , 78% yield.
 (ii) CH_4 (60 bar), $o\text{-C}_6\text{H}_4\text{F}_2$, 110°C , 61% yield.
 (iii) $\text{C}_6\text{D}_5\text{Br}$, 110°C , >95% NMR yield.

with 1. Upon 10 h of heating in a $o\text{-C}_6\text{H}_4\text{F}_2$ solution at 100°C , about 60% of 2 was found decomposed, in contrast to complete decomposition of 1 under identical conditions.

With the new borenium in hand, we set out to examine the reactivity of 2 with methane. Heating the solution of 2 in $o\text{-C}_6\text{H}_4\text{F}_2$ under 60 bar of CH_4 to 100°C resulted in the formation of the C–H borylation product $[\text{IBn}^{\text{F}}\text{B}(\text{Me})\text{Cb}^{\text{Me}}][\text{B}(\text{C}_6\text{F}_5)_4]$ (4), which can be isolated in 29% yield after recrystallization. Increasing the reaction temperature to 110°C resulted in a higher isolation yield of 61% (Scheme 1). Replacing isolated 2 with *in situ* generated 2 (from equimolar of 3 and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$) provided a lower isolation yield (28%). Further increase of the reaction temperature to 130°C has little impact on the isolation yield (60%). Decreasing the pressure of methane to 30 bar led to a diminished isolation yield (29%). Analysis of the overhead gas by GC revealed the presence of H_2 gas. The $o\text{-C}_6\text{H}_4\text{F}_2$ solvent appears critical for the activation of methane, as employing $\text{C}_6\text{H}_5\text{Br}$ or $o\text{-C}_6\text{H}_4\text{Cl}_2$ as solvent led to the formation of a trace amount of 4 (NMR yield < 10%). The molecular structure of borenium 4 was determined using a combination of multinuclear NMR analysis, HR-MS, and single-crystal X-ray analysis. In the ^1H NMR spectrum of 4, a singlet at 1.99 ppm was observed, which was assigned to the methyl substituent on the borenium center. The $^1\text{H}\text{-}^{13}\text{C}$ HSQC spectrum revealed this signal is correlated to a broad singlet at 20.5 ppm of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, which is close to those observed in other methylboranes, such as $\text{MeBAR}^{\text{F}}_2$ ($\text{Ar}^{\text{F}} = 2,4,6\text{-tris(trifluoromethyl)phenyl}$), 19.9 ppm).⁴⁰ The ^{11}B NMR spectrum of 4 reveals a broad signal at 82.7 ppm, in agreement with the existence of a tri-coordinated borenium center. In the solid structure of 4, the borenium center remains tri-coordinated as evidenced by the sum of $\angle\text{C-B-C}$ angles of the borenium center of 360.0° . The corresponding B–C bond lengths are in the range of 1.534(3)–1.609(3) Å, typical for B–C single bonds.⁴¹ When ^{13}C enriched methane was applied in the borylation reaction, as anticipated, the ^1H NMR of the resulting 4- ^{13}C exhibited a doublet ($^1J_{\text{C-H}} = 120.5$ Hz) at 1.99 ppm, assigned to the boron linked $^{13}\text{CH}_3$ moiety. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4- ^{13}C , a broad singlet at 20.5 ppm with enhanced intensity was observed, and this

signal appears as a quartet with $^1J_{C-H}$ of 120.5 Hz in the ^{13}C NMR spectrum. The appearance of a major peak corresponding to $[Bn^F B(Me)Cb^{Me}]^+ -^{13}C$ in HR-MS spectrum of $4-^{13}C$ further confirms that the formation of $4-^{13}C$ is the result of $^{13}CH_4$ activation. After **4** was treated with 50 bar of ^{13}C enriched methane in $o-C_6H_4F_2$ at $110^\circ C$ for 24 h, we found no detectable amount of $4-^{13}C$ in the reaction mixture via 1H NMR analysis. The facile activation of methane with **2** as well as the lack of reactivity of **4** are in contrast to the well-studied rare earth metallocene systems, in which Cp^*_2MH complexes show no reactivity with methane and $Cp^*_2MCH_3$ ($M = Sc, Y, Lu$) complexes readily undergo isotopic exchange with $^{13}CH_4$.^{11,12,14}

