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A NHC-Silyliumylidene Cation for Catalytic *N*-Formylation of Amines Using Carbon Dioxide

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ABSTRACT: This study describes the use of a silicon(II) complex, namely, the NHC-silyliumylidene cation complex $[(I_{Me})_2SiH]I$ (**1**, $I_{Me} = :C\{N(Me)C(Me)\}_2$), to catalyze the chemoselective *N*-formylation of primary and secondary amines using CO₂ and PhSiH₃ under mild conditions to afford the corresponding formamides as a sole product (average reaction time: 4.5 h; primary amines, average yield: 95%, average TOF: 8 h⁻¹; secondary amines, average yield: 98%, average TOF: 17 h⁻¹). The activity of **1** and product yields outperform the currently available non-transition-metal catalysts used for this catalysis. Mechanistic studies show that the silicon(II) center in complex **1** catalyzes the C–N bond formation via a different pathway in comparison with non-transition-metal catalysts. It sequentially activates CO₂, PhSiH₃, and amines, which proceeds via a dihydrogen elimination mechanism, to form formamides, siloxanes, and dihydrogen gas.

KEYWORDS: silylene, carbon dioxide, amines, silane, *N*-formylation

INTRODUCTION

Catalytic conversion of carbon dioxide (CO₂) into value-added chemicals and fuels has attracted much attention due to the increasing amount of anthropogenic CO₂ in the atmosphere and its corresponding climatic problems.¹ Considering that C–N bonds are commonly found in agrochemicals and pharmaceuticals,² investigation of catalytic C–N bond formation using CO₂ as C₁ building block becomes indispensable. Consequently, a large number of precious transition-metal catalysts have been developed to overcome the high thermodynamic stability of CO₂ for such catalyses.³ However, harsh conditions such as high pressure of CO₂ and long reaction time were required. Organocatalysis then emerged and was established as an alternative strategy, where N-heterocyclic carbenes (NHCs),^{4–6} superbases,^{7–10} and ionic liquids,^{3c,11,12,13,14,15,16,17,18} were used as catalysts to promote a range of C–N bond forming reactions between amines and CO₂.¹⁹ Mechanistic studies show that organocatalysts activate amines [R₂NH] (R = substituent) to form a [catalyst–H][R₂N] complex, which consequently reacts with CO₂ to form a carbamate salt in the form of [catalyst–H][R₂NCOO] (Figure 1).^{9,20–25} The carbamate anion subsequently acts as a nucleophile to reduce CO₂ in the presence of silane or borane derivatives, affording formamides, *N*-methylamines, and/or

aminals with the selectivity dependent upon reaction temperature, CO₂ pressure, and type of solvent and amines.^{9,10,15,16,20,24} In addition, organocatalytic C–N cyclization reactions using CO₂ were feasible in the synthesis of quinazoline-2,4-diones²⁶ and oxazolidinones.²⁷ Recently, a different catalytic platform was developed by employing main-group element compounds as catalysts. These main group elements are considered as sustainable alternatives to precious transition-metal species due to their high abundance and relatively low toxicity. A handful of examples were reported, whereby carbodicarbene,²⁸ proazaphosphatane,²⁹ 1,3,2-diazaphospholene,³⁰ and NHC-germaacylium cations³¹ undergo different mechanisms to mediate catalytic *N*-amination using CO₂. These results prompted us to search for other main-group element compounds that could promote more efficient catalytic C–N bond formation using CO₂ via new reaction pathways.

Figure 1. Organocatalytic C–N bond formation using CO₂.^{19a}

Among main-group elements, silylene compounds could be a good option due to their unique properties: the presence of a lone pair of electrons and a vacant p orbital on the silicon(II) atom of a silylene. These electronic properties enable them to possess both electrophilic and nucleophilic characters, leading to Lewis ambiphilicity. In this context, they can display reactivity similar to transition-metal complexes in the area of small molecules and enthalpically strong bond activation,³² thus showing possible application in catalyzing organic reactions.³³ To prove this concept, various silylene compounds have been shown to separately undergo CO₂ activation^{32n–q} and ammonia, amine, and hydrazine N–H bond activation.^{32e–m} However, there is still no example capable of stoichiometrically or catalytically activating both CO₂ and a N–H bond simultaneously, resulting in C–N bond formation. In addition, other coupling reactions between two small molecules mediated by a silylene compound are currently unknown. This aroused our interest to investigate the catalytic capability of a silicon(II) compound in C–N bond formation. Recently, we reported the synthesis of a NHC-silyliumylidene cation complex [(I_{Me})₂SiH]⁺I[–] (**1**, Figure 1),³⁴ which contains a base-stabilized silicon(II) cation. It showed transition-metal-like reactivity in functionalizing the *ortho*-C–H bond of fluorobenzene, leading to C–C bond formation.³⁴ Henceforth, complex **1** is anticipated to be an excellent candidate to activate both CO₂ and amines simultaneously for C–N bond formation. Herein, we report the NHC-silyliumylidene cation complex-catalyzed *N*-formylation of amines and CO₂ to selectively afford formamides (Figure 1).

