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硼氢正离子与烷基硅烷的烷基交换反应

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摘要 硼和硅的配体交换反应为有机硼化合物的合成提供了一种简便的方法, 虽然这一方法已经被广泛地应用于芳基硼化合物的制备, 但是利用烷基交换制备烷基硼化合物的报道非常少. 在本工作中发现氮杂环卡宾稳定的硼氢正离子可以在室温下与烷基硅试剂发生反应, 生成烷基硼正离子化合物. 理论计算表明对于烷基硅试剂的硅碳键的活化是通过 σ 键复分解的反应路径进行的.

关键词 硼; 硅; 碳硅键; σ-键复分解

Alkyl Exchange between Alkylsilanes and Hydroborenium Ion

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Abstract Ligand exchange between boron and silicon centers offers a convinient way for the synthesis of organoboron compounds. While such method is well-established for the preparation of arylboranes, examples of alkyl exchange between boron and silicon centers are very rare. Here, it was demonstrated that an *N*-heterocyclic carbene stablized hydroborenium ion readily reacts with alkylsilanes at ambient conditions to afford the corresponding alkylborenium complexes. Theoretical calculations suggest that the activation of Si—C(alkyl) bonds involves a σ-bond metathesis pathway.

Keywords boron; silicon; Si—C bond; σ-bond metathesis

1 Introduction

Boron and silicon, due to their diagonal relationship in the periodic table, share similar properties and reactivity at bonds to these elements.[1] Ligand redistribution between boron and silicon centers provides an efficient way to generate organoboron compounds from easily-accessible and air-stable organosilanes.[2] While this strategy is well established for the synthesis of arylboron species due to facile migration of aryl ligands from silicon to boron,[3] there are only two examples of ligand redistribution involving boron species and alkylsilanes, both of which involve strong Lewis acidic BBr_3 or BI_3.[4-6] In 1977, Nöth *et al.*[4] reported that $N(SiMe_3)_3$ reacts with BBr_3 to afford $MeBBr_2$ and $N(SiMe_2Br)_3$ (Scheme 1a). Following this report, Haubold *et al.*[5] discovered that the reaction of $SiMe_4$ with BX_3 (X=Br or I) resulted in the formation of Me_nBX_{3-n} (n=1 or 2) and Me_3SiBr (Scheme 1b). The paucity of alkyl transfer from organosilane to boron species may arise from the lack of suitable boron species which are strong Lewis acidic and bear labile substituents at the same time. Recently we[7-8] reported the synthesis of an *N*-heterocyclic carbene (NHC) stabilized hydroborenium complex with *o*-carboranyl substituent ([$IMe_4B(H)Cb$][$B(C_6F_5)_4$], IMe_4= 1,3,4,5-tetramethylimidazol-2-ylidene, Cb = *o*-carboran-1-yl, **1**), which readily forms a η^2-σ complex with $HSiEt_3$ and undergoes hydroboration when treated with cyclopropane derivatives. Taking into account of the strong Lewis acidity of complex **1** as well as its relatively labile hydrogen substituent, we envisioned that complex **1** could react with alkylsilanes to afford the corresponding alkylborenium and hydrosilane. Herein, we present our study of the reactivity of **1** with alkylsilanes, characterization of the resulting alkylborenium complexes and mechanistic investigations.

2 Results and discussion

Treating **1** with 1.5 equiv. of $SiMe_4$ in the solution of C_6H_5Br/hexane at room temperature resulted in the formation of methylborenium complex [$IMe_4B(Me)Cb$]-[$B(C_6F_5)_4$] (**2**), which can be isolated in a yield of 45% after recrystallization (Scheme 2). Analysis of the overhead gas by GC-MS revealed the presence of $HSiMe_3$. In

