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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.9b06714 • Publication Date (Web): 10 Oct 2019

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A Versatile NHC-Parent Silyliumylidene Cation for Catalytic Chemo- and Regioselective Hydroboration.

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ABSTRACT: This study describes the first use of a silicon(II) complex, NHC-parent silyliumylidene cation complex $[(I_{Me})_2SiH]I$ (**1**, I_{Me} = :C{N(Me)C(Me)}$_2$) as a versatile catalyst in organic synthesis. Complex **1** (loading: 10 mol %) was shown to act as an efficient catalyst (reaction time: 0.08 h, yield: 94 %, TOF = 113.2 h^{-1}; reaction time: 0.17 h, yield: 98 %, TOF = 58.7 h^{-1}) for the selective reduction of CO_2 with pinacolborane HBpin to form the primarily reduced formoxyborane [pinBOC(=O)H]. The activity is better than the currently available base-metal catalysts used for this reaction. It also catalyzed the chemo- and regioselective hydroboration of carbonyl compounds and pyridine derivatives to form borate esters and N-boryl-1,4-dihydropyridine derivatives with quantitative conversions, respectively. Mechanistic studies show that the silicon(II) center in complex **1** activated the substrates and then mediated the catalytic hydroboration. In addition, complex **1** was slightly converted into the NHC-borylsilyliumylidene complex $[(I_{Me})_2SiBpin]I$ (**3**) in the catalysis, which was also able to mediate the catalytic hydroboration.

Introduction

Heavier group 14(II) complexes with a formal oxidation state of +2 often consist of a vacant orbital and a lone pair of electrons on the group 14 centers. As a result, they display both electrophilic and nucleophilic characters, leading to Lewis ambiphilicity. These electronic properties should enable heavier group 14(II) complexes to display reactivity that closely resembles that of transition metal complexes in the area of catalysis.[1] This was evidenced by Jones *et al.* that the two-coordinate (amido)(hydrido)germylene and -stannylene [Ar*(*i*Pr$_3$Si)NËH] (E = Ge, Sn; Ar* =2,4,6-*i*Pr{C(H)Ph$_2$}$_2$C$_6$H$_2$) are efficient transition-metal-like catalysts in mediating the hydroboration of unsaturated compounds, due to their far more reactive E^{II}–H bonds in comparison with classical E^{IV}–H bonds.[2,3] In addition, the two-coordinate Ge^{II} and Sn^{II} centers preserve their Lewis ambiphilic characters, which enable the σ-bond metathesis, oxidative addition and reductive elimination processes in the catalyses. Moreover, research groups of Wesemann and Zhao showed that the base-stabilized germylene and stannylene compounds [Ar$_{i\text{Pr}}$ËC(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$_3$) and [HC{C(Me)N(Ar)}{C(=CH$_2$)N(Ar)}Ge:] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) can catalyze the hydroboration of carbonyl compounds with the aid of the non-innocent ligands, respectively.[4a-b] Furthermore, Power et al. used the methoxystannylene pre-catalyst [{Ar$_{Mes}$Sn(μ-OMe)}$_2$] (Ar$_{Mes}$ = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$) to catalytically dehydrocouple amine-borane adducts.[4c]

Similarly, silicon(II) compounds with a formal oxidation state of +2 such as silyliumylidene cations (RSi:$^+$, R = supporting ligand) and hydridosilylenes (R(H)Si:) can show transition-metal-like reactivity in the area of small molecules activation.[5] For example, Inoue et al. showed that the NHC–arylsilyliumylidene cation complex $[Ar_{Mes}Si(I_{Me})_2]^+$ (I_{Me} = :C{N(Me)C(Me)}$_2$) can reduce CO_2 to form CO and activate the C–H bond of phenylacetylene.[6] Moreover, Kato et al. illustrated that the base-stabilized (amido)(hydrido)silylenes underwent the reversible oxidative addition of Si^{IV}–H and P^{III}–H bonds at room temperature, in addition to the uncatalyzed insertion of the Si^{II}–H bonds with unsaturated C–X bonds (X = C, N, O, etc.).[7] However, catalytic organic transformations mediated by silicon(II) compounds surprisingly remain unexplored. It could be possibly due to the supporting ligands in a silicon(II) compound, which impart kinetic and thermodynamic stabilization effects on the highly reactive silicon center.[8] As a consequence, its Lewis ambiphilic character is not pronounced and the high catalytic potential of a silicon(II) compound is suppressed. To the best of our knowledge, only one example of silicon(II) compounds shows catalytic capability, whereby Jutzi et al. used the cyclopentadienyl silyliumylidene cation [Cp*Si]$^+$ (Cp* = C$_5$Me$_5$) to catalyze the controlled degradation of oligo(ethyleneglycol) diethers.[9] In this context, it is imperative to develop a strategy to activate

the catalytic ability of stable silicon(II) compounds, which would greatly advance sustainable catalysis due to the high abundance and non-toxicity of silicon.

Recently, we described the synthesis of an NHC-parent silyliumylidene cation complex [$(I_{Me})_2$SiH]I (**1**, Figure 1) and its transition-metal-like reactivity in functionalizing the *ortho*-C–H bond of fluorobenzene.[10] Considering the chemistry of the above-mentioned base-stabilized silyliumylidene cations and hydridosilylenes, it is anticipated that **1** could be a promising candidate to catalyze organic reactions due to its dual functionality: Si^{II} cation and reactive Si^{II}–H bond. In this context, we were highly interested in investigating its catalytic capability. Herein, we report the NHC-parent silyliumylidene cation-catalyzed chemo- and regioselective hydroboration of carbon dioxide, carbonyl compounds and pyridine derivatives (Figure 1).

