An Amidinato Isopropylmethylamidosilylene-Catalyzed Hydroboration of Carbonyl Compounds

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Dedicated to Prof. Cameron Jones on the occasion of his 60th Birthday

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# Equal Contribution

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Abstract: This study describes the use of an amidinato isopropylmethylamidosilylene [LSiN(Me)*i*Pr] (**1**, L = PhC(N*t*Bu)$_2$) to catalyze hydroboration of carbonyl compounds. Compound **1** (loading: 5 – 10 mol%) was shown to be an efficient catalyst for the chemoselective hydroboration of aldehydes (average yield = 97 %, average TOF = 8.8 h^{-1}) and ketones (average yield = 97 %, average TOF = 1.7 h^{-1}) with pinacolborane (HBpin) in C_6D_6 at 90 °C to form borate esters. Mechanistic studies shows that the Si lone pair electrons on **1** and the B vacant p orbital of HBpin activates the C=O double bond of aldehydes and ketones, the intermediates of which undergoes hydroboration to yield borate esters and regenerate compound **1**.

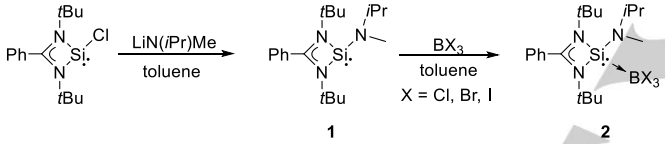
Introduction

Silylenes [R$_2$Si:] (R = supporting substituents) have a lone pair of electrons and vacant orbital on the silicon atom, and they possess Lewis ambiphilic character.[1] Their stability can be enhanced by coordinating with a Lewis base donor, where the vacant orbital is stabilized to form Lewis base-silylene complexes [R$_2$(L)Si:] (L = Lewis base donor). These two- and three-coordinate silylenes, [R$_2$Si:] and [R$_2$(L)Si:], were shown to act like transition metals in small molecule activation,[1] but their application in catalysis remains underexplored. Only two examples of silyliumylidene cation have been shown to catalyze organic reactions. The first example is the cyclopentadienyl silyliumylidene cation [Cp*Si]$^+$ (Cp* = C_5Me_5), which can catalyze the controlled degradation of oligo(ethyleneglycol) diethers, hydrosilylation of olefins and Piers-Rubinsztajn reaction.[2-3] Another example is the NHC-silyliumylidene cation complex [(I$_{Me}$)$_2$SiH]$^+$ (I$_{Me}$ = :C{N(Me)C(Me)}$_2$) that can catalyze the hydroboration of carbon dioxide, carbonyl compounds and pyridine derivatives, as well as the N-formylation of amines.[4-5] However, heavier congeners, germylenes and stannylenes, were shown to be competent in catalysis through a diversity of mechanisms.[6-16] The first example is the hydridogermylene [Ar*(*i*Pr$_3$Si)NGeH] (Ar* = 2,4,6-*i*Pr{C(H)Ph$_2$}$_2$C$_6$H$_2$) that catalyzes the hydroboration of carbonyl compounds via the Ge-H and B-H σ-bond metathesis reactions.[17] The second example is the phosphine-tetrylene complexes [Ar$_{i\text{Pr}}$EC(H)(Ph)PPh$_2$] (E = Ge, Sn; Ar$_{i\text{Pr}}$ = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$), which mediates the catalytic hydroboration of aldehyde via two mechanisms: the activation of aldehyde by forming adduct with the phosphine donor and tetrylene acceptor, as well as the activation of pinacolborane (HBpin) at the tetrylene center.[18] The third example is the NHC-germyliumylidene cation [$^{\text{Mes}}$TerGe(I$_{Me}$)$_2$]$^+$ ($^{\text{Mes}}$Ter = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) using the Lewis basicity of the Ge center to promote hydride transfer from PhSiH$_3$ to CO$_2$ in the catalytic N-methylation of amine with CO$_2$ and PhSiH$_3$.[19] The fourth example is the diaminogermylene mediating the catalytic hydroboration of aldehyde via the adduct formation between HBpin (Lewis base) and the Ge^{II} center (Lewis acid) to facilitate the insertion of the H-B bond with aldehyde.[20]

The fruitful germylene- and stannylene-mediated catalyses provide an indication that silylenes could likewise have catalytic capability. We recently reported an amidinato amidosilylene with a sterically hindered amido substituent, -N(SiMe$_3$)$_2$ or –N(SiMe$_3$)Ar (Ar = *i*Pr$_2$C$_6$H$_3$) stoichiometrically activating the B-H bond of borane.[21] We propose that fine-tuning the steric effect could possibly enable the amidinato amidosilylene in sequentially activating borane and substrate, leading to catalytic hydroboration. In this article, we report a smaller amido substituent, isopropylmethylamide, that unlocks the catalytic capability of an amidinato silylene in the hydroboration of carbonyl compounds with HBpin. The catalytic mechanism was also studied and rationalized by DFT calculations.