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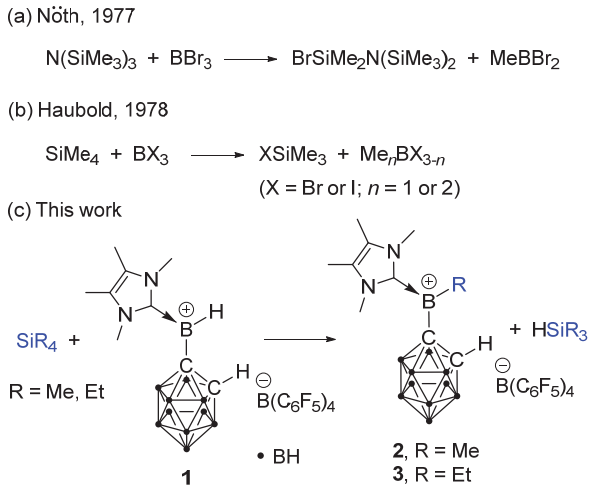
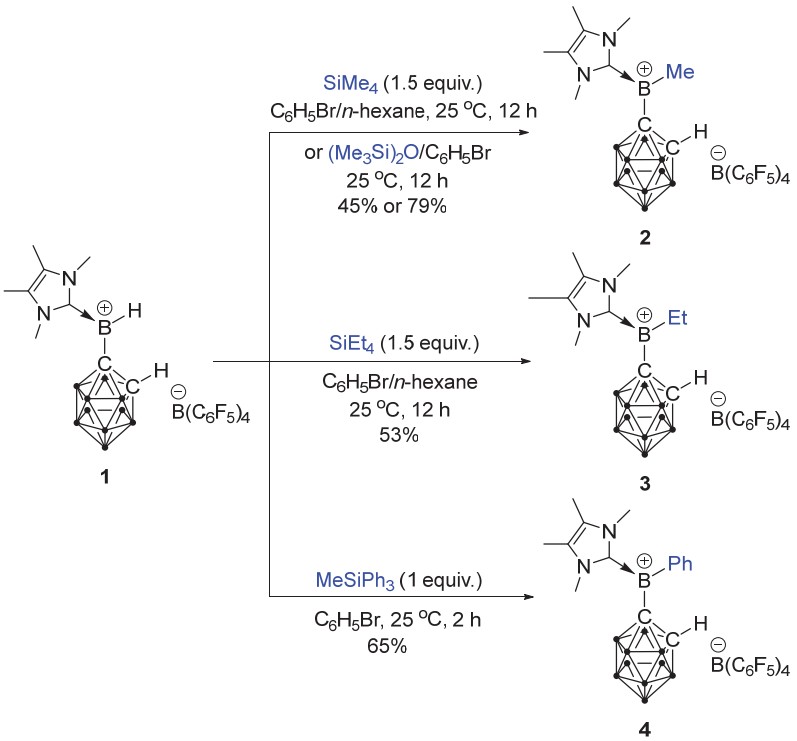


Scheme 1 Alkyl exchange between boron and silicon

the ^{1}H NMR spectrum of **2**, a broad singlet was observed at δ 1.50 which was assigned to the methyl substituent on the borenium center. The ^{1}H-^{13}C HSQC spectrum showed that this signal is correlated to a broad signal at δ 17.6 of the ^{13}C NMR spectrum, which is slightly up-field shifted compared to the one observed for [IBn^{F}B(Me)Cb^{Me}][B(C$_6$F$_5$)$_4$] (IBn = 1,3-bis(2,3,4,5,6-pentafluorobenzyl)imidazol-2-ylidene, Cb^{Me} = 2-methyl-*o*-carboran-1-yl, δ 20.5).[9] The ^{11}B NMR spectrum of **2** shows a broad singlet at δ 79.5, which is very close to the one observed for ([IMe$_4$B(*n*-propyl)Cb][B(C$_6$F$_5$)$_4$] (δ 79.9).[8] The identity of **2** was further confirmed by single-crystal X-ray analysis (Figure 1). The sum of C—B—C angles of the borenium center is 360.0°, revealing a planar tri-coordinated boron center. The B—C distances of the boron center range from 0.1530 nm to 0.1597 nm, typical for B—C single bonds.[10] Complex **2** can also be accessed by dissolving **1** in the 1∶1 mixture of C$_6$H$_5$Br and (Me$_3$Si)$_2$O, which can afford **2** in a yield of 79% after recrystallization.