RESULTS AND DISCUSSION

Optimization was first performed using diisopropylamine **4b** (Table 1, see Supporting Information, Table S1). The NHC-silyliumylidene cation complex **1** (10 mol %) was unable to catalyze the reaction of **4b** with CO₂ in the absence of a hydride source at 60 °C. Subsequently, three equivalents of hydride reagent (HBpin, Ph₃SiH, Ph₂SiH₂, PhSiH₃) was added into the reaction mixture to afford the *N*-formamide **5b**, demonstrating that complex **1** can mediate *N*-formylation regardless of the type of hydride source used (entries 2–5).

Table 1. Optimization of *N*-Formylation of Amines with CO₂ and PhSiH₃.^a

entry	X	H [–] source (equiv)	T (°C)	t (h)	yield (%)	TON	TOF (h ^{–1})
1	10	None	60	96	0	0.0	0.0
2	10	HBpin (3)	60	1	68	6.8	6.8
3	10	Ph ₃ SiH (3)	60	96	30	3.0	0.03
4	10	Ph ₂ SiH ₂ (3)	60	1	43	4.3	4.3
5	10	PhSiH ₃ (3)	60	1	91	9.1	9.1
6	10	PhSiH ₃ (3)	24	3	95	9.5	3.2
7	10	PhSiH ₃ (3)	40	1	75	7.5	7.5
8	10	PhSiH ₃ (3)	90	1	71	7.1	7.1
9	1	PhSiH ₃ (3)	60	1	84	8.4	8.4
10	5	PhSiH ₃ (1)	60	1	54	10.8	10.8
11 ^b	5	PhSiH ₃ (2)	60	1	90	18.0	18.0
12	5	PhSiH ₃ (3)	60	1	88	17.6	17.6

^aReaction conditions: amine **4b** (0.10 mmol), required amount of silane, C₆D₆ (0.5 mL), catalytic amount of complex **1** and CO₂. Catalyst loading is relative to amine. The yield was obtained by ¹H NMR using the CH₂ protons of cyclohexane as an internal standard. TON and TOF are assigned to the number of hydride transferred. All the catalytic trials were repeated in triplicate. ^bOptimized conditions.

Among the hydride reagents, PhSiH₃ showed the best activity in terms of TOF (entry 5). The catalytic loading of **1** (entries 5, 9, and 12), molar ratio of PhSiH₃ (entries 10–12), and reaction temperature (entries 5–8) were then modulated, where complex **1** showed the best performance in catalytic *N*-formylation under 5 mol % catalytic loading, reaction temperature of 60 °C, and two equivalents of PhSiH₃ (entry 11).

The catalytic reaction of primary amines with CO₂ and PhSiH₃ was then investigated (Table 2, Table S3) using the optimized conditions (Table 1, entry 11). First, isopropylamine **2a** did not undergo catalytic *N*-formylation under any conditions. Second, complex **1** (5 mol %) was found to be capable of catalyzing *N*-formylation of less sterically hindered aliphatic amines, namely, 2-methoxyethan-1-amine **2b** and *n*-butylamine **2c** to form the corresponding *N*-formamides (yield for **3b** and **3c**: >99%; TOF = 20.0 h^{–1}). The olefinic functionality in prop-2-yn-1-amine **2d** remained intact during the catalysis, showing the possibility of chemoselective *N*-formylation. Third, >99% yield was achieved for the *N*-formylation of aromatic aniline **2e** (TOF = 10.0 h^{–1}). Its derivatives with electron-donating, electron-withdrawing, and sterically hindered substituents were well tolerated (**2f–2t**). Fourth, benzylamine **2u** underwent catalytic *N*-formylation to form **3u** with >99% conversion (TOF: 6.7 h^{–1}). However, when electron-donating and electron-withdrawing groups were introduced at the *ortho* and *para* positions of **2u**, complex **1** was less active in these reactions (TOF = 4.1–6.1 h^{–1}). Fifth, diformylated products were not observed in most reactions. Only the *N*-formylation of **2k** afforded mono- and diformylated products in a 3:2 ratio. In these catalyses, the activity of complex **1** in terms of TOF and product yield are better than the *N*-heterocyclic carbene (NHC), IPr (:C{N(Ar)CH₃}₂, Ar = 2,6-*i*Pr₂C₆H₃). Examples of IPr, **2e**: yield = 35%, TOF = 0.3

