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Reaction of Lithium Silylamides with Carbon Monoxide Leading to Carbamoylsilanes

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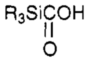
Summary: Carbamoylsilanes, a hitherto little known class of compounds, are obtained by the reaction of lithium silylamides with carbon monoxide followed by quenching with methyl iodide. The reaction involves initial formation of a carbamoyllithium species and subsequent rearrangement of the silyl group to give a lithium (silylcarbonyl)amide.

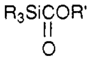
Introduction

A variety of acylsilanes have been synthesized, characterized, and utilized in synthetic reactions.[1] In contrast, silylcarbonyl compounds in which a heteroatom is directly connected to the $R_3SiC(O)$ group still remain rare. Compounds having a $R_3SiC(O)$ group connected to an oxygen atom, *i.e.* silanecarboxylic acids **1**[2] and their esters **2**,[2] are known.



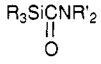
$R_3Si\underset{\underset{O}{\|}}{C}OH$

1



$R_3Si\underset{\underset{O}{\|}}{C}OR'$

2

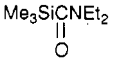


$R_3Si\underset{\underset{O}{\|}}{C}NR'_2$

3

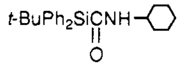
The nitrogen analogues, carbamoylsilanes **3**, remain almost unknown. Jutzi reported the synthesis of a carbamoylsilane,[3] but later Rautenstrauch pointed out that the product was a silyl formamide.[4] Ojima had reported that hydrosilylation of an isocyanate afforded a carbamoylsilane,[5] but this was also found out later to be a silyl formamide.[6] Widdowson reported that no carbamoylsilane could be detected in the reaction of (dialkylcarbamoyl)lithium with trialkylsilyl chloride despite many attempts.[7]

As far as we know, there have only been two carbamoylsilanes reported to date. Peddle described the first synthesis of (diethylcarbamoyl)silane **4** by the reaction of disilyl sulfide with carbamoylmercury, although the yield of the product was not stated.[8] Baldwin reported that addition of (*tert*-butyldiphenylsilyl)lithium to cyclohexyl isocyanate followed by quenching with exactly 1 equiv of water afforded (cyclohexylcarbamoyl)silane **5** in good yield.[6]



$Me_3Si\underset{\underset{O}{\|}}{C}NEt_2$

4



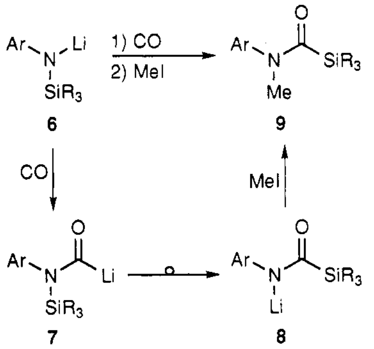
$t\text{-}BuPh_2Si\underset{\underset{O}{\|}}{C}NH-$

5

This paper describes a novel route to carbamoylsilanes.

Results and Discussion

We thought that the transformations shown in eq 1 seemed attainable. The reaction of lithium silylamide **6** with carbon monoxide would afford carbamoyllithium **7**.[3,4,7,9] The silyl group in **7** could undergo anionic rearrangement[10] to give a lithium (silylcarbonyl)amide **8** in the light of the topologically similar 1,2-silicon rearrangement that we had devised.[11] Subsequent N-alkylation would afford the desired compound, the carbamoylsilane **9**. This is the case, as described.



(1)

The reaction of the lithium amide **6** with carbon monoxide was carried out under atmospheric pressure and also at 30 atm. The latter conditions turned out to be better. When lithium (trimethylsilyl)(2,6-dimethylphenyl)amide (**6a**),[12] prepared in situ by successive reactions of the parent aniline with *n*-BuLi/Me_3SiCl and then *n*-BuLi in THF, was exposed to carbon monoxide at ambient pressure at 20 °C, it reacted over 8 h, but the desired carbamoylsilane **9a** was obtained only in trace

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[⊛] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

(1) (a) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95–155. (b) Ricci, A.; Degl'Innocenti, A. *Synthesis* **1989**, 647. (c) Page, P. C. B.; Klair, S. S.; Rosenthal, S. J. *Chem. Soc. Rev.* **1990**, *19*, 147.