To understand the mechanism of this methane C–H borylation reaction, we measured the initial rates of the reaction under CH_4 and CD_4 independently (Table S4). The resulting primary KIE value of 3.3(2) indicates that the activation of the C–H bond of methane is involved in the rate determining step. A similar KIE value (4.0) was also observed in $Cp^*_2ScCH_2CMe_3$ -mediated methane activation reported by Tilley et al.¹⁴ Furthermore, measuring the initial rates of the reaction with variant **2** concentrations (0.01 to 0.08 M) and methane pressures (51 to 79 bar) allows us to determine the rate law of this reaction, which shows first-order dependence on both **2** and the pressure of methane (Figures S10 and S11). Eyring analysis over a $30^\circ C$ range ($100^\circ C$ to $130^\circ C$) was also conducted, which revealed the enthalpy and entropy barriers ($\Delta H^\ddagger = 9.0(2) \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -63.1(4) \text{ e.u.}$) for this reaction (Figure S9), consistent with a highly ordered transition state. Collectively, these experimental data are all in agreement with a σ -bond metathesis mechanism in which the C–H and B–H bonds are cleaved in a single step.

To further elucidate the mechanism of the methane activation process, we carried out density functional theory (DFT MN15) calculations (the $[B(C_6F_5)_4]^-$ anion was omitted).⁴² This methane C–H borylation reaction is almost thermodynamically neutral with $\Delta G^\circ = +3.8 \text{ kcal mol}^{-1}$ at 298 K. The C–H activation process takes place via a four-centered transition state (TS) without prior coordination of methane with **2** (Figure 1). The calculated free energy barrier is $28.2 \text{ kcal mol}^{-1}$, in excellent agreement with the experimental value of $27.8(4) \text{ kcal mol}^{-1}$ (298 K). In TS, the C1–H1 bond is nearly broken with a bond length of 1.455 Å, whereas the C1–B1 bond is almost formed at a distance of 1.734 Å, suggesting TS as a late transition state in regard to the formation of **4**. Both H1 and H2 atoms are bonded to the B1 atom with a B1–H1 distance of 1.267 Å and a B1–H2 distance of 1.273 Å. The distance between H1 and H2 is 1.059 Å, substantially longer than the one for free H_2 (0.74 Å). Accordingly, the Wiberg bond indices (WBI) revealed fractional C1–H1 (0.211), B1–C1 (0.768), B1–H1 (0.399), B1–H2 (0.671), and H1–H2 (0.192) interactions. Overall, the bonding picture of TS agrees with a σ -bond metathesis.⁴³ Notably, Goldfuss and co-workers reported a similar transition state in their theoretical investigation of the reaction between BH_3 and CH_4 .⁴⁴

To examine the possibility of extending this stoichiometric methane borylation reaction to a catalytic one, we studied the reactivity of **4** with catecholborane (HBcat), a common borylation reagent. When equimolar of **4** and HBcat was heated in C_6D_5Br to $110^\circ C$ for 18 h, neutral borane **3** and MeBcat were observed in the reaction mixture along with around 60% of unreacted **4** as indicated by 1H NMR spectroscopy. When the amount of HBcat was increased to two equivalents, **4** was completely consumed after 6 h of heating at $110^\circ C$, and **3** and MeBcat were quantitatively generated (Scheme 1). Decomposition of the $B(C_6F_5)_4^-$ anion (about 70% according to ^{19}F NMR spectroscopy) was also observed with $B(C_6F_5)_3$, $(C_6F_5)Bcat$ and some unidentified compounds among the decomposition products. Methyl