Table 2. Scope of Primary Amine Substrates^a

$\text{CO}_2 + \text{R}-\text{NH}_2 \xrightarrow[\text{C}_6\text{D}_6, 60^\circ\text{C}]{\text{Catalyst 1 (5 mol \%), 2 equiv. PhSiH}_3} \text{R}-\text{NH}-\text{C}(=\text{O})\text{H}$			
2			3

3a 0 %	3b >99 (70) %, 20.0 h ⁻¹	3c >99 (70) %, 20.0 h ⁻¹	3d >99 (61) %, 10.0 h ⁻¹

3e >99 (99) %, 10.0 h ⁻¹	3f >99 (99) %, 6.7 h ⁻¹	3g >99 (99) %, 10.0 h ⁻¹	3h >99 (99) %, 1.4 h ⁻¹

3k^{b,c} 75 (40) %, 5.0 h ⁻¹	3m^b 93 (70) %, 1.0 h ⁻¹	3n >99 (99) %, 10.0 h ⁻¹	3p >99 (99) %, 13.3 h ⁻¹

3q >99 %, 5.0 h ⁻¹	3r >99 (99) %, 6.7 h ⁻¹	3s >99 (80) %, 6.7 h ⁻¹	3t 95 (42) %, 4.8 h ⁻¹

3u >99 (99) %, 6.7 h ⁻¹	3v^b 79 (43) %, 5.3 h ⁻¹	3w^b >99 (99) %, 6.1 h ⁻¹	3x^b 81 (31) %, 4.1 h ⁻¹

^aReaction conditions: primary amine (0.10 mmol), 2 equiv of PhSiH₃ (0.20 mmol), catalyst **1** (5 mol %), C₆D₆ (0.50 mL), CO₂ (~50.0 mg). Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard, on the basis of the consumption of the amine. The identity of the product was confirmed as RHNC(=O)H. Isolated yields were reported in parentheses. All the catalytic trials were repeated in triplicate. ^bReaction performed at 40 °C. ^cMono- and diformylations were observed in a 3:2 ratio.

h⁻¹; **2m**: 47%, 0.4 h⁻¹; **2n**: 86%, 0.7 h⁻¹; **2q**: 0%; **2u**: 85%, 0.7 h⁻¹.⁵ When the Ar substituent is replaced by Mes (2,4,6-Me₃C₆H₂), IMes (:C{N(Mes)CH₂})₂ can only mediate the reaction of amines with CO₂ and Ph₂SiH₂ to solely form *N*-methylamines.⁴ Another NHC, namely, thiazolium carbene (:C{N(Bn)CH=C(H)S})₂, Bn = CH₂Ph, was capable of catalyzing both *N*-formylation and *N*-methylation of amines with polymethylhydrosiloxane and CO₂ depending on the reaction temperature, but its activity (example of thiazolium carbene: **2e**: yield = 53%, TOF = 0.4 h⁻¹) is slower than **1**.⁶ Sixth, the activity of **1** is better than superbases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD (examples of TBD, **2e**: yield = 24%, TOF = 0.2 h⁻¹)⁷ and *N*-butyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, BTMG (examples of BTMG, **2e**: yield = 95%, TOF = 4.3 h⁻¹; **2u**: mixture of products).⁹ In particular, complex **1** exhibits better activity in comparison with ionic liquids, for example, 1-butyl-3-methylimidazolium chloride [BMIm]Cl (examples of [BMIm]Cl, **2e**: yield = 76%, TOF = 0.15 h⁻¹; **2u**: 60%, 0.12 h⁻¹),¹¹ glycine betaine (**2c**: 85%, 4.5

h⁻¹; **2m**: 43%, 4.5 h⁻¹; **2u**: 81%, 4.5 h⁻¹),¹⁵ and lecithin (**2c**: 89%, 1.7 h⁻¹; **2m**: no reaction; **2u**: 84%, 1.7 h⁻¹).¹⁸ Lastly, the formation of *N*-formamides in the catalyses was further confirmed by X-ray crystallography of **3m**, **3p**, and **3w** (Figures S71–S73). Moreover, it is noteworthy that the above-mentioned NHC,⁶ superbases,^{8,9} and ionic liquids^{16,17} mediated both catalytic *N*-formylation and *N*-methylation of amines and CO₂. However, complex **1** can only selectively mediate *N*-formylation regardless of reaction conditions. In other words, the *N*-formamides formed in the catalyses (Tables 2 and 3) did not undergo further reduction to form *N*-methylamines.