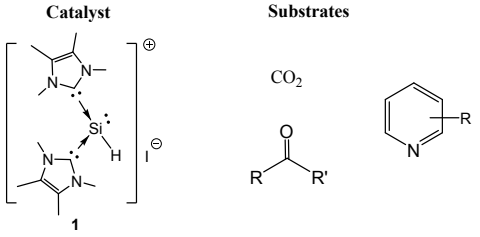


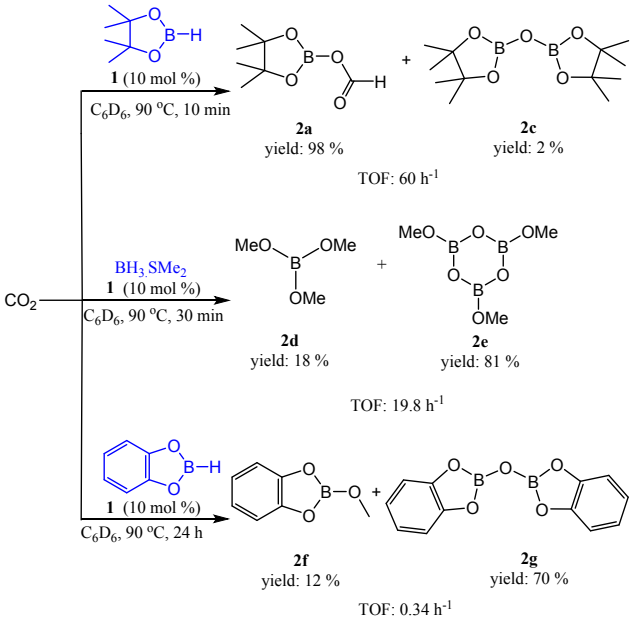
Figure 1. The NHC-parent silyliumylidene cation complex **1** and substrates.

Results and Discussion

The catalytic ability of the NHC-parent silyliumylidene cation complex **1** toward hydroboration of CO_2 with pinacolborane HBpin was first examined, considering that non-metal compounds have been rarely used as homogeneous catalysts for such reaction, the obtained turnover frequencies (TOF) and selectivity are often low, leading to a mixture of methoxyborane [pinBOMe] (**2b**) and diborate ether [$(pinB)_2O$] (**2c**). To begin with, there was no reaction between CO_2 and borane (HBpin, $BH_3.SMe_2$, HBcat) in C_6D_6 at 90 °C. However, in the presence of **1** (10 mol %), the reduction of CO_2 with HBpin in C_6D_6 at 90 °C was extremely clean, resulting in the formation of the formoxyborane [pinBOC(O)H] (**2a**, reaction time: 0.08 h, yield: 94 %, TOF = 113.2 h^{-1}; reaction time: 0.17 h, yield: 98 %, TOF = 58.7 h^{-1}; Scheme 1; see the Supporting Information, Table S1), along with trace amount of the diborate ether **2c** (Yield: <2 %). No other identifiable boron-containing products such as methoxyborane **2b** were found in the reaction mixture when increasing the reaction time or temperature. Moreover, complex **1** (10 mol %) was able to catalyze the reduction of CO2 under air and/or in wet C_6D_6 to afford **2a** and **2c**, but the yield of **2a** decreased (Table S2). It is because HBpin decomposed in these reaction conditions to give **2c** and hence the yield of the latter increased. When the amount of complex **1** decreased (5 mol %), the catalytic hydroboration was incomplete (90 % conversion, Table S1) in 0.5 h, but the selectivity was still observed. It is noteworthy that complex **1** is the first non-metal catalytic system that selectively delivers the primarily reduced formoxyborane **2a**. Complex **1** is one of the very few examples that catalyze the selective reduction of CO_2, including the main-group and transition metal catalysts, namely an amine-lithium borohydride [(L)Li][$HBPh_3$] (L = $N(CH_2CH_2NMe_2)_3$, TOF = 10 h^{-1}),[11] a NHC-copper [I_{Ar}Cu(O*t*Bu)] (yield: 85 %, TOF = 0.35 h^{-1})[12] and a PSiP-pincer-palladium complex [{^{Ph}PSiP}PdOTf] [^{Ph}PSiP = $Si(Me)(2\text{-}PPh_2\text{-}C_6H_4)_2$] (yield: 93 %, TOF = 1550 h^{-1}).[13] Moreover, **1** exceeds the base-metal catalysts, [(L)Li][$HBPh_3$] and [I_{Ar}Cu(O*t*Bu)], in terms of both reaction time and TOF. Furthermore, the TOF of the hydroboration of CO_2 with HBpin far surpasses the TOF values of the activated non-transition metal catalysts (TOF = 0.07 - 2.5 h^{-1}) and even the non-metal catalysts (TOF = 0.40 - 14.5 h^{-1}).[14]

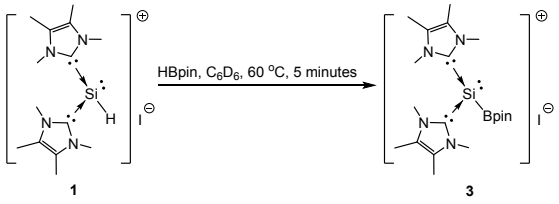
When more potent [$BH_3.SMe_2$] was used instead of HBpin, 10 mol % of complex **1** catalyzed the reduction of CO_2 with >99 % conversion to form a mixture of the borate ethers [$B(OMe)_3$] (**2d**) and [$BO(OMe)]_3$ (**2e**) in a ratio of 1:4 in 0.5 h (TOF = 19.8 h^{-1}, Scheme 1, Table S3), but selectivity cannot be achieved.