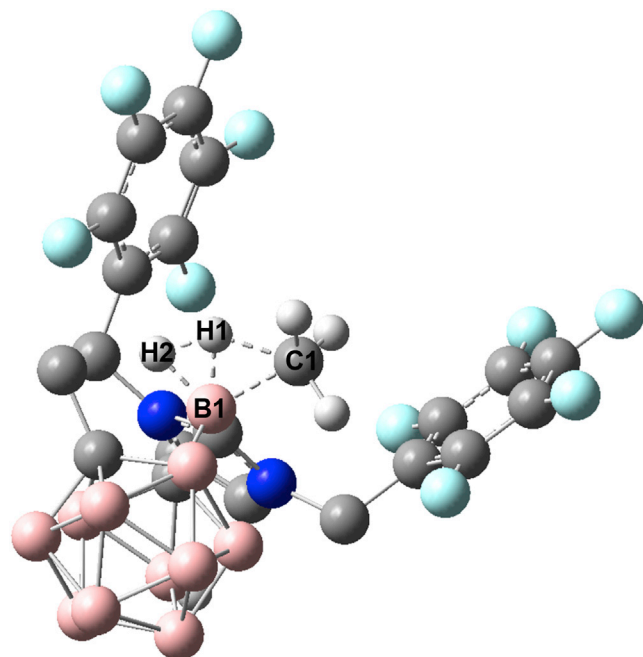
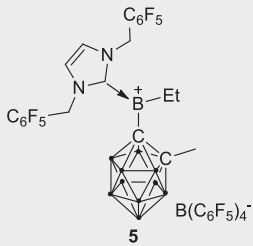
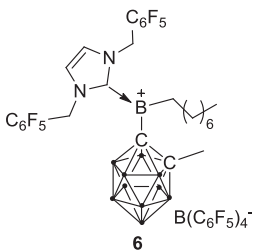
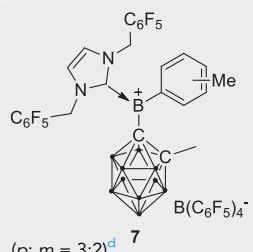


Figure 1. Geometry of TS (hydrogen atoms except H₂ and those in CH₄ are omitted for clarity)

exchange likely takes place between **4** and HBcat, affording MeBcat and **2**, and the resulting **2** reacts further with HBcat to yield **3** and [Bcat][B(C₆F₅)₄], the latter of which is known to undergo decomposition to form B(C₆F₅)₃ and (C₆F₅)Bcat.⁴⁵ Consistent with this hypothesis, heating of equimolar of **2** and HBcat in C₆D₅Br to 110°C quantitatively affords **3**, with both B(C₆F₅)₃ and (C₆F₅)Bcat being present in the reaction mixture. Without regeneration of **2**, it is unlikely **2** can catalyze methane borylation with HBcat. Indeed, after the solution of HBcat in the presence of 20 mol% of **2** in *o*-C₆H₄F₂ was heated at 110°C under 60 bar of CH₄ for 24 h, no formation of MeBcat was observed. **3** was the only observable species containing IBn^F moiety in the reaction mixture. Nonetheless, the successful transfer of the methyl group from **4** to HBcat revealed a synthetic cycle for the conversion of methane to MeBcat, which could serve as a proof of concept for the development of borenium catalyzed methane borylation reaction.

After achieving borylation of methane with borenium **2**, we set out to explore whether such a borylation reaction can be extended to other alkanes (Table 1). Treatment of **2** with ethane (30 bar) at 110°C resulted in the formation of ethane activation product [IBn^FB(Et)Cb^{Me}][B(C₆F₅)₄] (**5**) in 46% yield after recrystallization. Decreasing the reaction temperature to 90°C improved the isolation yield to 56%, which can be attributed to the thermal instability of **5** at a higher temperature (*t*_{1/2} ≈ 10 h at 110°C in *o*-C₆H₄F₂). No ethylene glycol was detected by gas chromatography-mass spectrometry (GC-MS) if conventional oxidative workup with NaOH/H₂O₂ was applied, indicating the absence of bisborylation products. Besides gaseous alkanes, we also examined the reactivity of **2** against *n*-octane. Heating **2** with octane (300 equiv) in *o*-C₆H₄F₂ at 110°C led to the formation of octyl-substituted borenium **6** in 18% NMR yield along with a substantial amount of decomposition products. The lower yield compared with methane or ethane could be due to the decreased polarity of the *n*-octane/*o*-C₆H₄F₂ solvent, which enhances the interaction between the ion pairs, resulting in acceleration of decomposition. GC-MS analysis of the mixture

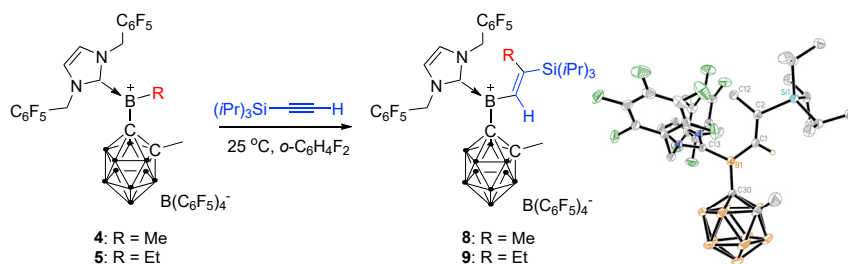
Table 1. Borylation of alkanes with borenium 2