(2) (a) Steward, O. W.; Dziedzic, J. E.; Johnson, J. S.; Frohliger, J. O. *J. Org. Chem.* **1971**, *36*, 3480. (b) Brook, A. G.; Yau, L. *J. Organomet. Chem.* **1984**, *271*, 9.

(3) Jutzi, P.; Schröder, F.-W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 339.

(4) Rautenstrauch, V.; Joyeux, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 85.

(5) (a) Ojima, I.; Inaba, S. *Tetrahedron Lett.* **1973**, *44*, 4363. (b) Ojima, I.; Inaba, S. *J. Organomet. Chem.* **1977**, *140*, 97.

(6) Baldwin, J. E.; Derome, A. E.; Riordan, P. D. *Tetrahedron* **1983**, *39*, 2989.

(7) Lindsay, C. M.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 569.

(8) Peddle, G. J. D.; Walsingham, R. W. *J. Chem. Soc. D* **1969**, 462.

(9) (a) Rautenstrauch, V.; Joyeux, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 83. (b) Narayana, C.; Periasamy, M. *Synthesis* **1985**, 253. (c) Peretz, D. G.; Nudelman, N. S. *J. Org. Chem.* **1988**, *53*, 408. (d) Mizuno, T.; Nishiguchi, I.; Hirashima, T. *Tetrahedron* **1993**, *49*, 2403.

(10) Note that insertion of a N–Si bond into a lithioxycarbene to give the imidate form of **8a** is another possibility. The lithioxycarbene character of carbamoyllithium has been suggested in ref 3.

(11) Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 2440.

(12) Generation of lithium (trimethylsilyl)(2,6-dimethylphenyl)amide (**6a**) was detected by another experiment. Treatment of **6a** with 10 equiv of methyl iodide at −78 °C gave methyl(trimethylsilyl)(2,6-dimethylphenyl)amine in 74% yield. Methyl(trimethylsilyl)(2,6-dimethylphenyl)amine: bp 143 °C/4.0 Torr; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, CH_3Si), 2.25 (s, 6H, CH_3), 2.68 (s, 3H, CH_3N), 6.94 (dd, J = 8.6, 6.2 Hz, 1H, *p*-H), 7.03 (d, J = 8.6 Hz, 1H, *m*-H), 7.03 (d, J = 6.2 Hz, 1H, *m*-H).

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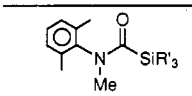
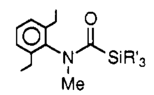
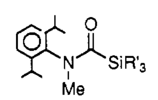
Table 1. Synthesis of Carbamoylsilane 9 from Lithium silylamide 6, CO (30 atm, 20 °C, 15 min), and Methyl Iodide

product	R'₃Si	no.	isolated yield, %	mp, °C	IR (ν_{CO}), cm^{-1}	^{13}C NMR, ppm
	Me$_3$Si	**9a**	28 (trace)[a]	80–82	1576 (KBr)	188.3[b]
	PhMe$_2$Si	**9b**	36	53–55	1562 (KBr)	186.5[c]
	Me$_3$Si	**9c**	27	liquid	1576 (neat)	188.6
	PhMe$_2$Si	**9d**	17	liquid	1574 (neat)	186.9
	Me$_3$Si	**9e**	40 (31)[a]	83–85	1566 (Kbr)	189.3
	PhMe$_2$Si	**9f**	17	liquid	1570 (neat)	187.0

[a] Conditions: CO 1 atm, 20 °C, 8 h. [b] $^1J_{C-Si}$ = 75.0 Hz, ^{29}Si NMR −9.0 ppm from TMS. [c] $^1J_{C-Si}$ = 76.8 Hz, ^{29}Si NMR −15.7 ppm from TMS.