On the other hand, the **1**-catalyzed reduction of CO_2 with catecholborane HBcat was slowly proceeded (24 h, >99 % conversion, TOF = 0.34 h^{-1}, Table S4) to afford a mixture of diborate ether [$(catB)_2O$] (major product, yield: 70 %) and methoxyborane [catBOMe] (minor product, yield: 12 %). In comparison with other examples, the above-mentioned NHC-copper complex [I_{Ar}Cu(O*t*Bu)] did not catalyze the selective reduction of CO_2 with HBcat,[12] whereas the (amido)(hydrido)stannylene [Ar*(*i*Pr_3Si)NSnH] outperformed **1** using HBcat to non-selectively reduce CO_2 into [(catB)OMe] and [$(catB)_2O$] (TOF = 1188 h^{-1}, yield of each compound was not reported).[3]



Scheme 1. **1**-catalyzed reduction of CO_2. (All the catalytic trials were repeated in triplicate)

Upon completing the catalytic hydroboration of CO_2 with HBpin, a weak singlet at ca. δ 0.9 ppm, in addition to the signal of **2a**, was observed in ^{11}B (Figure S12b) and ^{11}B{^{1}H} NMR spectroscopy. These indicate that a new boron compound, which does not have any H atom on the boron atom, was formed in the catalysis. To clarify these phenomena, complex **1** was treated with excess HBpin in C_6D_6 at 60 °C for five minutes, whereby same ^{11}B NMR signal at δ 0.92 ppm (singlet) was observed, indicating formation of the new boron compound. The reaction was further analyzed by ^{1}H and ^{29}Si NMR spectroscopy. The ^{1}H NMR spectrum shows a set of signals due to methyl protons of I_{Me} and B*pin*. The ^{29}Si NMR spectrum displays a singlet at δ -93.0 ppm (^{29}Si{^{1}H} NMR: δ -95.6 ppm, singlet; Figures S4 - S5), which is an intermediate value between that of **1** (δ -77.9 ppm, $^1J_{Si-H}$ = 283 Hz) and the NHC-hydridosilylene complex [I_{Me}–:SiH(Si*t*Bu$_3$)] (δ -137.8 ppm).[10,15] The upfield Si NMR signal corresponds to a Si^{II} cationic center and there is no hydrogen atom on the Si center. On the basis of NMR spectroscopic data, the new boron compound formed in the reaction is an NHC-borylsilyliumylidene complex [(I_{Me})$_2$SiBpin]I (**3**, Scheme 2). Its composition is also supported by the theoretical ^{29}Si NMR value (δ -94.0 ppm, B3LYP/6-311^{++}G(2df,2pd)//B3LYP/6-31G**, Table S12) and HRMS. After work-up, complex **3** was isolated as colorless solid (yield: ca 30 % for 5-min reaction time). Compound **3** is highly unstable in solution and hence obtaining suitable single crystals for X-ray crystallography is still in progress. In this context, its structure was simulated by DFT calculations (Figure S89). Complex **3** easily decomposed in toluene and ethereal solvents to form a white insoluble precipitate, which comprises a mixture of an NHC-boronium cation [(I_{Me})$_2$Bpin]I (^{11}B NMR: δ 2.37 ppm), an imidazolium salt [I_{Me}–H]I (see Figure S88) and unidentified products. However, they are inactive in any catalytic hydroboration.



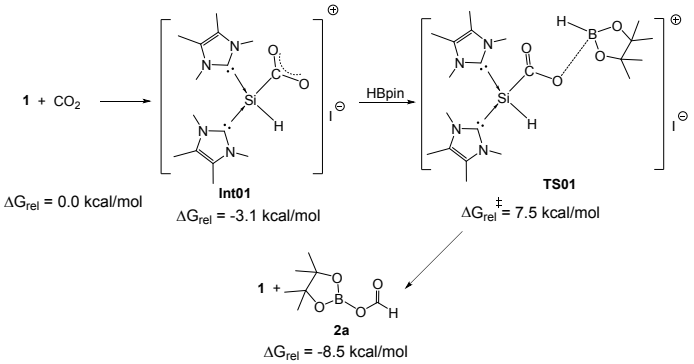
Scheme 2. Synthesis of compound **3.**

In supporting complex **3** that involves in the catalysis, it was used to catalyze the hydroboration of carbon dioxide with HBpin, whereby selective reduction of CO_2 was achieved to obtain **2a** (2.5 mol %; time: 0.17 h, yield: 94 %, TOF = 227 h^{-1}, Table S1).

These results brought up a question of whether complex **1** or **3** is a genuine catalyst in the hydroboration of CO_2.