Substrates	Temperature (°C)	Products	Yield
CH ₃ CH ₃ (30 bar) ^a	90		56% ^b
<i>n</i> -octane (300 equiv) ^a	110		18% ^c
toluene (350 equiv) ^a	110		44% ^b

^a2 (0.16 mmol) in *o*-C₆H₄F (3 mL).^bIsolation yield.^cNMR yield.^dDetermined by ¹H NMR analysis.

after NaOH/H₂O₂ workup revealed the presence of *n*-octanol and no other isomers were detected, implying that the primary C–H bonds is substantially favored over the secondary ones in this borylation reaction, a phenomenon also observed in transition-metal-catalyzed borylation reactions.⁴⁶ In the case of toluene, however, the borylation took place at the aryl ring, resulting in the formation of a mixture of *para*- and *meta*-tolylborenium complexes (7) in a 3:2 *para:meta* ratio.⁴⁷ In agreement with this observation, theoretical calculations indicate that the free energy barrier for the activation of the benzylic C–H bond (30.0 kcal mol^{−1}) is higher than those for the activation of aryl C–H bonds (27.5 kcal mol^{−1} for *para*-C–H; 28.0 kcal mol^{−1} for *meta*-C–H) (Figure S71).

One attractive feature of this alkane borylation reaction is that the formed alkylborenium complexes can be directly employed in alkyne functionalization, introducing both the alkyl and boryl moieties onto organic scaffolds. Treatment of 4 with tri(isopropyl)silylacetylene in *o*-C₆H₄F₂ at room temperature results in the quantitative formation of *syn*-1,2-methylboration product 8 (Scheme 2). After recrystallization, 8 can be isolated in 55% yield and its identity was confirmed by multinuclear NMR analysis, HR-MS, and single-crystal X-ray analysis. Similar reactivity was also observed for 5, which affords *syn*-1,2-ethylboration product 9 in 66% isolation yield. While the works from Ingleson,⁴⁸ Shoji,^{49–51} and others^{25,52} have shown that arylborenium,



Scheme 2. Synthesis of borenium 8 and 9 via 1,2-alkylboration and the molecular structure of methylborenium 8 (for clarity, $[B(C_6F_5)_4]^-$ anion and the hydrogen atoms except the one on the alkenyl moiety were removed)

arylborinium, or arylboranes can react with alkynes to afford 1,2-arylboration products, uncatalyzed 1,2-alkylboration of alkynes, to the best of our knowledge, has not been reported previously.

Conclusions

To conclude, we found that a well-defined NHC carbene-stabilized hydroborenium complex can react with methane or ethane under relatively mild conditions to afford the corresponding methyl- or ethylborenium complexes. Mechanistic studies indicate that the C–H bond of methane is activated via a σ -bond metathesis pathway. The utility of the methylborenium complex as a methyl source was evidenced by the methyl exchange reaction with HBcat as well as selective 1,2-alkylboration of alkynes. This work not only offers a route to functionalize alkanes in the absence of metals but also underscores the potential of main group elements mediated σ -bond metathesis, which could rival *d*- or *f*-elements in enthalpically strong bond activation.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.chempr.2021.03.010>.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Huadong Wang (huadongwang@fudan.edu.cn).

Materials availability

Unique and stable reagents generated in this study will be made available on request, but we might require a payment and/or a completed materials transfer agreement if there is potential for commercial application.

Data and code availability

The crystal structure data of complexes 3, 2-py, 4, and 8 have been deposited in the Cambridge structural database under reference numbers 2005260, 2008556, 2005185, and 2008557.