Table 3. Scope of Secondary Amine Substrates^a

$\text{CO}_2 + \text{R}^1\text{N}(\text{R}^2)\text{H} \xrightarrow[\text{C}_6\text{D}_6, 60^\circ\text{C}]{\text{Catalyst 1 (5 mol \%), 2 equiv. PhSiH}_3} \text{R}^1\text{N}(\text{R}^2)\text{C}(=\text{O})\text{H}$			
4			5

5a >99 (46) %, 40.0 h ⁻¹	5b 85 (72) %, 17.0 h ⁻¹	5c >99 (70) %, 20.0 h ⁻¹	5d^c 0 %

5e^b 95 (95) %, 6.3 h ⁻¹	5f^d >99 (99) %, 20.0 h ⁻¹	5g >99 (69) %, 20.0 h ⁻¹	5h >99 (70) %, 20.0 h ⁻¹

5k^b >99 (90) %, 20.0 h ⁻¹	5m^b >99 (97) %, 20.0 h ⁻¹	5n^c >99 %, 20.0 h ⁻¹	5p >99 %, 10.0 h ⁻¹

5q >99 %, 6.7 h ⁻¹	5r^c >99 %, 20.0 h ⁻¹		

^aReaction conditions: secondary amine (0.10 mmol), 2 equiv of PhSiH₃ (0.20 mmol), catalyst **1** (5 mol %), C₆D₆ (0.50 mL), CO₂ (~50.0 mg). Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard on the basis of the consumption of the amine. The identity of the product was confirmed as R¹R²NC(=O)H. Isolated yields were reported in parentheses. All the catalytic trials were repeated in triplicate. ^bReaction performed at 40 °C. ^cReaction performed at 90 °C. ^dReaction was also performed in a 1 g scale, leading to full conversion, under the same reaction conditions.

The catalytic reaction of secondary amines with CO₂ and PhSiH₃ was further investigated (Table 3, Table S4). First, 5 mol % **1** was able to catalyze the *N*-formylation of aliphatic secondary amines, namely, diethylamine (**4a**) and diisopropylamine (**4b**), to afford the corresponding *N*-formamides in high yield. Selective *N*-formylation was observed for the product **5c**, where the olefinic functionality in *N*-methylprop-2-yn-1-amine **4c** remained intact during the catalysis. In particular, the activity of **1** toward sterically hindered **4f** is much higher than

that of the superbases DBU (yield = 54%, TOF = 0.1 h⁻¹)⁸ and ionic liquids [BMIm]Cl (69%, 0.14 h⁻¹)¹¹ and glycine betaine (77%, 0.8 h⁻¹).¹⁵ Second, less activity was found in aromatic *N*-methylaniline **4e** (95%, 6.3 h⁻¹), but the TOF of **1** is still higher than those of NHC, IPr (>99%, 0.8 h⁻¹),⁵ superbases, TBD (40%, 0.16 h⁻¹),⁷ and ionic liquid, [BMIm]Cl (95%, 0.19 h⁻¹).¹¹ Third, excellent yields (85 to >99%) and high activity (TOF: 20.0 h⁻¹) were found in the **1**-catalyzed *N*-formylation of cyclic amines such as piperidine **4g**, morpholine **4h**, indoline **4k**, and 1,2,3,4-tetrahydroquinoline **4m**. >99% yield and high activity (TOF: 6.7–10 h⁻¹) were also achieved for the *N*-formylation of *N*-heterocycles, namely, dimethylpyrazole **4n**, imidazole **4p**, and benzimidazole **4q**. The catalytic activity outperformed that of NHC catalysts found in the literature.⁵ Notably, complex **1** shows better selectivity in comparison with other main-group element compounds, where 1,3,2-diazaphospholene unselectively catalyzes *N*-formylation of secondary amines leading to a mixture of *N*-formylated and *N*-methylated products.³⁰ It is noteworthy that complex **1** is capable of showing selective *N*-formylation of both primary and secondary amines.

In order to shed some light into the practical utility of our catalytic protocol using complex **1**, a gram-scale reaction was carried out. Under the standard reaction conditions, dibenzylamine **4f** was fully converted to **5f** (yield: >99%, TOF: 20.0 h⁻¹) as the sole product. In other words, both selectivity and yield were preserved upon upscaling of our catalytic protocol.

Upon completing the above catalytic *N*-formylation of amines, a weak singlet at $\delta \sim 4.5$ ppm was observed (Figures S1, S6, S15, S24, S33, S38, S43, S48, S57, S60, and S63), which is attributable to H₂ gas. To clarify these phenomena, *N*-methylaniline **4e** was treated with PhSiH₃ in C₆D₆ at room temperature or 60 °C, whereby no reaction occurred. This demonstrates that the N–H proton of **4e** and Si–H hydride of PhSiH₃ did not react to form H₂ and the silylamine [Ph(Me)NSiH₂Ph] in C₆D₆ in the absence of complex **1**. This result is consistent with the recent findings, where a catalyst is essential for the dehydrocoupling of silanes and amines to form silylamines and H₂.³⁵ Moreover, there was no reaction between complexes **1** and **4e**, which demonstrates that the Si–H bond in complex **1** did not react with the N–H proton of **4e** in C₆D₆ to form H₂ and the amidosilyliumylidene cation [(I_{Me})₂SiN(Me)Ph]⁺. In this context, complex **1** behaves differently from other organocatalysts, which activate amine (R₂NH) to form [catalyst–H][R₂N] (Figure 1, R = substituent).^{19a} Furthermore, complex **1** does not react with PhSiH₃ at 60 °C in C₆D₆, which illustrates that they are not involved in the first step of catalysis. Therefore, the first step of catalysis should involve the interaction of complex **1** with CO₂.^{33a} In addition, H₂ can only be formed when **1** was reacted with *N*-methylaniline, CO₂, and PhSiH₃ together. Such a hypothesis is evidenced by the following DFT calculations.