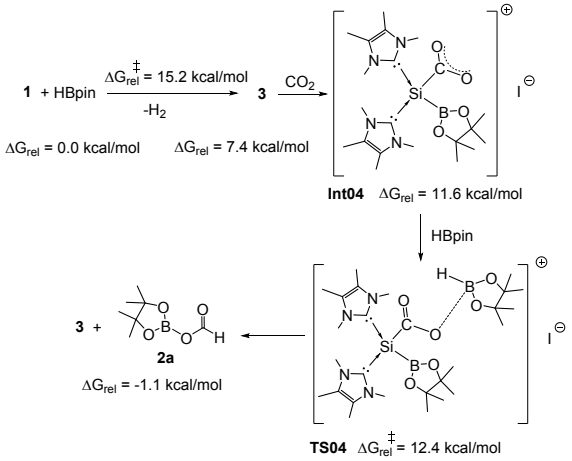
Considering that the conversion of complex **1** into complex **3** is slight (see above), it is suggested that complex **1** could prefer to react with CO_2 instead of HBpin in the first step of catalysis. To gain insight, complex **1** was used to react with CO_2 in C_5D_5N at -40 °C, whereby the ^{29}Si NMR signal (-68.9 ppm, $^1J_{SiH}$ = 202 Hz, -40 °C, Figure S10) is downfield shifted in comparison with that of **1**, indicating that the Si lone pair electrons interact with CO_2 to form **Int01** (Scheme 3). The Si–H coupling constant, as well as the absence of signal for formate –C(O)H moiety in the ^{1}H NMR spectrum, indicate that CO_2 did not insert into the Si–H bond in **1** during the catalysis.[19a] When stoichiometric amount of HBpin was subsequently added to the reaction mixture, compound **2a** was afforded, along with regeneration of complex **1**. Notably, the reaction of complex **1** and CO_2 was found to be reversible upon the removal of CO_2 and volatiles of the reaction mixture *in vacuo* at room temperature. As a result, complex **1** does not resemble the (amido)(hydrido)germylene and -stannylene to catalyze hydroboration through σ-E–H bond metathesis mechanism (E = Ge, Sn).[2,3]

DFT calculations were then performed (Scheme 3). It was found out that complex **1** is capable of mediating the catalysis, whereby the Si lone pair electrons interact with CO_2 to form **Int01** (ΔG = -3.1 kcal/mol). The HOMO-3 of **Int01** shows that the Si lone pair orbital interacts with the π* orbital of CO_2 (Figure S91). Accordingly, the NBO analysis shows that the Si–C_{CO_2} bond results from the overlap of a *sp*$^{2.14}$ hybrid on Si with a *sp*$^{2.59}$ hybrid on C (Table S13). In the formation of **Int01**, the natural charge of the Si atom increases from 0.44 (compound **1**) to 1.02 (**Int01**), while that of the C_{CO_2} atom decreases from 1.03 (**1**) to 0.54 (**Int01**). Subsequently, the H–B bond of HBpin inserts into the C=O bond via a low kinetic barrier (**TS01**; $\Delta G_{\mathbf{Int01}\rightarrow\mathbf{TS01}}$ = 10.6 kcal/mol at 24 °C, Scheme S2), which results in the formation of the formoxyborane **2a** and regeneration of **1** (ΔG = -8.5 kcal/mol, Scheme S2). In other words, the Si lone pair of electrons in complex **1** is Lewis basic enough to activate CO_2 for subsequent hydroboration, whereas the Si–H bond is not sufficiently hydridic to activate CO_2. The mechanism is in contrast to σ-E–H bond metathesis mechanism (E = main-group element) in main-group element catalyzed hydroboration.[14c] Moreover, the interaction of the Si lone pair in **1** with **2a** is endergonic (ΔG = 7.0 kcal/mol, Scheme S5), whereas that with CO_2 is exergonic (Scheme 3). This suggests that complex **1** does not prefer to further react with **2a** after a catalytic cycle, while it chooses to react with CO_2 again and achieves the selective reduction.



Scheme 3. Calculated Gibbs free energies (ΔG_{rel}) for the reaction of **1**, CO_2 and HBpin at 24 °C (M06-2X/def2-

TZVP). Int and TS stands for intermediate and transition state. For the detailed mechanism with arrow pushing, see Scheme S3.



Scheme 4. Calculated Gibbs free energies (ΔG_{rel}) via **3** at 24 °C (M06-2X/def2-TZVP).

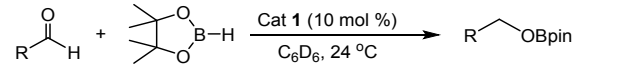
DFT calculations also support that the catalytic hydroboration of CO_2 via complex **3** is feasible (ΔG = -1.1 kcal/mol; M06-2X/def2-TZVP, Scheme 4, Scheme S1), especially complex **3** catalyzes the hydroboration of CO_2 via a lower kinetic barrier ($\Delta G_{3\rightarrow TS04}$ = 5.0 kcal/mol) in comparison with the mechanism via **TS01**. It is consistent with experimental results that the activity of **3** in terms of TOF is much higher than that of **1** (Table S1). However, the kinetic barrier for the formation of **3** is relatively high ($\Delta G_{1\rightarrow 3}$ = 15.2 kcal/mol), which suggests that the mechanism via **TS01** should be more dominant than that via **3** and **TS04** in the catalysis.

Inoue et al. reported that the NHC-arylsilyliumylidene cation $[RSi(I_{Me})_2]Cl$ with steric hindered substituent 2,6-$Mes_2C_6H_3$ (R = Ar_{Mes}) reacted with CO_2 at room temperature to afford the NHC-arylsilaacylium $[RSi(=O)(I_{Me})_2]Cl$.[6] In contrast, when the Ar_{Mes} substituent was replaced by a lesser steric hindered substituent 2,4,6-$i Pr_3C_6H_2$ (R = Tipp), only insoluble amorphous precipitates were formed in the reaction at room temperature. Considering the steric environment of complex **1** and the catalytic conditions, it is anticipated that the **1**-catalyzed reduction of CO_2 with HBpin via an NHC-parent silaacylium intermediate is not possible. To support this hypothesis, the reaction of **1** with CO_2 was studied by DFT calculations. The kinetic barrier and free energy for the formation of an NHC-parent silaacylium intermediate $[(I_{Me})_2Si(=O)H]I$ (kinetic barrier: ΔG = 13.4 kcal/mol, Scheme S4) are energetically less favorable in comparison with those for the formation of formoxyborane **2a** (Scheme 3).