This alkyl transfer reaction can be extended to ethyl group. Stirring a mixture of **1** with 1.5 equiv. of SiEt$_4$ at room temperature for 12 h led to the formation of ethylborenium complex [IMe$_4$B(Et)Cb][B(C$_6$F$_5$)$_4$] (**3**) in an isolation yield of 53% (Scheme 2). The formation of HSiEt$_3$ was confirmed by GC-MS analysis of the reaction mixture. Complex **3** was fully characterized by multinuclear NMR analysis, HRMS as well as single-crystal X-ray analysis. The ^{1}H NMR spectrum of **3** shows one triplet signal and one quartet signal at δ 1.00 and 1.89, respectively, with an integration ratio of 3∶2, in agreement with the presence of ethyl group. A broad singlet at δ 79.9 in the ^{11}B NMR spectrum of **3** was assigned to the borenium center.

The reactivity of **1** with Ph$_3$SiMe, an organosilane containing both aryl and alkyl substituents, was also examined. After treating **1** with 1.0 equiv. of Ph$_3$SiMe in C$_6$H$_5$Br at room temperature, no formation of **2** was observed. Instead, phenylborenium complex [IMe$_4$B(Ph)Cb][B(C$_6$F$_5$)$_4$] (**4**) was obtained in a yield of 65% after recrystallization (Scheme 2). The GC-MS analysis of the reaction mixture supports the formation of Ph$_2$MeSiH as well. The identity of complex **4** was confirmed by multinuclear NMR analysis, HRMS and single-crystal X-ray analysis (Figure 1). This result points to the preference of aryl substituent over alkyl during the ligand transfer between boron and silicon species.



Scheme 2 Synthesis of compounds **2**～**4** via alkyl exchange

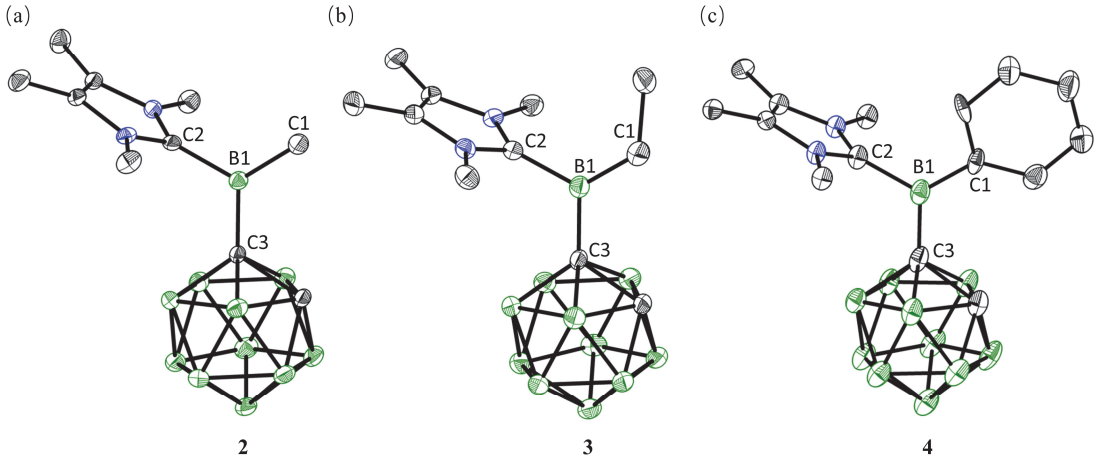


Figure 1 Molecular structures of complexes **2** (a), **3** (b) and **4** (c)
Hydrogen atoms, counteranion $B(C_6F_5)_4^-$, and a solvent molecule C_6H_5Br in **2** are omitted for clarity.