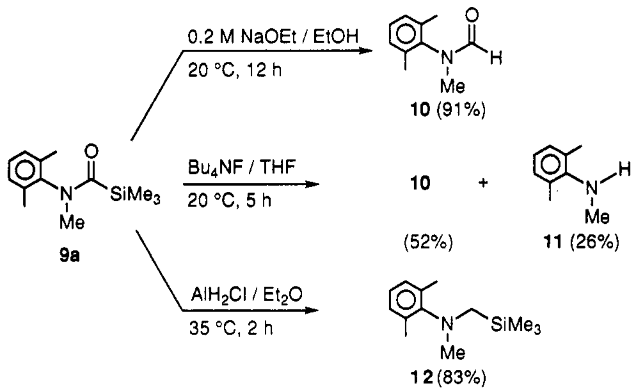
amounts after quenching with an excess of methyl iodide.[13] From lithium (trimethylsilyl)(2,6-diisopropylphenyl)amide (**6e**), however, the desired carbamoylsilane **9e** was obtained in 31% yield by reaction with carbon monoxide (1 atm) for 8 h followed by quenching with methyl iodide. While lithium amide **6a** did not react with carbon monoxide at 1 atm, it reacted with carbon monoxide at 30 atm at 20 °C for 15 min to give **9a** in 28% yield after quenching with methyl iodide. These and similar results are shown in Table 1.

Less hindered or aliphatic amides such as lithium (trimethylsilyl)benzylamide, (trimethylsilyl)phenylamide, and (trimethylsilyl)(1,1,3,3-tetramethylbutyl)amide gave complex mixtures of products in low yields. Lithium bis(trimethylsilyl)amide did not absorb carbon monoxide.

The structures of the carbamoylsilanes **9** have been unequivocally established by their NMR and IR spectra. The observed weak ^{29}Si satellites with $^1J_{C-Si}$ = 75.0 Hz at the ^{13}C NMR signal of the carbonyl carbon (δ 188.3) of **9a** indicates that the silyl group is directly attached to the carbonyl carbon atom. The ^{29}Si NMR of **9a** revealed a signal at −9.0 ppm ((CH$_3$)$_4$Si as an internal standard), which shows that the silicon atom is shielded by a carbonyl group, similar to the situation observed in acylsilanes.[1c] In the IR of **9a** there is a strong CO absorption at 1576 cm^{-1}, which is lowered by 54 cm^{-1} from that (1630 cm^{-1}) for a corresponding carbon analogue, *N*-(2,6-dimethylphenyl)-*N*-methyl-2,2-dimethylpropanamide.[14] It has been well established that IR absorption bands of acylsilanes, R(CO)SiR$_3$, are substantially lowered from those of the corresponding carbon analogues,[1] *i.e.*, ketones RC(O)R'. The IR and NMR data are also shown in Table 1.[15]

The chemical properties of the carbamoylsilanes **9** were examined briefly. The carbamoylsilane **9a** is a white solid and is fairly stable in air or to atmospheric moisture. At room temperature, treatment of **9a** in ether with water for 1 h and of **9a** in benzene with 10% sulfuric acid for 1 h resulted in 92% and 78% recoveries, respectively.[16] This stability allows the use of aqueous workup (H$_2$O–Et$_2$O) as an alternative, sometimes cleaner, method for the isolation of **9** in its preparation without significant decrease in the yields.

Scheme 1



Treatment of **9a** with 0.2 M NaOEt/EtOH for 12 h gave formamide **10** in 91% yield,[17] and hydrolysis of the amide linkage was not observed (Scheme 1). Similar desilylation was observed when **9a** was treated with a fluoride ion.[18] That the reaction was accompanied by the formation of the decarbonylation product **11** suggested the possible intervention of a carbamoyl anion as an intermediate. One standard reaction of an amide is the reduction to an amine with LiAlH$_4$.[19] Although reducing agents such as LiAlH$_4$, DIBAL-H, NaBH$_4$, and NaBH$_4$/AlCl$_3$ reacted with **9a** only sluggishly, clean reduction was attained when AlH$_2$Cl (prepared in situ from 1:1 AlCl$_3$ and LiAlH$_4$ in Et$_2$O[20]) was used (Scheme 1).