Results and Discussion

The amidinato isopropylmethylamidosilylene [LSiN(Me)*i*Pr] (**1**, L = PhC(N*t*Bu)$_2$) was prepared by the reaction of the amidinato chlorosilylene[22] with lithium isopropylmethylamide in toluene for 12 h (Scheme 1), which was isolated as colorless crystals. The ^{1}H NMR and ^{29}Si{^{1}H} NMR spectroscopy of compound **1** shows one set of signals attributed to the ligand backbone and a singlet at -4.6 ppm accountable to the three-coordinate silicon center respectively. The molecular structure of compound **1** obtained by X-ray crystallography (Figure 1) shows that the Si center adopts a trigonal pyramidal geometry, indicating the presence of a lone pair of electrons. This is supported by the reaction of **1** with trihaloborane BX_3 (X = Cl, Br, I) in toluene for 3 h to form the silylene-trihaloborane adducts **2** [X = Cl (**2a**), Br (**2b**), I (**2c**)]. Compound **1** is one of the few silylenes capable of coordinating with trihaloboranes instead of undergoing oxidative addition.[23] The ^{29}Si{^{1}H} NMR signals (-14.3 - -21.5 ppm) of compound **2** are upfield shifted in comparison with that of **1**, confirming the formation of a four-coordinate silicon center in **2**. The presence of the Si-B coordinative covalent bond is further confirmed by X-ray crystallographic data (Si-B: 1.997(4) – 2.018(3) Å, Figure 1 and Figure S80-81). Both compounds **1** and **2** are stable in solution from room temperature to 90 °C and hence compound **1** should be suitable for catalysis.



Scheme 1. Synthesis of compounds **1** and **2**.

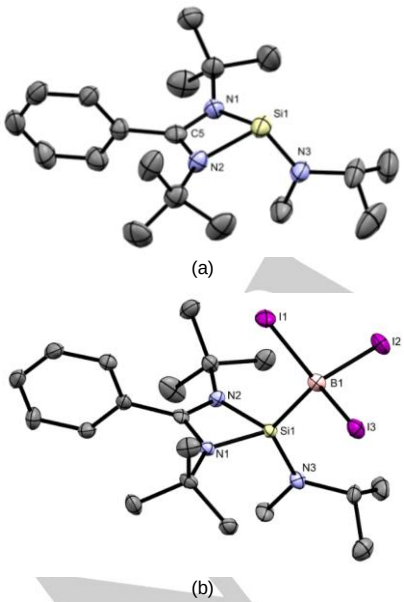
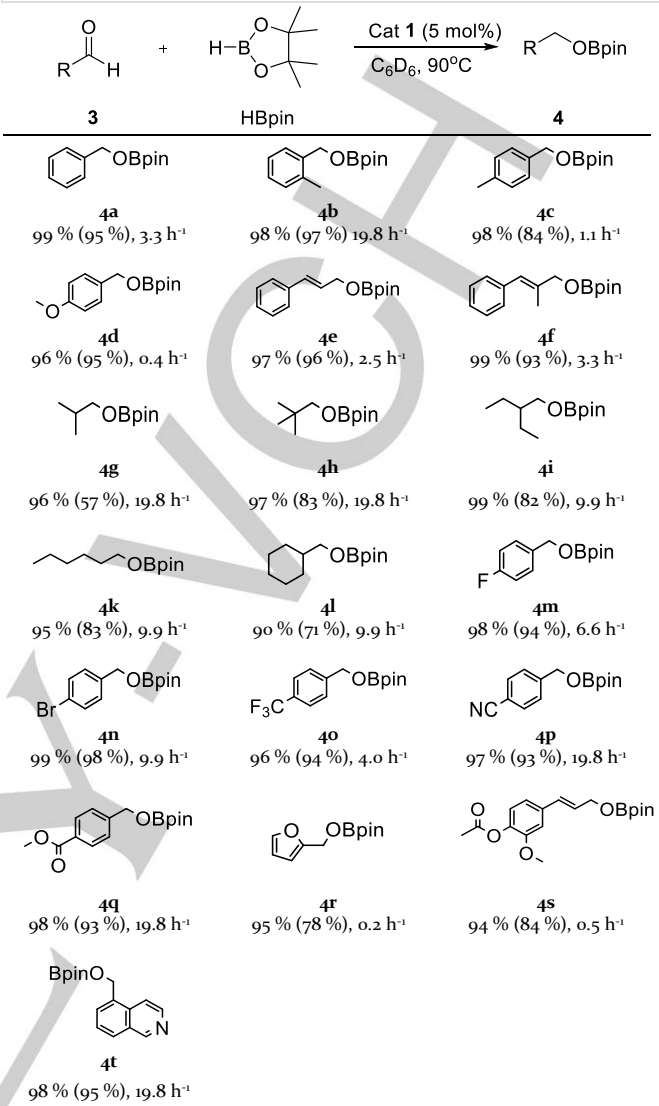