The presence of I_{Me} in complex **1** also brought up a question of whether I_{Me} dissociates from complex **1** and then catalyzes the hydroboration of CO_2. As such, 0.1 mol % of I_{Me}, which presumes small amount of the NHC ligand being dissociated during the catalysis, was used to mediate the reduction of CO_2 with HBpin in C_6D_6 at 90 °C for 0.25h, resulting in non-selective catalysis (19 % conversion, Table S1) to afford a mixture of [pinBOC(O)H] (**2a**), [pinBOMe] (**2b**) and [$(pinB)_2O$] (**2c**). In comparison with the catalytic results mediated by **1**, it is suggested that I_{Me} did not dissociate and involve in the hydroboration of CO_2.

Theoretical studies and experimental results show that complex **1** is the first stable silicon(II) species undergoing catalytic selective hydroboration with CO_2. Interestingly, the proposed mechanism is very similar to a recent report of the PNP pincer ligand-iron(II) hydride complex-catalyzed hydroboration of alkynes, whereby the iron(II) hydride complex [LFeH] (L = 2,5-bis-(phosphinomethyl)pyrrolide) can convert into the corresponding iron(II) boryl complex [LFeBpin] in the catalysis, along with both complexes were capable of catalyzing the hydroboration.[16]

Table 1. Scope of Aldehyde Substrates[a]



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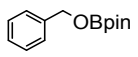
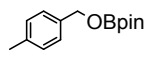
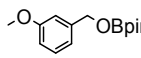
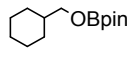
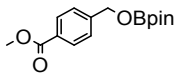
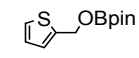
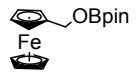
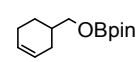
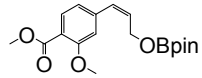
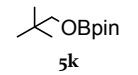
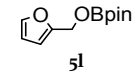
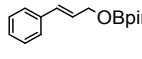
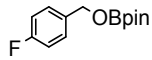
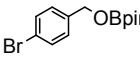
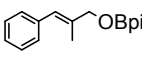
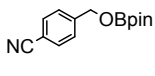
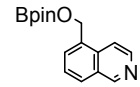
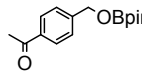
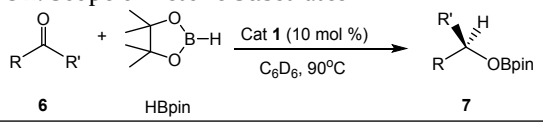
 **5a** >99 % (89 %), 115.8 h^{-1}	 **5b** >99 % (91 %) 115.8 h^{-1}	 **5c** >99 % (87 %), 115.8 h^{-1}
 **5d** >99 % (87 %), 115.8 h^{-1}	 **5e** >99 % (83 %), 115.8 h^{-1}	 **5f** >99 % (82 %), 115.8 h^{-1}
 **5g** >99 % (86 %), 118.8 h^{-1}	 **5h** >99 % (86 %), 115.8 h^{-1}	 **5j** >99 % (85 %), 115.8 h^{-1}
 **5k** >99 % (83 %), 19.8 h^{-1}	 **5l** >99 % (89 %), 23.8 h^{-1}	 **5m** >99 % (89 %), 115.8 h^{-1}
 **5n** >99 % (85 %), 115.8 h^{-1}	 **5p** >99 % (89 %), 17.0 h^{-1}	 **5q** >99 % (85 %), 29.7 h^{-1}
 **5r** >99 % (91 %), 39.6 h^{-1}	 **5s** >99 % (89 %), 39.6 h^{-1}	 **5t**[b] >99 % (91 %), 14.9 h^{-1}

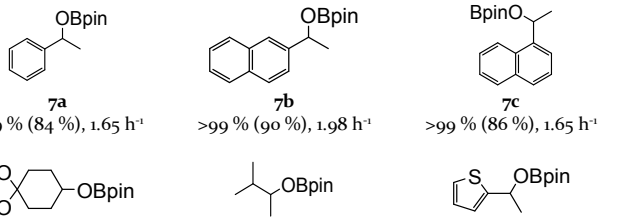
[a]Reaction conditions: aldehyde substrates (0.10 mmol), HBpin (0.11 mmol), C_6D_6 (0.50 mL), catalyst **1** (10 mol %). [b]Reaction performed at 40 °C. NMR yields are determined by ^1H NMR spectroscopy on the basis of the consumption of the aldehyde and the identity of the product was confirmed by RCH_2OBpin or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate.