To understand the mechanism of the reaction between **1** and $SiMe_4$, density functional theory (DFT M06-2x) calculations (the $[B(C_6F_5)_4]^-$ anion was omitted) were carried out.[11] Our studies reveals that **1** and $SiMe_4$ first form a high-energy adduct **IM1** via **TS1** (Figure 2). In **IM1**, the B1—H1 bond is slightly weakened, as indicated by the B1—H1 distance of 0.1201 nm and a Wiberg bond index (WBI) of 0.903. On the other hand, the Si—C1 bond is significantly elongated to 0.2123 nm with a WBI of 0.304. A short interaction between B1 and C1 was observed with a B1—C1 distance of 0.1728 nm and a WBI of 0.749. **IM1** needs to overcome a free energy barrier of 9.2 kJ•mol^{-1} via **TS2** to yield **2** and $HSiMe_3$. In **TS2**, both of the Si—C1 and B1—H1 bonds are further weakened, with distances of 2.322 and 0.1218 nm and WBIs of 0.191 and 0.835, respectively. The interaction between B and C becomes stronger with a B1—C1 distance of 0.1681 nm and a WBI of 0.830. Unlike **IM2**, **TS2** shows a noticeable interaction between H and Si with a distance of 0.1997 nm and a WBI of 0.095. Natural bonding orbital analysis revealed that in **TS2**, 0.54*e* charge transfers from the σ-bonding orbital of Si—C1 to the empty p orbital of the borenium center. At the same time, 0.12*e* charge also transfers from the occupied σ-bonding orbital of B1—H1 to the Si—C1 σ*-antibonding orbital. In summary, these results support a σ-bond metathesis pathway for the alkyl transfer process.[12]

3 Conclusions

In conclusion, it was demonstrated that hydroborenium **1** readily reacts with tetraalkylsilanes, such as $SiMe_4$ and $SiEt_4$ to afford the corresponding alkylborenium complexes. When an organosilane bearing both aryl and alkyl substituents was applied, aryl, instead of alkyl, exchange was observed, resulting in formation of an arylborenium complex. Theoretical calculations support a σ-bond metathesis pathway for the alkyl exchange between the silicon and boron centers.

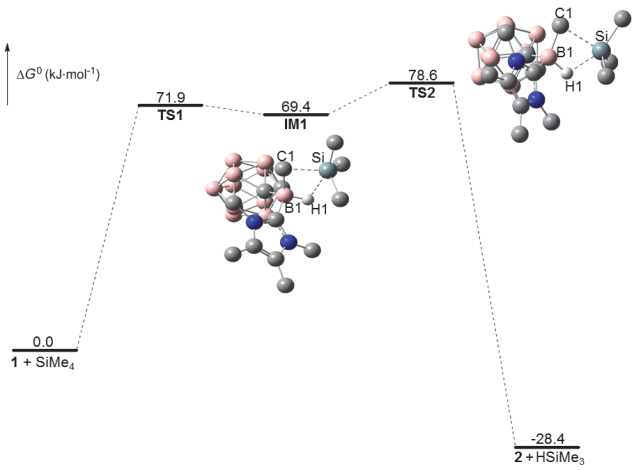


Figure 2 Gibbs free energy profile at 298 K for the reaction between **1** and $SiMe_4$, and the simulated structure of **IM1** and **TS2**
Hydrogen atoms except H1 are omitted by clarity.

4 Experimental section

4.1 General experimental information

Solvents were dried by refluxing under N_2 over sodium or CaH_2 and freshly distilled prior to use. Air sensitive compounds were handled under a N_2 atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on a Bruker SPECT NMR (400 MHz for ^{1}H NMR, 376 MHz for ^{19}F NMR, 100 MHz for ^{13}C NMR, 128 MHz for ^{11}B NMR) spectrometers. Most assignments were based on a series of 2D NMR experiments. HRMS analyses were performed on a Bruker micrOTOF II. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC 2225760, 2225761 and 2225762 (complex **2**, **3** and **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. **1** was prepared as

reported.[6]

4.2 Synthesis of methylborenium complex [IMe4B(Me)Cb][B(C6F5)4] (2)

Method I: To a 1∶1 mixture of C_6H_5Br/$(SiMe_3)_2O$ (5.0 mL) was added **1** (300.0 mg, 0.313 mmol) at room temperature. After 12 h stirring, hexane (6.0 mL) was added to the reaction mixture, resulting in formation of a white precipitate. The supernatant was removed by filtration and the residue was washed with hexane (5.0 mL×2) and dried under vacuum, affording **2** as a white solid, 240.0 mg, yield 79%.