The reaction mechanism was studied by DFT calculations (M06-2X/def2-TZVP, Scheme 1, Scheme S1). It was found that complex **1** is capable of mediating the catalysis, whereby the Si lone pair of electrons interact with CO₂ first to form **Int01** ($\Delta G_{\text{rel}} = -3.1$ kcal/mol).^{33a} The O center in **Int01** attacks PhSiH₃, and subsequently, the Si–H bond reacts with the N–H bond of **2u** to form H₂. The N center of **2u** simultaneously attacks the C=O bond via a low kinetic barrier of 13.2 kcal/mol (**TS01**: $\Delta G_{\text{rel}}^\ddagger = 10.1$ kcal/mol) to form **Int02** ($\Delta G_{\text{rel}} = -0.7$ kcal/mol). The O center in **Int02** then attacks the second PhSiH₃, where the Si–H bond of PhSiH₃

Scheme 1. DFT Calculations for Catalytic *N*-Formylation of Amines with CO₂ and PhSiH₃

inserts into the C–O bond via a low kinetic barrier (**TS02**, $\Delta G_{\text{rel}}^\ddagger = 20.3$ kcal/mol), resulting in the formation of **Int03** and regeneration of **1** ($\Delta G_{\text{rel}} = -15.7$ kcal/mol). Siloxane (PhH₂Si)₂O is then eliminated from **Int03** via a kinetic barrier of 15.9 kcal/mol (**TS03**: 0.2 kcal/mol) to form **3u** ($\Delta G_{\text{rel}} = -38.7$ kcal/mol). The DFT calculations are consistent with the catalytic conditions, whereby two equivalents of PhSiH₃ are sufficient for the completion of catalysis (Table 1). In addition, the mechanism is different from that of the abovementioned organocatalytic *N*-formylation of amines and CO₂ using NHCs, superbases, and ionic liquids as catalysts, where they activate the amine (R₂NH) to form [catalyst–H][R₂N] in the first step of catalyses.^{9,20–25}

To further support the proposed mechanism for the dehydrogenation step occurring between **TS01** and **Int02**, a deuterium-labeling study was performed using *d*₁₁-piperidine **4g-D** (*D*, 98%, Scheme 2). First, the catalysis was carried out

Scheme 2. Deuterium-Labeling Study Using *d*₁₁-Piperidine (*D*, 98%) (All Catalytic Trials Were Repeated at Least in Triplicate)

using the standard reaction conditions, where HD (triplet, 4.43 ppm) and formyl –C(=O)H (7.76 ppm) signals were observed in the ¹H NMR after an hour (Figure S66). The formation of HD proves the mechanism in Scheme 1, which proceeds via a dihydrogen elimination mechanism. Second, **4g** and **4g-D** in a 1:1 ratio were subjected to catalytic *N*-formylation using the standard reaction conditions (Scheme 3). Full conversion was observed where H₂ and HD were formed, as well as **5g-D** and **5g** were afforded in a 1:1 ratio (Figure S67). Third, **4g** or **4g-D** did not react with PhSiH₃ in the absence of complex **1** at any temperature, refuting the

Scheme 3. Scrambling Reaction with d_{11} -Piperidine (D , 98%) and Piperidine in a 1:1 Ratio (All Catalytic Trials Were Repeated at Least in Triplicate)

possibility of H_2 formation from the coupling reaction between $PhSiH_3$ and amine. Fourth, no reaction was observed in the reaction of $PhSiH_3$ and piperidine (**4g-D** and/or **4g**) in the presence of catalyst **1** at any reaction temperature (Figure S68). This illustrates that complex **1** cannot attack $PhSiH_3$ and the subsequent amine to form H_2 and silylamide [$Ph(H)_2SiNR_2$]. In other words, the mechanism via **Int01** and **TS01** should be feasible.