Figure 1. Molecular structures of (a) **1** and (b) **2c** obtained by X-ray crystallography. Thermal ellipsoids are shown at 50% probability. All hydrogen atoms are removed for clarity. (a) Selected bond lengths (Å) and angles (deg) of **1**: Si1-N1 1.896(4), Si1-N2 1.890(4), Si1-N3 1.729(3), N1-Si1-N2 68.0(2), N1-Si1-N3 102.6(2), N2-Si1-N3 103.3(2). (b) Selected bond lengths (Å) and angles (deg) of **2c**: Si1-N1 1.829(6), Si1-N2 1.813(5), Si1-N3 1.676(5), Si1-B1 2.008(6), B1-I1 2.244(7), B1-I2 2.257(8), B1-I3 2.258(8), N1-Si1-N2 72.1(2), N1-Si1-N3 113.5(3), N2-Si1-N3 111.9(3), I1-B1-I2 108.6(3), I1-B1-I3 109.7(3), I2-B1-I3 108.6(3), B1-Si1-N1 115.3(3), B1-Si1-N2 116.9(3), B1-Si1-N3 118.5(3).

Table 1. 1-Catalyzed Hydroboration of Aldehyde Substrates[a]

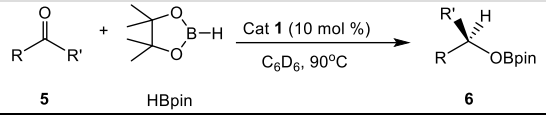


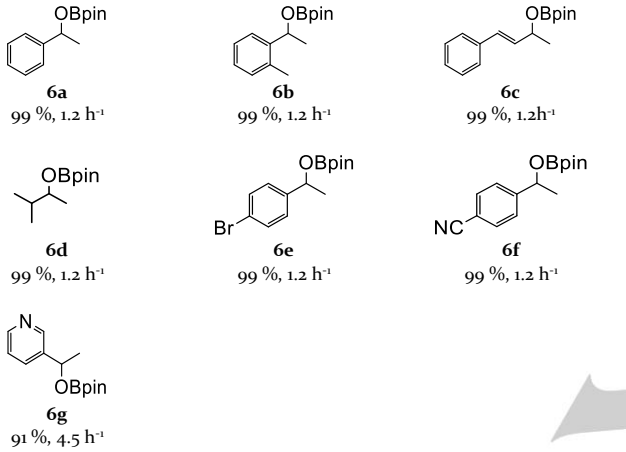
[a] Reaction conditions: aldehyde substrates (0.20 mmol), HBpin (0.22 mmol), C_6D_6 (0.40 mL), catalyst **1** (5 mol %). [b] Reaction performed at 90 °C. NMR yields are determined by ^{1}H NMR spectroscopy on the basis of an internal standard (1,3,5-trimethoxybenzene or cyclohexane) and the identity of the product was confirmed by the RCH_2OBpin resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate

The catalytic ability of compound **1** towards hydroboration of carbonyl compounds was examined. First, there was no reaction between PhC(O)H (**3a**) and HBpin in C_6D_6 at any temperature. In addition, compound **1** is unable to catalyze the hydroboration of carbonyl compounds in C_6D_6 at room temperature. Second, when the reaction temperature was increased to 90 °C, compound **1** (5 mol%) promoted the catalytic hydroboration of aromatic aldehyde PhC(O)H (**3a**) and its derivatives with electron donating and withdrawing substituents at different positions (**3b** – **3d**, **3m** – **3q**), to afford the corresponding borate esters in high yield (yield: 94 – 99%, Table 1). Third, 90 – 99% yield was achieved for the hydroboration of non-aromatic aldehydes (**3g** – **3l**). Fourth, functional groups such as C=C double bond (**3e** – **3f, 3s**), furan (**3r**) and pyridine (**3t**) remained intact after the catalysis, showing that the chemoselective

hydroboration of aldehydes is feasible. Fifth, as expected, a higher catalytic loading (10 mol%) and longer reaction times were required for the chemoselective hydroboration of ketones **5** as compared to aldehydes **3** due to the less electrophilic nature of ketones (Table 2). Various functional groups in aromatic ketones (**5c**, **5f**, **5g**) were also well tolerated in these reactions and the corresponding borate esters were afforded in high yields (86 – 99%).

Table 2. 1-Catalyzed Hydroboration of Ketone Substrates[a]





[a] Reaction conditions: ketone substrates (0.50 mmol), HBpin (0.55 mmol), C_6D_6 (0.40 mL), catalyst **1** (10 mol %). NMR yields are determined by ^{1}H NMR spectroscopy on the basis of an internal standard (1,3,5-trimethoxybenzene or cyclohexane) and the identity of the product was confirmed by the RC(R')(H)OBpin resonances. All the catalytic trials were repeated in triplicate

The catalyses were quenched by adding elemental sulphur to the reaction mixtures, after which they were changed from pale yellow to yellow/orange solution. The ^{29}Si{^{1}H} NMR spectroscopy shows a singlet at – 10.6 ppm, which is comparable with that of the amidinato amidosilanethione [L{(Me$_3$Si)$_2$N]Si=S] (– 16.9 ppm).[24] Together with HRMS data (*m*/*z* calcd for $C_{19}H_{33}N_3SSi$: 364.2243 $[(M + H)]^+$; found: 364.2242), an amidosilanethione appeared to be formed in the quencing. To further support the observation, compound **1** was reacted with elemental sulphur in benzene for 12 h at room temperature to afford the amidinato amidosilanethione [L{*i*Pr(Me)N}Si=S] (**7**) as dark yellow crystals (Figure 2, Scheme 2a). The ^{29}Si{^{1}H} NMR and HRMS data of dark yellow crystals are same as those obtained in the quenching (Figure S74). The results suggest that compound **1** was regenerated after the catalysis and underwent an oxidation with elemental sulphur to form compound **7** in the quenching. In other words, compound **1** should be the active catalyst in the hydroboration of carbonyl compounds.

After quenching, the catalytic reactions were filtered and volatiles were removed under reducted pressure. Compounds **4** and **6** were isolated by extracting the crude products with pentane or benzene.

Recently, Thomas et al. showed that nucleophiles such as NaO*t*Bu, Na[N(SiMe$_3$)$_2$], *n*Bu$_2$Mg, and *n*BuLi promoted decomposition of HBpin to form BH_3,[25] which was the active catalyst to mediate hydroboration of alkyne and alkene. To clarify whether BH_3 or compound **1** is the actual catalyst, TMEDA was added to the catalytic reactions, but the latter were unaffected (Scheme 2d, Figure S74), indicating that BH_3 did not form in the catalysis and coordinate with TMEDA.