The lithium (silylcarbonyl)amide **8** (or **13**) was expected to afford the isocyanide **15** upon heating (eq 2), since a similar lithium amidate involved in Baldwin's reaction[6] had been reported to give an isocyanide upon warming. The autoclave containing lithium *N*-(silyl)anilides **6**, prepared in situ as described above, was pressurized with 30 atm of CO at 25 °C for 30 min and then heated to 100

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[13] This reaction was accompanied by the formation of *N*-(2,6-diisopropylphenyl)-*N*-methylformamide (22%) and 2,6-diisopropylphenyl isocyanide (**15b**; 10%).

[14] *N*-(2,6-Dimethylphenyl)-*N*-methyl-2,2-dimethylpropanamide: ^{1}H NMR (CDCl$_3$) δ 0.99 (s, 9H, *t*-Bu), 2.24 (s, 6H, CH$_3$), 3.10 (s, 3H, CH$_3$N), 7.06 (d, *J* = 9.0 Hz, 1H, *m*-H), 7.06 (*J* = 5.5 Hz, 1H, *m*-H), 7.13 (dd, *J* = 9.0, 5.5 Hz, 1H, *p*-H). This compound was prepared using a general method described in: *Organic Functional Group Preparations*, 2nd ed.; Sandler, S. R., Karo, W., Eds.; Academic Press: New York, 1983; Vol. 1, pp 323–330.

[15] These data are in accordance with reported data for **4** (IR 1560 cm^{-1})[8] and for **5** (IR 1593 cm^{-1} in CHCl$_3$; ^{13}C NMR 182.6 ppm; ^{29}Si NMR −17.5 ppm).[6]

[16] In contrast, it has been reported that (diethylcarbamoyl)silane reacted completely with water within 30 min to give a formamide.[8]

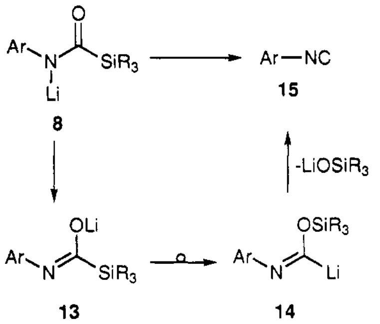
[17] It has been reported that the bond between the silicon and carbonyl carbon in acylsilanes is cleaved by base to afford the corresponding aldehydes and/or alkoxysilanes: (a) Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373. (b) Brook, A. G. *J. Org. Chem.* **1960**, *25*, 1072. (c) Brook, A. G.; Schwartz, N. V. *J. Org. Chem.* **1962**, *27*, 2311. See also ref 1.

[18] Desilylation of an acylsilane to an aldehyde by F$^-$ has been reported: (a) Page, P. C. B.; Rosenthal, S.; Williams, R. V. *Tetrahedron Lett.* **1987**, *28*, 4455. (b) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881. See also refs 1b,c.

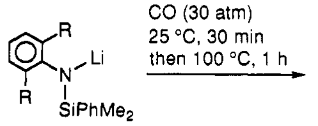
[19] Barrett, A. G. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 8, pp 249–251.

[20] Ojima, I.; Zhao, M.; Yamato, T.; Nakahashi, K.; Yamashita, M.; Abe, R. *J. Org. Chem.* **1991**, *56*, 5263.

°C for 1 h. The yields of isocyanides were fair (~50%) for Me_3Si and excellent for the case of Me_2PhSi (eq 3).



(2)



(3)

R = Et **15a** 77% (GLC yield 94%)

i-Pr **15b** 80% (GLC yield 93%)

In summary, a unique entry to several (arylcarbamoyl)silanes has been found. It has been demonstrated that these carbamoylsilanes are stable and can be manipulated in a conventional manner.