Method II: To a solution of tetramethylsilane (TMS, 10.0 mg, 0.11 mmol) in hexane (1.0 mL) was added a solution of **1** (70.0 mg, 0.073 mmol) in C_6H_5Br (1.0 mL) at room temperature. After 12 h stirring, hexane (6.0 mL) was added to the reaction mixture. The supernatant was removed by filtration and the residue was recrystallized with a mixture solution of *o*-$C_6H_4F_2$/*n*-hexane (*V*∶*V*=1∶2), affording **2** as a white solid, 32.0 mg, yield 45%.

[$IMe_4B(Me)Cb][B(C_6F_5)_4$] (**2**): ^1H NMR (400 MHz, CD_2Cl_2, 25 ℃) *δ*: 3.89 (s, 1H, $CH_{Carborane}$), 3.58 (s, 6H, NCH_3), 2.25 (s, 6H, $=CCH_3$), 1.50 (s, 3H, BCH_3); $^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2, 25 ℃) *δ*: 3.89 (s, 1H, $CH_{Carborane}$), 3.58 (s, 6H, NCH_3), 2.66 (s, 1H, $BH_{Carborane}$), 2.50～2.32 (m, 7H, $BH_{Carborane}$), 2.25 (s, 6H, $=CCH_3$), 1.83 (s, 2H, $BH_{Carborane}$), 1.50 (s, 3H, BCH_3); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 ℃) *δ*: 148.60 (dm, $^1J_{C\text{-}F}$=241 Hz, *o*-C_6F_5), 138.60 (dm, $^1J_{C\text{-}F}$=245 Hz, *p*-C_6F_5), 136.71 (dm, $^1J_{C\text{-}F}$ = 245 Hz, *m*-C_6F_5), 130.86 (= *C*CH_3), 58.29 ($CH_{Carborane}$), 35.19 (NCH_3), 17.59 (BCH_3), 8.61 (=*C*CH_3); ^{11}B NMR (128 MHz, CD_2Cl_2, 25 ℃) *δ*: 79.5 (br s, 1B, $BIMe_4$), 3.0 (d, $^1J_{H\text{-}B}$=146 Hz, 1B, $B_{Carborane}$(12)), −0.8 (d, $^1J_{H\text{-}B}$=155 Hz, 1B, $B_{Carborane}$(9)), −6.9 (d, $^1J_{H\text{-}B}$=152 Hz, 2B, $B_{Carborane}$(8 and 10)), −9.6～−16.2 (m, 6B, $B_{Carborane}$(3 to 7 and 11)), −16.9 (s, 1B, $B(C_6F_5)_4$); $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, 25 ℃) *δ*: 79.4 (br s, 1B, $BIMe_4$), 3.0 (s, 1B, $B_{Carborane}$(12)), −0.7 (s, 1B, $B_{Carborane}$(9)), −6.9 (s, 2B, $B_{Carborane}$(8 and 10)), −9.6～−16.2 (m, 6B, $B_{Carborane}$(3 to 7 and 11)), −16.9 (s, 1B, *B*$(C_6F_5)_4$); ^{19}F NMR (376 MHz, CD_2Cl_2, 25 ℃) *δ*: −133.06 (br s, 8F, *o*-C_6F_5), −163.44 (t, 4F, $^3J_{F\text{-}F}$=20 Hz, *p*-C_6F_5), −167.44 (t, $^3J_{F\text{-}F}$=18 Hz, 8F, *m*-C_6F_5); HRMS calcd for $C_{10}H_{26}B_{11}N_2$ $[M-BC_{24}F_{20}]^+$ 295.3120, found 295.3136.