It is noteworthy that complex **1** (10 mol %) was able to catalyze the hydrosilylation of CO_2 with $PhSiH_3$ in C_6D_6 to form a mixture of silylformates [$PhSiH_x\{OC(O)H\}_{3-x}$] and siloxanes (Scheme 4, $x = 1-2$; conversion: >99%; TOF = 19.4

Scheme 4. 1-Catalyzed Hydrosilylation of CO_2 (All Catalytic Trials Were Repeated at Least in Triplicate)

h^{-1}), which was confirmed by 1H and $^{13}C\{^1H\}$ NMR spectroscopy (Figures S69a,b and S70) and HRMS. Hydrosilylation of CO_2 mediated by a low-oxidation state silicon compound was not reported yet. These results brought up a question of whether the mechanism of **1**-catalyzed N -formylation should proceed via silylformates [$PhSiH_x\{OC(O)H\}_{3-x}$], which then react with amines to form N -formamides and siloxanes.

To answer this question, the mechanism of the **1**-catalyzed hydrosilylation of CO_2 was elucidated by DFT calculations (Scheme 5, Scheme S2), whereby the Si lone pair electrons interact with CO_2 to form **Int01** ($\Delta G_{rel} = -3.1$ kcal/mol).^{33a} Subsequently, the Si-H bond of $PhSiH_3$ inserts into the C-O bond in **Int01** via **TS04** ($\Delta G_{rel}^\ddagger = 13.9$ kcal/mol) to form the silylformate [$PhH_2SiOC(O)H$] ($\Delta G_{rel} = -5.7$ kcal/mol) and regenerates complex **1**. The reaction occurs with higher activation barrier (17.0 kcal/mol) in comparison with the reaction of **1**, **2u**, CO_2 and $PhSiH_3$ via **TS01** (13.2 kcal/mol). This suggests that the **1**-catalyzed N -formylation of amines with CO_2 and $PhSiH_3$ should not proceed via a silylformate intermediate. Our results are in contrast to the DFT calculations of the mechanism of the 1,3,2-diazaphospholene-catalyzed N -formylation and N -methylation, which involve the formation of silylformate [$PhSiH_x\{OC(O)H\}_{3-x}$] intermediate via σ -P-H bond metathesis mechanism pathway.³⁶

Scheme 5. DFT Calculations for Catalytic Hydrosilylation of CO_2

In particular, the silylformates [$PhSiH_x\{OC(O)H\}_{3-x}$] formed further reacted with $PhSiH_3$ to form siloxanes in the **1**-catalyzed hydrosilylation of CO_2 (Scheme 4). This result indicates that the **1**-catalyzed N -formylation (Tables 2 and 3) should not proceed via silylformates; otherwise, low yields of formamides would occur. Even if the **1**-catalyzed N -formylation proceeds via silylformates, which then react with amine, silanol $PhSiH_x(OH)_{3-x}$ formed could hydrolyze complex **1** and then impede its activity. However, complex **1** shows high activity toward the N -formylation of amines with CO_2 and $PhSiH_3$, signifying the implausible mechanism via a silylformate intermediate.

To support our hypothesis, a stepwise mechanistic study was implemented, where **1**-catalyzed hydrosilylation of CO_2 was performed as the first step followed by the removal of CO_2 and addition of amine **2f** or **2m** (Table 4). The results showed that

Table 4. N -Formylation of Amines via Silylformates Resulting in Low Yields of **3^a**

entry	T (°C)	t (h)	consumption of silane (%)	product	yield (%)
1	60	3	15	3f	11
2	40	19	24	3m	21
3	90	2	23	control reaction	

^aReaction conditions: $PhSiH_3$ (0.20 mmol), C_6D_6 (0.5 mL), catalytic amount of complex **1** and CO_2 (~50.0 mg). After the hydrosilylation reaction, CO_2 was removed with its crude mixture filtered into another J Young NMR tube loaded with amine (0.10 mmol). Catalyst loading is relative to amine. The yield was obtained by 1H NMR using the CH_2 protons of cyclohexane as an internal standard. All the catalytic trials were repeated in triplicate.

the conversion of the silylformates [$PhSiH_x\{OC(O)H\}_{3-x}$] were found to be exceedingly low at 40 and 60 °C, which resulted in the poor yield of **3f** (11%) and **3m** (21%), indicative of minimal contribution of silylformates [$PhSiH_x\{OC(O)H\}_{3-x}$] in **1**-catalyzed N -formylation. The low conversion of [$PhSiH_x\{OC(O)H\}_{3-x}$] at 40 and 60 °C is in line with a higher kinetic barrier in DFT calculations (Scheme 5).

■ CONCLUSIONS

The NHC–silyliumylidene cation complex **1** is a low-oxidation-state group 14 element catalytic system to promote the metal-free chemoselective *N*-formylation of amines with carbon dioxide, which efficiently and selectively delivers *N*-formamides. The byproducts of the reactions are dihydrogen gas and siloxane. The activity of **1** and product yields are better than that of currently available nonmetal catalysts used for such catalysis. The outperformance of **1** is due to its transition-metal-like catalysis, whereby the silicon(II) center sequentially activates CO₂, PhSiH₃, and amines, which proceeds via a dihydrogen elimination mechanism, to form formamides, siloxanes, and dihydrogen gas.