Following the hydroboration of CO_2, the catalytic ability of complex **1** towards hydroboration of carbonyl compounds was further examined. First, there were no reaction between carbonyl compounds with HBpin in C_6D_6 at room temperature. Second, complex **1** (10 mol %) was

found to be capable of catalyzing hydroboration of aromatic aldehyde ArC(O)H (Ar = Ph, **4a**, Table 1, Table S5) as well as its derivatives with electron donating (Ar = MeC_6H_4 **4b**, $MeOC_6H_4$ **4c**) and withdrawing substituents ($MeCO_2C_6H_4$ **4e**, FC_6H_4 **4n**) at different positions in 10 minutes, which quantitatively afforded the corresponding borate esters. In these reactions, the activity of **1** in terms of TOF (17 - 115.8 h^{-1}) is intermediate between the heavier group 14 element(II) compounds, namely (amido)(hydrido)germylene (17 - 67 h^{-1}) and -stannylene (400 - 800 h^{-1}).[2] Third, >99 % yield was achieved for the hydroboration of non-aromatic aldehydes, namely cyclohexanecarboxaldehyde **4d** and 2,2-dimethylpropanal **4k**. Complex **1** is less active in these reactions (TOF = 19.8 - 115.8 h^{-1}) in comparison with those catalyzed by the (amido)(hydrido)germylene and -stannylene (TOF = >2000 h^{-1}).[2] Fourth, the olefinic functionality in 3-cyclohexene-1-carboxaldehyde **4h**, cinnamaldehyde **4m** and 2-methyl-3-phenylprop-2-enal **4q** remains intact in the catalyses, showing that the chemoselective hydroboration of aldehydes is possible. Such selectivity is also observed in the hydroboration of thiophene-2-carbaldehyde **4f**, ferrocenecarboxaldehyde **4g**, furan-2-carbaldehyde **4l**, 4-formylbenzonitrile **4r** and isoquinoline-5-carboxaldehyde **4s** in which the functional groups such as nitrile and pyridine were not hydroborated. Such chemoselective catalyses have not been reported before for heavier group 14 element(II) compounds.[2] In addition, excellent chemoselectivity of aldehydes over ketones was observed in the catalytic hydroboration of 4-acetylbenzaldehyde **4t**. Fifth, as expected, a higher reaction temperature (90 °C) and longer reaction time were required for the chemoselective hydroboration of ketones when compared to aldehydes due to their steric nature (Table 2, Table S6). Various functional groups in aromatic and aliphatic ketones were well tolerated in these reactions and the corresponding borate esters were afforded in high yields.

Table 2. Scope of Ketone Substrates[a]

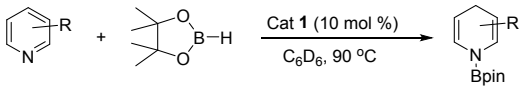


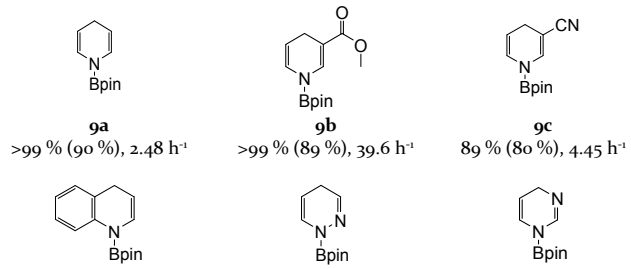


[a]Reaction conditions: ketone substrates (0.10 mmol), HBpin (0.11 mmol), C_6D_6 (0.50 mL), catalyst **1** (10 mol %). NMR yields are determined by ^{1}H NMR spectroscopy on the basis of the consumption of the ketone and the identity of the product was confirmed by RC(R')(H)OBpin or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate.

The catalytic ability of complex **1** toward the hydroboration of pyridine derivatives was also studied (Table 3, Table S7). First, there was no hydroboration reaction between HBpin and pyridine derivatives in C_6D_6 at 90 °C. Second, 10 mol % of **1** catalyzed the reaction of pyridine **8a** with one equivalent of HBpin in C_6D_6 at 90 °C to quantitatively form N-boryl-1,4-dihydropyridine **9a** as the only regioisomer (TOF = 2.48 h^{-1}), whereas the 1,2-hydroborated product was not formed. Such regioselectivity is comparable with metal-free $B(C_6F_5)_3$ catalyst (yield of **9a**: >99 %)[17] and the 1,3,2-diazaphosphenium triflate catalyst (yield of **9a**: 96 %).[18] In addition, such catalysis has not been reported for heavier group 14 element(II) compounds. Third, both chemo- and regioselectivity were observed in the **1**-catalyzed hydroboration of functionalized pyridines **8b**-**c** and ring-fused pyridine **8d**. Third, the scope of substrates can further be extended to 1,2- and 1,3-pyrazines **8e**-**f**.

Table 3. Scope of Pyridine Substrates[a]





[a]Reaction conditions: pyridine substrates (0.10 mmol), HBpin (0.11 mmol), C_6D_6 (0.50 mL), catalyst **1** (10 mol %). NMR yields are determined by ^{1}H NMR spectroscopy on the basis of the consumption of the pyridine and the identity of the product was confirmed by C=C or resonances. Isolated yields are shown in parentheses. All the catalytic trials were repeated in triplicate.

Upon completing the above-mentioned catalysis (Tables 1 – 3), complex **3** was observed (Figures S18 - 20, S33a, S43, S45, S47, S49, S53, S65, S79, S81, S83a and S85a). These indicate that both complexes **1** and **3** are involved in the catalyses. Similar to the case of CO_2, it is suggested that the Si lone pair of electrons in complexes **1** and **3** activate the carbonyl compounds, which are then reacted with HBpin to form the corresponding hydroborated products, along with the regeneration of the catalysts.[19b,21] In case of pyridine derivatives, it is proposed that the catalysis proceeds through coordination of **8** with HBpin first,[17] which induces nucleophilic attack of complexes **1** and **3** at the para-position of **8** due to lesser steric congestion.[20,21] Subsequent dearomatization of **8** results in displacing the hydride from the borane moiety, which then attacks at the para-position to afford **9**, along with the regeneration of the catalysts. In supporting complex **3** that involves in

these catalyses, it was used to catalyze the hydroboration of benzaldehyde **4a** (Table S8), 1,4-dioxaspiro[4.5]decan-8-one **6d** (Table S9) and pyridine **8a** (Table S10), whereby complex **3** shows better activity in terms of TOF in comparison with complex **1**.