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AUTHOR CONTRIBUTIONS

H.W. conceived the research and designed the project. Y.L. and W.D. performed the experimental work. Z.H.L. undertook the DFT calculations. H.W. wrote the manuscript with input from all authors. All authors analyzed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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REFERENCES

- Huang, K., Miller, J.B., Huber, G.W., Dumesic, J.A., and Maravelias, C.T. (2018). A general framework for the evaluation of direct nonoxidative methane conversion strategies. *Joule* 2, 349–365.
- Caballero, A., and Pérez, P.J. (2013). Methane as raw material in synthetic chemistry: the final frontier. *Chem. Soc. Rev.* 42, 8809–8820.
- Meng, X., Cui, X., Rajan, N.P., Yu, L., Deng, D., and Bao, X. (2019). Direct methane conversion under mild condition by thermo-, electro-, or photocatalysis. *Chem* 5, 2296–2325.
- Gunsalus, N.J., Koppaka, A., Park, S.H., Bischof, S.M., Hashiguchi, B.G., and Periana, R.A. (2017). Homogeneous functionalization of methane. *Chem. Rev.* 117, 8521–8573.
- Hashiguchi, B.G., Konnick, M.M., Bischof, S.M., Gustafson, S.J., Devarajan, D., Gunsalus, N., Ess, D.H., and Periana, R.A. (2014). Main-group compounds selectively oxidize mixtures of methane, ethane, and propane to alcohol esters. *Science* 343, 1232–1237.
- Konnick, M.M., Hashiguchi, B.G., Devarajan, D., Boaz, N.C., Gunnoe, T.B., Groves, J.T., Gunsalus, N., Ess, D.H., and Periana, R.A. (2014). Selective CH functionalization of methane, ethane, and propane by a perfluoroarene iodine(III) complex. *Angew. Chem. Int. Ed. Engl.* 53, 10490–10494.
- Koppaka, A., Park, S.H., Hashiguchi, B.G., Gunsalus, N.J., King, C.R., Konnick, M.M., Ess, D.H., and Periana, R.A. (2019). Selective C–H functionalization of methane and ethane by a molecular Sb^V complex. *Angew. Chem. Int. Ed. Engl.* 58, 2241–2245.
- Gunsalus, N.J., Park, S.H., Hashiguchi, B.G., Koppaka, A., Smith, S.J., Ess, D.H., and Periana, R.A. (2019). Selective N functionalization of methane and ethane to aminated derivatives by main-group-directed C–H activation. *Organometallics* 38, 2319–2322.
- Waterman, R. (2013). σ -bond metathesis: a 30-year retrospective. *Organometallics* 32, 7249–7263.
- Labinger, J.A., and Bercaw, J.E. (2002). Understanding and exploiting C–H bond activation. *Nature* 417, 507–514.
- Watson, P.L. (1983). Methane exchange reactions of lanthanide and early-transition-metal methyl complexes. *J. Am. Chem. Soc.* 105, 6491–6493.
- Watson, P.L., and Parshall, G.W. (1985). Organolanthanides in catalysis. *Acc. Chem. Res.* 18, 51–56.
- Thompson, M.E., Baxter, S.M., Bulls, A.R., Burger, B.J., Nolan, M.C., Santarsiero, B.D., Schaefer, W.P., and Bercaw, J.E. (1987). σ -bond metathesis for carbon-hydrogen bonds of hydrocarbons and Sc-R (R = H, alkyl, aryl) bonds of permethylscandocene derivatives. Evidence for noninvolvement of the π system in electrophilic activation of aromatic and vinylic C–H bonds. *J. Am. Chem. Soc.* 109, 203–219.