■ 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.³³ C₆D₆ was dried over potassium metal and distilled prior to use. CDCl₃ was dried over CaH₂ and distilled prior to use. *d*₁₁-piperidine (**D**, 98%) was purchased from Cambridge Isotope Laboratories, Inc. and dried with 4 Å molecular sieves prior to use. All amine substrates are commercially available and dried using CaH₂. The ¹H and ¹³C{¹H} NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C₆D₆ or CDCl₃, and the chemical shifts are relative to SiMe₄ for ¹H and ¹³C. The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. Coupling constants *J* are given in Hertz (Hz). Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University.

Optimization for the Reductive Functionalization of CO₂ Using PhSiH₃ and Diisopropylamine **4b.** Catalyst **1** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μL, 0.10 mmol, 20 equiv), phenylsilane (24.6 μL, 0.20 mmol, 40 equiv), diisopropylamine **4b** (14.0 μL, 0.10 mmol, 20 equiv), and C₆D₆ (0.5 mL) were loaded into a J Young NMR tube. The J Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO₂ gas was then added. The freeze–pump–thaw cycle was repeated twice. The reaction conditions are indicated in Table S1 in the Supporting Information, and the reaction was monitored by NMR spectroscopy, which confirmed the formation of (*i*Pr)₂NC(=O)H **5b**. Formation of methylated amine was not observed throughout the catalytic reaction. The yields of products were reported according to the integration of ¹H NMR signals of (*i*Pr)₂NC(=O)H at 8.17 ppm with reference to the –CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. The catalytic studies were repeated at least in triplicate.

General Procedures for the Catalytic Functionalization of CO₂ Using PhSiH₃ and Amines. Catalyst **1** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μL, 0.10 mmol, 20 equiv), phenylsilane (24.6 μL, 0.20 mmol, 40 equiv), required amount of amine (0.10 mmol, 20 equiv), and C₆D₆ (0.5 mL) were loaded into a J Young NMR tube. The J Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO₂ gas was then added. The freeze–pump–thaw cycle

was repeated twice. The reaction conditions are indicated in Tables S3 and S4 in the Supporting Information, and the reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. The yields of products were reported according to the integration of ¹H NMR signals of R¹R²NC(=O)H at ~8 ppm with reference to the CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. Formation of methylated amine was not observed throughout the catalytic reaction. The resulting formamides were purified by silica plug or silica gel chromatography using either ethyl acetate/hexane or tetrahydrofuran as the eluent to give the corresponding *N*-formamides as an oil or crystalline solid. The NMR data of **3a–3x** and **5a–5m** can be found in the Supporting Information.

Procedures for the Gram-Scale Catalytic Functionalization of CO₂ Using PhSiH₃ and Dibenzylamine **4f.** Catalyst **1** (0.102 g, 0.253 mmol), internal standard cyclohexane (1.00 mL, 5.07 mmol, 20 equiv), phenylsilane (1.25 mL, 10.1 mmol, 40 equiv), dibenzylamine **4f** (1.00 g, 0.97 mL, 5.07 mmol, 20 equiv), and C₆D₆ (25 mL) were loaded into a Schlenk bottle. The Schlenk bottle was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO₂ gas was then added. The freeze–pump–thaw cycle was repeated twice. The reaction mixture was heated from room temperature to 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. Full conversion was observed after an hour. A 99% yield was reported according to the integration of ¹H NMR signals of (PhCH₂)₂NC(=O)H (**5f**) at 8.07 ppm with reference to the CH₂ protons (1.40 ppm) of the internal standard, cyclohexane. Formation of methylated amine was not observed throughout the catalytic reaction. **5f** was purified by silica gel chromatography using ethyl acetate/hexane as the eluent, which was isolated as an oil (99% yield).

Deuterium-Labeling Study of Catalytic *N*-Formylation Using *d*₁₁-Piperidine **4g-D.** Catalyst **1** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μL, 0.10 mmol, 20 equiv), phenylsilane (24.6 μL, 0.20 mmol, 40 equiv), *d*₁₁-piperidine **4g-D** (**D**, 98%, 9.87 μL, 0.10 mmol, 20 equiv), and C₆D₆ (0.5 mL) were loaded into a J Young NMR tube. The J Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO₂ gas was then added. The freeze–pump–thaw cycle was repeated twice. The reaction mixture was heated from room temperature to 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic trials were repeated at least in triplicate. The identity of the product was determined according to the ¹H NMR signals of R¹R²NC(=O)H (**5g-D**) at 7.76 ppm. A mixture of H₂ (4.47 ppm) and HD (triplet, 4.43 ppm, ¹*J*_{HD} = 42.7 Hz) were observed in the crude reaction after an hour due to piperidine (2%) and *d*₁₁-piperidine (98%), respectively.