Conclusion

The NHC-parent silyliumylidene cation complex **1** is a versatile catalyst to catalyze the metal-free chemo- and regioselective hydroboration of carbon dioxide, carbonyl compounds and pyridine derivatives with HBpin to form formoxyborane, borate esters and N-boryl-1,4-dihydropyridine derivatives, respectively. In particular, complex **1** is the first non-metal catalytic system that efficiently and selectively delivers the primarily reduced formoxyborane. Its activity is better than that of currently available base-metal catalysts used for such reaction. Mechanistic studies show that complex **1** exhibits transition-metal-like catalysis, whereby the silicon(II) center in complex **1** activates the substrates and then mediates the catalytic hydroboration. In addition, complex **1** was slightly converted into the NHC-borylsilyliumylidene complex $[(I_{Me})_2SiBpin]I$ (**3**) in the catalysis, which was also able to mediate the catalytic hydroboration. It seems reasonable that complex **1** will find a range of other catalytic applications (e.g. C–C bond formation, C–H bond functionalization[10]). We are currently investigating this possibility and will report on our findings in due course. The trapping of reactive intermediates with various Lewis bases and acids will also be reported in the course of time.

Experimental Procedure

General procedures. All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Compound **1** was prepared according to the literature procedure.[10] Toluene was dried over Na/K alloy and distilled prior to use. C_6D_6 and d_5-pyridine were dried over K metal and distilled prior to use. CH_2Cl_2 and $CDCl_3$ were dried over CaH_2 and distilled prior to use. Chemicals were purchased and used directly without further purification. The ^1H, ^{11}B, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, ^{29}Si and $^{29}Si\{^1H\}$ NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C_6D_6, $CDCl_3$ or d_5-pyridine, and the chemical shifts are relative to $SiMe_4$ for ^1H, ^{13}C and ^{29}Si; $BF_3{\cdot}Et_2O$ for ^{11}B, respectively. The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Coupling constants *J* are given in Hertz (Hz). Melting points were measured in sealed glass tubes and were not corrected. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University.

Synthesis of 2a – 2c. Catalyst **1** (4.0 mg, 0.01 mmol), internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol, 5 equiv.) and 0.5 mL of C_6D_6 were mixed in a J-Young NMR tube. Pinacolborane, HBpin (14.5 µL, 0.10 mmol, 10 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO_2 gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ^1H NMR signals of pinBOC(=O)H (**2a**) at 0.93 ppm and $(pinB)_2O$ (**2c**) at 1.02 ppm with reference to the –OMe and C_{Ar}–H protons (3.36, 6.20 ppm) of the internal standard, 1,3,5-trimethoxybenzene. The NMR data of **2a** and **2c** can be found in the Supporting Information.

Synthesis of 2d – 2e. Catalyst **1** (4.0 mg, 0.01 mmol), internal standard methyltriphenylsilane (27.4 mg, 0.10 mmol, 10 equiv.) and 0.5 mL of C_6D_6 were mixed in a J-Young NMR tube. Borane dimethylsulfide, $BH_3.SMe_2$ (9.5 µL, 0.10 mmol, 10 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO_2 gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ^1H NMR signals of $B(OMe)_3$ (**2d**) at 3.42 ppm and $(MeOBO)_3$ (**2e**) at 3.34 ppm with reference to the –Me protons (0.71 ppm) of the internal standard, methyltriphenylsilane. The NMR data of **2d** and **2e** can be found in the Supporting Information.

Synthesis of 2f – 2g. Catalyst **1** (4.0 mg, 0.01 mmol), internal standard 1,3,5-tri-*tert*-butylbenzene (2.5 mg, 0.01 mmol, 1 equiv.) and 0.5 mL of C_6D_6 were mixed in a J-Young NMR tube. Catecholborane, HBcat (10.7 µL, 0.10 mmol, 10 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO_2 gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ^1H NMR signals of catBOMe (**2f**) at 3.39 ppm and $(catB)_2O$ (**2g**) at 6.72 – 6.75 ppm with reference to the -Me and C_{Ar}-H protons (1.35, 7.42 ppm) of the internal standard, 1,3,5-tri-*tert*-butylbenzene. The NMR data of **2f** and **2g** can be found in the Supporting Information.