- Sadow, A.D., and Tilley, T.D. (2003). Homogeneous catalysis with methane. A strategy for the hydromethylation of olefins based on the nondegenerate exchange of alkyl groups and σ -bond metathesis at scandium. *J. Am. Chem. Soc.* 125, 7971–7977.
- Sadow, A.D., and Tilley, T.D. (2003). Catalytic functionalization of hydrocarbons by σ -bond metathesis chemistry: dehydroisilylation of methane with a scandium catalyst. *Angew. Chem. Int. Ed. Engl.* 42, 803–805.
- MacDonald, M.R., Langeslay, R.R., Ziller, J.W., and Evans, W.J. (2015). Synthesis, structure, and reactivity of the ethyl yttrium metallocene, $(C_5Me_5)_2Y(CH_2CH_3)$, including activation of methane. *J. Am. Chem. Soc.* 137, 14716–14725.
- Burger, P., and Bergman, R.G. (1993). Facile intermolecular activation of carbon-hydrogen bonds in methane and other hydrocarbons and silicon-hydrogen bonds in silanes with the iridium(III) complex $Cp^*(PMe_3)Ir(CH_3)(OTf)$. *J. Am. Chem. Soc.* 115, 10462–10463.
- Arndtsen, B.A., and Bergman, R.G. (1995). Unusually mild and selective hydrocarbon C–H bond activation with positively charged iridium(III) complexes. *Science* 270, 1970–1973.
- The possibility of HF/SbF₅ mediated methane activation via σ bond metathesis was recently raised via theoretical calculation to address the reactivity of methane in superacids, see: King, C.R., Holdaway, A., Durrant, G., Wheeler, J., Suaava, L., Konnick, M.M., Periana, R.A., and Ess, D.H. (2019). Supermetal: SbF₅-mediated methane oxidation occurs by C–H activation and isobutane oxidation occurs by hydride transfer *Dalton Trans* 48, 17029–17036.
- Lu, Z., Cheng, Z., Chen, Z., Weng, L., Li, Z.H., and Wang, H. (2011). Heterolytic cleavage of dihydrogen by “frustrated Lewis pairs” comprising bis(2,4,6-tris(trifluoromethyl)phenyl)borane and amines: stepwise versus concerted mechanism. *Angew. Chem. Int. Ed. Engl.* 50, 12227–12231.
- Wang, Y., Chen, W., Lu, Z., Li, Z.H., and Wang, H. (2013). Metal-free HB(C₆F₅)₂-catalyzed hydrogenation of unfunctionalized olefins and mechanism study of borane-mediated σ -bond metathesis. *Angew. Chem. Int. Ed. Engl.* 52, 7496–7499.
- Fan, C., Mercier, L.G., Piers, W.E., Tuononen, H.M., and Parvez, M. (2010). Dihydrogen activation by antiaromatic pentaarylboroles. *J. Am. Chem. Soc.* 132, 9604–9606.
- Houghton, A.Y., Karttunen, V.A., Fan, C., Piers, W.E., and Tuononen, H.M. (2013). Mechanistic studies on the metal-free activation of dihydrogen by antiaromatic pentaarylboroles. *J. Am. Chem. Soc.* 135, 941–947.
- Nikonov, G.I., Vyboishchikov, S.F., and Shirobokov, O.G. (2012). Facile activation of H–H and Si–H bonds by boranes. *J. Am. Chem. Soc.* 134, 5488–5491.
- Devillard, M., Brousses, R., Miqueu, K., Bouhadir, G., and Bourissou, D. (2015). A stable