Catalytic *N*-Formylation Using Piperidine **4g and *d*₁₁-Piperidine **4g-D** in a 1:1 Ratio.** Catalyst **1** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μL, 0.10 mmol, 20 equiv), phenylsilane (24.6 μL, 0.20 mmol, 40 equiv), piperidine **4g** (4.94 μL, 0.05 mmol, 10 equiv), *d*₁₁-piperidine **4g-D** (**D**, 98%, 4.94 μL, 0.05 mmol, 10 equiv), and C₆D₆ (0.5 mL) were loaded into a J-Young NMR tube. The J Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO₂ gas was then added. The freeze–pump–thaw cycle

was repeated twice. The reaction mixture was heated from room temperature to 60 °C. The reaction was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate. The yield was calculated based on consumption of the amine **4g** in addition to the integration of the formoxy $-CHO$ and non-labeled $-CH_2$ functional groups of the corresponding *N*-formamide against the $-CH_2$ integration of the internal standard cyclohexane. The identity of the product was determined according to the 1H NMR signals of $R^1R^2NC(=O)H$ of **5g** and **5g-D** at 7.76 ppm and corresponding **5g** signals of 3.22–3.25 (m, 2H, CH_2), 2.51–2.54 (m, 2H, CH_2), 1.04–1.13 (m, 4H, CH_2), 0.91–0.96 (m, 2H, CH_2) in C_6D_6 . A mixture of H_2 (4.47 ppm) and HD (4.33, 4.43, 4.54 ppm, $^1J_{HD} = 42.7$ Hz) was observed in the crude reaction after an hour.

Reaction of $PhSiH_3$ with d_{11} -Piperidine **4g-D.** Internal standard cyclohexane (10.8 μ L, 0.10 mmol), phenylsilane (24.6 μ L, 0.20 mmol, 2.0 equiv), d_{11} -piperidine **4g-D** (*D*, 98%, 9.87 μ L, 0.10 mmol, 1.0 equiv), and C_6D_6 (0.5 mL) were loaded into a J Young NMR tube. The reaction was monitored by NMR spectroscopy at 24, 60, and 90 °C over 24 h. The catalytic studies were repeated at least in triplicate. Consumption of $PhSiH_3$ was not observed based on the integration of the silane signal $-SiH_3$ against the $-CH_2$ integration of the internal standard cyclohexane. H_2 and HD signals were absent. In addition, no reaction was observed when piperidine **4g** (9.88 μ L, 0.10 mmol, 1 equiv) was used instead of d_{11} -piperidine.

General Procedure for Stepwise Hydrosilylation and Subsequent Amine Addition. Catalyst **1** (2.0 mg, 0.005 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 20 equiv), phenylsilane (24.6 μ L, 0.20 mmol, 40 equiv), and C_6D_6 (0.5 mL) were loaded into a J Young NMR tube. The J Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO_2 gas was then added. The freeze–pump–thaw cycle was repeated twice. The reaction conditions are indicated in Table 4, and the reaction was monitored by NMR spectroscopy. After catalytic hydrosilylation, CO_2 was removed *in vacuo* and the resulting solution was filtered into another J Young NMR tube. Subsequently, the required amount of amine (0.10 mmol, 20 equiv) was added. The resultant mixture was then heated and was monitored by NMR spectroscopy. The catalytic studies were repeated at least in triplicate.

Catalytic Hydrosilylation of Carbon Dioxide Using $PhSiH_3$. Catalyst **1** (4.0 mg, 0.01 mmol), internal standard cyclohexane (10.8 μ L, 0.10 mmol, 10 equiv), phenylsilane (24.6 μ L, 0.20 mmol, 20 equiv), and C_6D_6 (0.5 mL) were loaded into a J Young NMR tube. The J Young NMR tube was immersed in liquid nitrogen under vacuum to obtain a frozen solution for freeze–pump–thaw cycle, and 1 bar of CO_2 gas was then added. The freeze–pump–thaw cycle was repeated twice. The reaction mixture was heated from room temperature to 90 °C. The reaction was monitored by NMR spectroscopy, which confirmed the formation of silylformates and siloxanes as the major products after 1 h. All catalytic trials were repeated at least in triplicate. The existence of intermediates and products (silylformates and siloxanes) was confirmed by 1H , $^{13}C\{^1H\}$, and ^{29}Si NMR spectroscopy and HRMS spectrometry. The NMR data of the products 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 at <https://pubs.acs.org/doi/10.1021/acscatal.0c03795>.

Experimental section; selected spectra; X-ray data collection and structural refinement; and theoretical studies (PDF)

X-ray crystallographic data for **3m**, **3p**, and **3w** (CIF)

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Notes

The authors declare no competing financial interest.

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