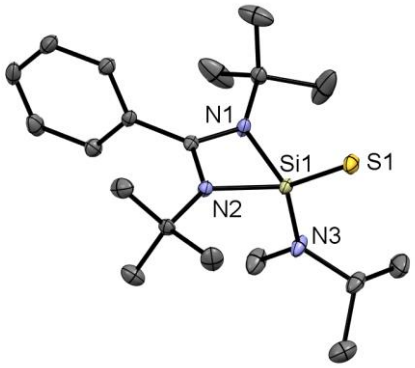
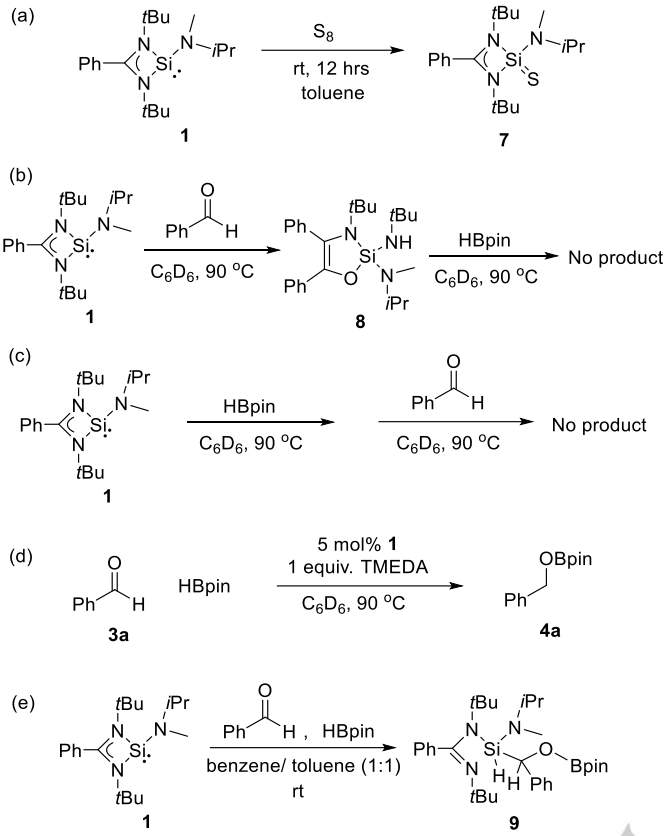


Figure 2. Molecular structure of **7** obtained by X-ray crystallography. Thermal ellipsoids are shown at 50% probability. All non-essential hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): Si1-N1 1.833(16), Si1-N2 1.835(15), Si1-N3 1.704(17) Si1-S1 1.985(7), N1-Si1-N2 71.1(7), N1-Si1-N3 107.8(8), N2-Si1-N3 108.4(8), N1-Si1-S1 121.3(6), N2-Si1-S1 120.6(6), N3-Si1-S1 118.4(6).

To understand the catalytic mechanism, compound **1** was treated stoichiometrically with compound **3a** in toluene or C_6D_6 at 90 °C for 3 hours to form compound **8** (Isolated yield: 42%, Scheme 2b, Figure S82), where the C–H bond of compound **3a** was activated along with expansion of the amidinate ring.[26] Compound **8** did not react with HBpin in C_6D_6 at 90 °C to form any hydroborated compounds. Together with long reaction time and low yield for the formation of compound **8**, it is suggested that compound **8** could not be an intermediate in the catalysis. In addition, compound **1** was treated stoichiometrically with HBpin in toluene at 90 °C overnight to form a mixture of unidentified products (Scheme 2c), which did not react with compound **3a** to form compound **4a**. These results suggest that the catalysis could proceed via a trimolecular mechanism. As such, compound **1** was then stoichiometrically reacted with a mixture of benzaldehyde **3a** and HBpin in a benzene/toluene mixture at room temperature to form compound **9** (Scheme 2e) and isolated as colorless crystals from the concentrated reaction mixture. The ^{11}B{^{1}H} (22.9 ppm) and ^{29}Si NMR signals (-44.3 ppm, J_{Si-H} = 197.8 Hz) are consistent with the presence of three-coordinate B and four-coordinate Si atoms in the molecular structure obtained by X-ray crystallography (Figure 3). The Si1-C16 (1.911(1) Å) and O1-B1 (1.352(2) Å) bond lengths indicate that they are single bonds. To understand whether compound **9** is the active catalyst, it was reacted with compound **3a** and/or HBpin in C_6D_6 at room temperature and 90 °C, but no reaction was observed for all conditions. Hence, compound **9** is deemed to be an off-catalytic-cycle product, this being consistent with the reaction conditions of **1**-catalyzed hydroboration where no catalysis was observed at room temperature.