Synthesis of 3. Compound **1** (4.0 mg, 0.01 mmol) and pinacolborane, HBpin (14.5 µL, 10 equiv, 0.10 mmol) were mixed with 0.5 mL of C_6D_6 in a J-Young NMR tube at room temperature. The resulting mixture was stirred at 60 °C for 5 min. Volatiles were immediately removed at 60 °C *in vacuo*. The residue was extracted with benzene (1 mL). After filtration, the filtrate was removed *in vacuo* to afford compound **3** as a colorless solid (1.6 mg, Yield: 30 %). When the reaction was performed for 16 hours, the yield of compound **3** is 63 % (3.3 mg). Mp: 167 °C (dec.). HRMS (ESI): m/z calcd for $C_{20}H_{37}BIN_4O_2Si$ $[M\text{-}H]^+$: 531.18236; found: 531.18240. Satisfactory elemental analysis data could not be obtained due to compound **3** being highly sensitive to moisture and air. ^1H NMR (395.9 MHz, 24 °C, C_6D_6, ppm): δ = 3.69 (s, 12H, N-CH_3), 1.75 (s, 12H, C-CH_3), 1.08 (s, 12H,

Bpin-CH_3). ^{11}B NMR (128.41 MHz, 24 °C, C_6D_6, ppm): δ = 0.92. ^{11}B{^{1}H} NMR (128.41 MHz, 24 °C, C_6D_6, ppm): δ = 0.95. ^{29}Si NMR (78.65 MHz, 24 °C, C_6D_6, ppm): δ = -93.0. ^{29}Si{^{1}H} NMR (78.65 MHz, 24 °C, C_6D_6, ppm): δ = -95.6. The Si NMR signal is relatively weak due to quadrupolar broadening with the boron nucleus (I = 3/2).

The catalytic hydroboration of carbon dioxide using 3 as the catalyst. Catalyst **3** (1.3 mg, 0.0025 mmol), internal standard 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol, 20 equiv.) and 0.5 mL of C_6D_6 were mixed in a J-Young NMR tube. Pinacolborane, HBpin (14.5 μL, 0.10 mmol, 40 equiv.) was then added. The NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution. The J-Young NMR tube was lifted from liquid nitrogen and 1 bar of CO_2 gas was then added. The reaction mixture was warmed to room temperature and then heated at 90 °C. The reaction was monitored by NMR spectroscopy. The yields of products were reported according to the integration of ^{1}H NMR signals of pinBOC(=O)H (**2a**) at 0.93 ppm and $(pinB)_2O$ (**2c**) at 1.02 ppm with reference to the –OMe and C_{Ar}–H protons (3.36, 6.20 ppm) of the internal standard, 1,3,5-trimethoxybenzene. The NMR data of **2a** and **2c** can be found in the Supporting Information.

General procedures for the catalytic hydroboration of carbonyl compounds and pyridine derivatives using 1 as the catalyst. Catalyst **1** (4.0 mg, 0.01 mmol) and 0.5 mL of C_6D_6 were added into a J-Young NMR tube. Pinacolborane, HBpin (16.0 μL, 0.11 mmol, 10.1 equiv.) and substrates (0.10 mmol, 10 equiv.) were then added. The reaction conditions are indicated in Tables S5 – S7 in the Supporting Information and the reactions were followed by NMR spectroscopy to determine their yields. The NMR data of substrates can be found in the Supporting Information.

General procedures for the catalytic hydroboration of carbonyl compounds and pyridine derivatives using 3 as the catalyst. Catalyst **3** (5.3 mg, 0.01 mmol), HBpin (16.0 μL, 0.11 mmol, 1.1 equiv.) and substrates (0.10 mmol, 1 equiv.) were mixed with 0.5 mL of C_6D_6 in a J-Young NMR tube at ambient temperature. The reaction mixture was stirred with the reaction conditions stated in Tables S8 – S10. The reactions were monitored by NMR spectroscopy to determine their yields. The NMR data of substrates can be found in the Supporting Information.

A full description of experimental methods and theoretical studies can be found in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and theoretical studies (PDF)
X-ray crystallographic data for $[(I_{Me})_2Bpin]I$ and $[I_{Me}–H]I$ (CIF)

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Notes

The authors declare no competing financial interests.

Author Contributions

The manuscript was written through contributions of all authors.

ACKNOWLEDGMENT

This work is supported by ASTAR SERC PSF grant and AcRF Tier 1 grant (C.-W. So.). M.-C. Yang and M.-D. Su are grateful to the National Center for High-Performance Computing of Taiwan for generous amounts of computing time, and the Ministry of Science and Technology of Taiwan for the financial support.

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(19) (a) DFT studies (M06-2X/def2-TZVP) show that the insertion of CO_2 into the Si–H bond of **1** is not possible. (b) Complex **1** was treated with aldehyde PhC(O)H in C_6D_6, whereby the ^{1}H NMR spectroscopy did not show any signal for $-CH_2O$ moiety, indicating that PhC(O)H did not insert into the Si–H bond in **1** during the catalysis. DFT studies show that the insertion of PhC(O)H into the Si–H bond in **1** is not favorable ($\Delta G^{\ddagger}$ = 48.4 kcal/mol, M06-2X/def2-SVP). It is suggested that the catalysis should proceed through the activation of PhC(O)H by the Si lone pair electrons in **1**, followed by reacting with HBpin.

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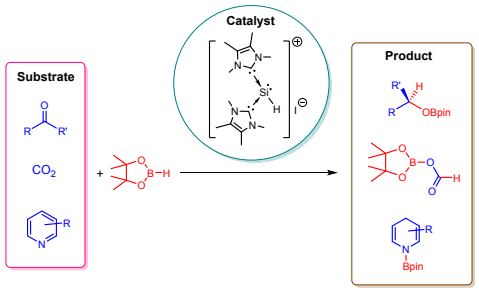
(21) 0.1 mol% of I_{Me} cannot mediate the hydroboration of ketone compounds and pyridine derivatives with HBpin in C_6D_6 at 90°C for 6 h.

SYNOPSIS TOC



NHC-Parent Silyliumylidene Cation

- Metal-free catalysis
- Green chemistry
- 1st silicon(II) species in catalytic CO_2 hydroboration
- High selectivity