4.3 Synthesis of ethylborenium complex [IMe4B(Et)Cb][B(C6F5)4] (3)

To a solution of tetraethylsilane (15.9 mg, 0.109 mmol) in *n*-hexane (1.0 mL) was added a solution of **1** (70.0 mg, 0.073 mmol) in C_6H_5Br (1.0 mL) at room temperature, resulting in a white slurry. After 12 h stirring, the supernatant was removed by filtration and the residue was recrystallized with a mixture of dichloromethane/*n*-hexane (*V*∶*V*=1∶1), affording **3** as a yellow solid, 38.0 mg, yield 53%. ^1H NMR (400 MHz, CD_2Cl_2, 25 ℃) *δ*: 3.88 (s, 1H, $CH_{Carborane}$), 3.58 (s, 6H, NCH_3), 2.28 (s, 6H, $=CCH_3$), 1.89 (q, $^3J_{H\text{-}H}$=7.4 Hz, 2H, CH_2CH_3), 1.00 (t, $^3J_{H\text{-}H}$=7.4 Hz, 3H, CH_2CH_3); $^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2, 25 ℃) *δ*: 3.88 (s, 1H, $CH_{Carborane}$), 3.58 (s, 6H, NCH_3), 2.68 (s, 1H, $BH_{Carborane}$), 2.47 (s, 3H, $BH_{Carborane}$), 2.39 (s, 4H, $BH_{Carborane}$), 2.28 (s, 6H, $=CCH_3$), 1.89 (q, $^3J_{H\text{-}H}$=7.4 Hz, 2H, CH_2CH_3), 1.81 (s, 2H, $BH_{Carborane}$), 1.00 (t, $^3J_{H\text{-}H}$=7.4 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 ℃) *δ*: 148.55 (dm, $^1J_{C\text{-}F}$=246 Hz, *o*-C_6F_5), 138.62 (dm, $^1J_{C\text{-}F}$ = 241 Hz, *p*-C_6F_5), 136.78 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *m*-C_6F_5), 130.66 (= *C*CH_3), 58.56 ($CH_{Carborane}$), 35.22 (NCH_3), 26.80 (CH_2CH_3), 8.94 (=C*C*H_3), 8.35 (CH_2CH_3); ^{11}B NMR (128 MHz, CD_2Cl_2, 25 ℃) *δ*: 79.9 (br s, 1B, $BIMe_4$), 3.3 (d, $^1J_{H\text{-}B}$=144 Hz, 1B, $B_{Carborane}$(12)), −0.7 (d, $^1J_{H\text{-}B}$=150 Hz, 1B, $B_{Carborane}$(9)), −7.0 (d, $^1J_{H\text{-}B}$=150 Hz, 2B, $B_{Carborane}$(8 and 10)), −9.8～−15.6 (m, 6B, $B_{Carborane}$(3 to 7 and 11)), −16.9 (s, 1B, $B(C_6F_5)_4$); $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, 25 ℃) *δ*: 79.9 (br s, 1B, $BIMe_4$), 3.2 (s, 1B, $B_{Carborane}$(12)), −0.6 (s, 1B, $B_{Carborane}$(9)), −6.9 (s, 2B, $B_{Carborane}$(8 and 10)), −9.8～−15.6 (m, 6B, $B_{Carborane}$(3 to 7 and 11)), −16.9 (s, 1B, $B(C_6F_5)_4$); ^{19}F NMR (376 MHz, CD_2Cl_2, 25 ℃) *δ*: −133.12 (br s, 8F, *o*-C_6F_5), −163.60 (t, $^3J_{F\text{-}F}$=20 Hz, 4F, *p*-C_6F_5), −167.54 (t, $^3J_{F\text{-}F}$=18 Hz, 8F, *m*-C_6F_5); HRMS calcd for $C_{11}H_{28}B_{11}N_2$ $[M-BC_{24}F_{20}]^+$ 309.3276, found 309.3271.