Scheme 2. Mechanistic experiments

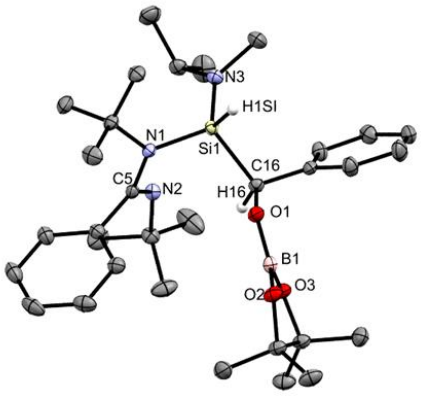
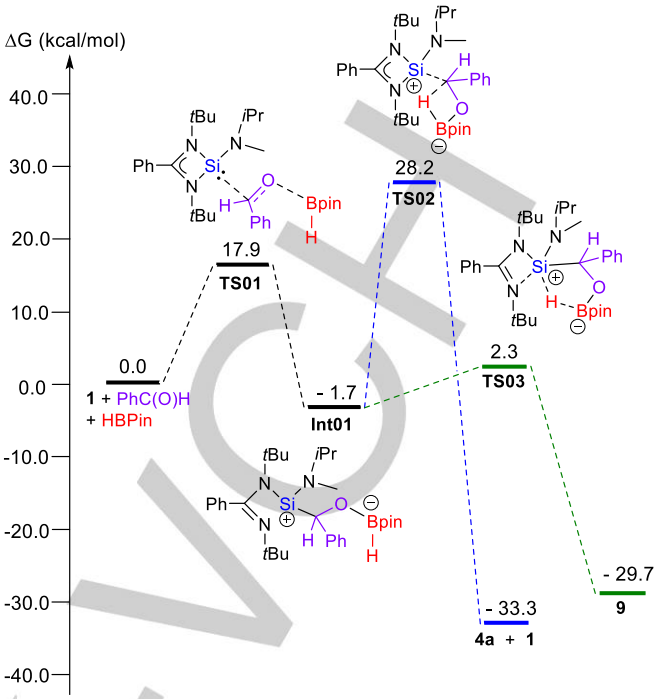


Figure 3. Molecular structure of **9** obtained by X-ray crystallography. Thermal ellipsoids are shown at 50% probability. All non-essential hydrogen atoms are removed for clarity. Selected bond lengths (Å) and angles (deg): C5-N2 1.285(2), C5-N1 1.413(2), N1-Si1 1.751(1), Si1-H1SI 1.40(2), Si1-C16 1.911(1), C16-H16 1.000, O1-B1-O2 121.6(1), O1-B1-O3 124.4(1), O2-B1-O3 114.0(1), B1-O1-C16 117.6(1), H16-C16-O1 109.6, H16-C16-Si1 109.6, O1-C16-Si1 104.7(9), C16-Si1-N1 109.5(6), C16-Si1-H1SI 99.6(8), N1-Si1-H1SI 108.5(8), N1-Si1-N3 115.03(7).



Scheme 3. Proposed mechanism for the formation of **9** and catalytic hydroboration.

On the basis of the molecular structure of compound **9**, the catalytic cycle for the hydroboration of PhC(O)H (**3a**) with HBpin is proposed and studied by DFT calculations (M06-2X-D3/def2-TZVPP//M06-2X-D3/def2-TZVP/SMD(Benzene)). In the reaction, the Si lone pair electrons on compound **1** attacks the C=O double bond of PhC(O)H (**3a**) and the oxygen atom further interacts with the vacant p orbital of HBpin via **TS01** (17.9 kcal/mol) to form a zwitterionic intermediate **Int01** (-1.7 kcal/mol). When the B-H bond in **Int01** attacks the silicon cation, the reaction proceeds via a five-membered ring **TS03** (2.3 kcal/mol; kinetic barrier: 4.0 kcal/mol) to form compound **9** (-29.7 kcal/mol). On the other hand, when the B-H bond in **Int01** attacks the carbon, the reaction goes through a four-membered ring **TS02** (28.2 kcal/mol, kinetic barrier: 29.9 kcal/mol) to form the borate ester [$Ph(H)_2COBpin$] (**4a**) and regenerate the catalyst, compound **1** (-33.3 kcal/mol). In this context, compounds **4a** and **9** are thermodynamic and kinetic products, respectively. **TS02** has a higher kinetic barrier than **TS03** probably due to the strong Si-C bond as well as the steric effect among the substituents at the four-coordinate silicon center. The DFT calculations are in accordance with the experimental conditions and observations. Reaction temperature of 25 °C resulted in the formation of compound **9**, but reaction temperature of 90 °C provides sufficient energy to overcome the kinetic barrier (**TS02**) for the catalytic hydroboration. It is expected that if the isopropylmethylamide is replaced by more sterically hindered substituents in **TS02**, the steric effect exerted at the silicon center could increase the free energy of the resulting transition state, making catalytic hydroboration infeasible. The hypothesis has been supported by a recent report where the amidinato silylenes with $–Si(SiMe_3)_3$ and $–N(SiMe_3)_2$ substituents do not show any catalytic capability toward hydroboration of carbonyl compounds.[27]

Conclusion

The amidinato isopropylmethylamidosilylene **1** is an efficient catalyst for the chemoselective hydroboration of aldehydes and ketones with HBpin to form borate esters. Mechanistic studies show that the Si lone pair electrons of compound **1** and the B vacant p orbital of HBpin activated the C=O double bond of aldehydes and ketones, the intermediates of which then underwent hydroboration with HBpin to yield the borate esters and regenerate compound **1**.