- but highly reactive phosphine-coordinated borenium: metal-free dihydrogen activation and alkyne 1,2-carbaboration. *Angew. Chem. Int. Ed. Engl.* **54**, 5722–5726.
26. De Vries, T.S., Prokofjevs, A., and Vedejs, E. (2012). Cationic tricoordinate boron intermediates: borenium chemistry from the organic perspective. *Chem. Rev.* **112**, 4246–4282.
 27. Su, B., Li, Y., Li, Z.H., Hou, J.-L., and Wang, H. (2020). Activation of C–C bonds via σ -bond metathesis: hydroborenium-catalyzed hydrogenolysis of cyclopropanes. *Organometallics* **39**, 4159–4163.
 28. Benhamou, L., Chardon, E., Lavigne, G., Bellemin-Lapponnaz, S., and César, V. (2011). Synthetic routes to N-heterocyclic carbene precursors. *Chem. Rev.* **111**, 2705–2733.
 29. Grimes, R.N. (2011). *Carboranes* (Academic Press).
 30. Bissinger, P., Braunschweig, H., Damme, A., Dewhurst, R.D., Kupfer, T., Radacki, K., and Wagner, K. (2011). Generation of a carbene-stabilized bora-borylene and its insertion into a C–H bond. *J. Am. Chem. Soc.* **133**, 19044–19047.
 31. Prokofjevs, A., and Vedejs, E. (2011). N-directed aliphatic C–H borylation using borenium cation equivalents. *J. Am. Chem. Soc.* **133**, 20056–20059.
 32. Farrell, J.M., Posaratnanathan, R.T., and Stephan, D.W. (2015). A family of N-heterocyclic carbene-stabilized borenium ions for metal-free imine hydrogenation catalysis. *Chem. Sci.* **6**, 2010–2015.
 33. Rochette, É., Courtemanche, M.A., and Fontaine, F.G. (2017). Frustrated Lewis pair mediated Csp^3 -H activation. *Chemistry* **23**, 3567–3571.
 34. Kaese, T., Trageser, T., Budy, H., Bolte, M., Lerner, H.W., and Wagner, M. (2018). A redox-active diborane platform performs $C(sp^3)$ -H activation and nucleophilic substitution reactions. *Chem. Sci.* **9**, 3881–3891.
 35. Khoo, S., Siu, C.K., and So, C.W. (2020). A base-stabilized silylene-promoted $C(sp^3)$ -H borylation and H_2 activation. *Inorg. Chem.* **59**, 9551–9559.
 36. Cook, A.K., Schimler, S.D., Matzger, A.J., and Sanford, M.S. (2016). Catalyst-controlled selectivity in the C–H borylation of methane and ethane. *Science* **351**, 1421–1424.
 37. Smith, K.T., Berritt, S., González-Moreiras, M., Ahn, S., Smith, M.R., 3rd, Baik, M.H., and Mindiola, D.J. (2016). Catalytic borylation of methane. *Science* **351**, 1424–1427.
 38. Kitano, H., Ito, H., and Itami, K. (2018). Palladium-catalyzed esterification of carboxylic acids with aryl iodides. *Org. Lett.* **20**, 2428–2432.
 39. Liu, Y., Su, B., Dong, W., Li, Z.H., and Wang, H. (2019). Structural characterization of a boron(III) η^2 - σ -silane-complex. *J. Am. Chem. Soc.* **141**, 8358–8363.
 40. Fan, X., Zheng, J., Li, Z.H., and Wang, H. (2015). Organoborane catalyzed regioselective 1,4-hydroboration of pyridines. *J. Am. Chem. Soc.* **137**, 4916–4919.
 41. Pyykkö, P., and Atsumi, M. (2009). Molecular single-bond covalent radii for elements 1–118. *Chemistry* **15**, 186–197.
 42. Yu, H.S., He, X., Li, S.L., and Truhlar, D.G. (2016). MN15: a Kohn–Sham global-hybrid exchange–correlation density functional with broad accuracy for multi-reference and single-reference systems and noncovalent interactions. *Chem. Sci.* **7**, 5032–5051.
 43. Lin, Z. (2007). Current understanding of the σ -bond metathesis reactions of $LnMR^+R^-H \rightarrow LnMR^+R-H$. *Coord. Chem. Rev.* **251**, 2280–2291.
 44. Goldfuss, B., Knochel, P., Bromm, L.O., and Knapp, K. (2000). C–H activation by direct borane-hydrocarbon dehydrogenation: kinetic and thermodynamic aspects. *Angew. Chem. Int. Ed. Engl.* **39**, 4136–4139.
 45. Del Grosso, A., Pritchard, R.G., Muryn, C.A., and Ingleson, M.J. (2010). Chelate restrained boron cations for intermolecular electrophilic arene borylation. *Organometallics* **29**, 241–249.
 46. Mkhali, I.A., Barnard, J.H., Marder, T.B., Murphy, J.M., and Hartwig, J.F. (2010). C–H activation for the construction of C–B bonds. *Chem. Rev.* **110**, 890–931.
 47. Ingleson, M.J. (2015). Fundamental and applied properties of borocations. *Topics in Organometallic Chemistry* **49**, 39–71.
 48. Cade, I.A., and Ingleson, M.J. (2014). syn-1,2-carbaboration of alkynes with borenium cations. *Chemistry* **20**, 12874–12880.
 49. Shoji, Y., Tanaka, N., Muranaka, S., Shigeno, N., Sugiyama, H., Takenouchi, K., Hajjaj, F., and Fukushima, T. (2016). Boron-mediated sequential alkyne insertion and C–C coupling reactions affording extended π -conjugated molecules. *Nat. Commun.* **7**, 12704.
 50. Tanaka, N., Shoji, Y., Hashizume, D., Sugimoto, M., and Fukushima, T. (2017). Formation of an isolable divinylboronium ion through twofold 1,2-carbaboration between a diarylboronium ion and diphenylacetylene. *Angew. Chem. Int. Ed. Engl.* **56**, 5312–5316.
 51. Shoji, Y., Shigeno, N., Takenouchi, K., Sugimoto, M., and Fukushima, T. (2018). Mechanistic study of highly efficient direct 1,2-carbaboration of alkynes with 9-borofluorenes. *Chemistry* **24**, 13223–13230.
 52. Hasenbeck, M., Müller, T., and Gellrich, U. (2019). Metal-free gem selective dimerization of terminal alkynes catalyzed by a pyridonate borane complex. *Catal. Sci. Technol.* **9**, 2438–2444.