4.4 Synthesis of phenylborenium complex [IMe4B(Ph)Cb][B(C6F5)4] (4)

To a solution of **1** (383.3 mg, 0.4 mmol) in C_6H_5Br (2.0 mL) was added a solution of methyltriphenylsilane (109.8 mg, 0.4 mmol) in C_6H_5Br (2.0 mL). After 2 h stirring at room temperature, hexane (6.0 mL) was added to the reaction mixture. The supernatant was removed by filtration and the residue was recrystallized with a mixture solution of dichloromethane/*n*-hexane (*V*∶*V*=2∶1), affording **4** as a white solid, 270.0 mg, yield 65%. ^1H NMR (400 MHz, CD_2Cl_2, 25 ℃) *δ*: 7.92 (t, $^3J_{H\text{-}H}$=7.4 Hz, 1H, *p*-C_6H_5), 7.65 (d, $^3J_{H\text{-}H}$=7.4 Hz, 2H, *o*-C_6H_5), 7.59 (t, $^3J_{H\text{-}H}$=8 Hz, 2H, *m*-C_6H_5), 4.19 (s, 1H, $CH_{Carborane}$), 3.59 (s, 6H, NCH_3), 2.30 (s, 6H, $=CCH_3$); $^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2, 25 ℃) *δ*: 7.93 (t, $^3J_{H\text{-}H}$=7.4 Hz, 1H, *p*-C_6H_5), 7.65 (d, $^3J_{H\text{-}H}$=7.4 Hz, 2H, *o*-C_6H_5), 7.59 (t, $^3J_{H\text{-}H}$=8 Hz, 2H, *m*-C_6H_5), 4.19 (s, 1H, $CH_{Carborane}$), 3.59 (s, 6H, NCH_3), 2.70 (s, 3H, $BH_{Carborane}$), 2.51～2.38 (m, 5H, $BH_{Carborane}$), 2.31 (s, 6H, $=CCH_3$), 1.98 (s, 2H, $BH_{Carborane}$); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 ℃) *δ*: 148.53 (dm, $^1J_{C\text{-}F}$=246 Hz, *o*-C_6F_5), 141.41 (*p*-C_6H_5), 140.13 (*o*-C_6H_5), 138.67 (dm, $^1J_{C\text{-}F}$ = 241 Hz, *p*-C_6F_5), 136.72 (dm, $^1J_{C\text{-}F}$ = 246 Hz, *m*-C_6F_5), 130.98 (*m*-C_6H_5), 130.46 (= *C*CH_3), 60.23 ($CH_{Carborane}$), 35.73 (NCH_3), 8.84 (=C*C*H_3); ^{11}B NMR (128 MHz, CD_2Cl_2, 25 ℃) *δ*: 63.1 (br s, 1B, $BIMe_4$), 3.4 (d, $^1J_{H\text{-}B}$=145 Hz, 1B, $B_{Carborane}$(12)), −1.1 (d, $^1J_{H\text{-}B}$=145 Hz, 1B, $B_{Carborane}$(9)), −6.9 (d, $^1J_{H\text{-}B}$=150 Hz, 2B, $B_{Carborane}$(8 and 10)), −9.0～−15.1 (m, 6B, $B_{Carborane}$(3 to 7 and 11)), −16.9 (s, 1B, $B(C_6F_5)_4$); $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, 25 ℃) *δ*: 64.3 (br s, 1B, $BIMe_4$), 3.4 (s, 1B, $B_{Carborane}$(12)), −1.0 (s, 1B, $B_{Carborane}$(9)), −6.9 (s, 2B, $B_{Carborane}$(8 and 10)), −9.0～−15.1 (m, 6B, $B_{Carborane}$(3 to

7 and 11)), −16.9 (s, 1B, $B(C_6F_5)_4$); ^{19}F NMR (376 MHz, CD_2Cl_2, 25 ℃) δ: −133.07 (br s, 8F, *o*-C_6F_5), −163.55 (t, $^3J_{F\text{-}F}$=20 Hz, 4F, *p*-C_6F_5), −167.49 (t, $^3J_{F\text{-}F}$=18 Hz, 8F, *m*-C_6F_5); HRMS calcd for $C_{15}H_{28}B_{11}N_2$ $[M-BC_{24}F_{20}]^+$ 357.3276, found 357.3294.

Supporting Information Calculation details; ^1H NMR, ^{11}B NMR, ^{13}C NMR and ^{19}F NMR spectra of complexes **2**, **3** and **4**; Cartesian coordinates for simulated structures of **1**, **2**, **TS1**, **TS2** and **IM1**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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