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Benzene, toluene and pentane were dried over Na/K alloy and distilled prior to use. C_6D_6 was dried over K metal and distilled prior to use. $CDCl_3$ was dried over CaH_2 and distilled prior to use. Chemicals were purchased from Sigma-Aldrich and used directly without further purification. The amidinato chlorosilylene [PhC(N*t*Bu)$_2$SiCl] was prepared according to literature.[22]

Synthesis of 1. Toluene (65 mL) was added into a 100 mL Schlenk flask containing the amidinato chlorosilylene[22] (10.0 mmol, 2.95 g) and lithium N-methylisopropyl amide (10.5 mmol, 0.83 g) at -78 ºC, following which, the resulting mixture was raised to room temperature and was stirred for 12 h. The dark orange suspension was filtered. The filtrate was concentrated and was kept at room temperature for two days to obtain colourless crystals in 75 % yield (2.49 g). M.p.: 167 ºC. ^{1}H NMR (399.5 MHz, C_6D_6, 25 °C): δ 7.05 – 7.07 (m, 1 H, Ar*H*), 6.86 – 7.05 (m, 4 H, Ar*H*) 4.19 (sept, 1 H, C*H*(CH$_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz), 2.52 (s, 3 H, NC*H*$_3$), 1.33 (d, 6 H, CH(C*H*$_3$)$_2$, $^3J_{H,H}$ = 6.4 Hz), 1.18 (s, 18 H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): 160.2 (N*C*N), 134.9 (Ar-*C*), 130.0 (Ar-*C*), 128.8 (Ar-*C*), 127.4 (Ar-*C*), 52.5 (*C*(CH$_3$)$_3$), 50.6 (NCH$_3$), 31.3 (C(*C*H$_3$)$_3$), 25.7 (*C*H(CH$_3$)$_2$), 22.5 (CH(*C*H$_3$)$_2$). ^{29}Si{^{1}H} NMR (79.4 MHz, C_6D_6, 25 °C): -4.6 (s).

Compound **1** (aldehydes: 3.3 mg, catalytic loading: 5 mol %; ketones: 16.6 mg, catalytic loading: 10 mol %) was added into a J-Young NMR tube and was washed down with 0.2 mL of C_6D_6. HBpin (aldehyde: 282 mg, 0.22 mmol, 1.1 equiv; ketone: 1408 mg, 0.55 mmol, 1.1 equiv.) was then added to the solution, followed by the addition of the substrate (aldehyde: 0.20 mmol, ketone: 0.5 mmol). The compounds were then washed down with 0.2 mL of C_6D_6 and the J-Young NMR tube was then shaken to ensure that all compounds have dissolved to obtain a homogeneous solution before heating the reaction mixture in a 90 ºC oil bath. The reaction was monitored via NMR spectroscopy and the yields were determined using a suitable internal standard. The chemical shifts of the products are in good agreement with the reported values in the literatures.[4]

Detailed experimental procedures and theoretical studies can be found in the Supporting Information.

Acknowledgements

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Keywords: silicon • silylene • carbene homolog • carbonyl • hydroboration

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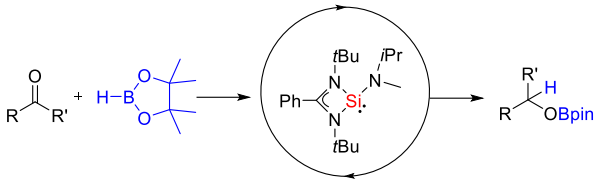
Entry for the Table of Contents



The amidinato isopropylmethylamidosilylene [LSiN(Me)*i*Pr] (L = PhC(N*t*Bu)$_2$) is an efficient catalyst for the chemoselective hydroboration of aldehydes and ketones with pinacolborane to form borate esters.