Experimental Section

All glassware was flame-dried under a stream of nitrogen prior to use. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. A hexane solution of *n*-butyllithium (Nacalai Tesque, Inc.) was purchased and titrated prior to use by the Gilman method.[21] ^1H NMR spectra were recorded on JEOL JNM-GSX 270 and Bruker AM 600 spectrometers as solutions in $CDCl_3$. IR spectra were recorded on a Hitachi 270–50 infrared spectrophotometer as KBr pellets or in neat form. Mass spectra and HRMS were recorded on a JEOL JMS-DX303 spectrometer. Melting points are uncorrected.

Synthesis of Carbamoylsilanes under 30-atm Pressure of Carbon Monoxide. A representative procedure was as follows. A 30-mL one-necked reaction flask equipped with a magnetic stirrer bar and a rubber septum, through which a short needle connected to a nitrogen line was inserted, was flame-dried under a stream of nitrogen. In the reaction flask was placed 8 mL of anhydrous THF and 0.606 g (5.0 mmol) of 2,6-dimethylaniline, and the solution was cooled to −78 °C with a dry-ice/methanol bath. To the stirred solution was added dropwise 3.7 mL of a hexane solution of *n*-BuLi (1.35 M, 5.0 mmol) by syringe. After 10 min, 0.635 mL (5.0 mmol) of trimethylsilyl chloride was added by syringe at −78 °C. After the resulting solution was stirred at −78 °C for 15 min, 3.7 mL of a hexane solution of *n*-BuLi (1.35 M, 5.0 mmol) was added again and the solution was warmed to 20 °C over 1 h. After the nitrogen line was removed from the short needle, the reaction vessel was quickly placed into an autoclave. The system was flushed and filled with a 30-atm pressure of carbon monoxide, and the mixture was stirred at 20 °C for 15 min. After the pressure of carbon monoxide was released, the vessel was taken out, a nitrogen line was connected again to the short needle, and the temperature was lowered to −78 °C with a cold bath. To the reaction mixture was added dropwise 3.1 mL (50 mmol) of methyl iodide, and the mixture was warmed gradually to 20 °C. To the mixture was added 10 mL of a saturated aqueous solution of NH_4Cl and 10 mL of ether. The organic layer and the aqueous layer were separated. The aqueous layer was extracted with ether (3 × 20 mL). The organic layers were combined, washed with brine, and dried over potassium carbonate. The solvents were removed under reduced pressure to provide a yellow oil, which was subjected to column chromatography on Florisil (20:1 CH_2Cl_2–ether) to give pure ((2,6-dimethylphenyl)methylcarbamoyl)trimethylsilane (**9a**; 0.565 g, 28% yield).

((2,6-Dimethylphenyl)methylcarbamoyl)trimethylsilane (9a): 28% yield; white solid, mp 80–82 °C; ^1H NMR ($CDCl_3$) δ −0.14 (s, 9H, CH_3Si), 2.20 (s, 6H, CH_3), 3.10 (s, 3H, CH_3N), 7.10 (d, *J* = 8.8 Hz, 1H, *m*-H), 7.11 (d, *J* = 5.5 Hz, 1H, *m*-H), 7.18 (dd, *J* = 8.8, 5.5 Hz, 1H, *p*-H); ^{13}C NMR ($CDCl_3$) δ −1.6 (CH_3Si), 17.8 (CH_3), 32.8 (CH_3N), 128.4 (*p*-C), 128.6 (*m*-C), 137.3 (*o*-C), 141.0 (*i*-C), 188.3 (C=O, J_{C-Si} = 75.0 Hz); ^{29}Si NMR ($CDCl_3$) δ −9.0; IR (KBr) 1596 (Ph), 1576 (C=O) cm^{-1}; MS *m/z* (relative intensity) 236 (22), 235 (M^+, 98), 73 (100). Anal. Calcd for $C_{13}H_{21}NOSi$: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.49; H, 9.09; N, 5.95.

((2,6-Dimethylphenyl)methylcarbamoyl)dimethylphenylsilane (9b): 36% yield; white solid, mp 53–55 °C; ^1H NMR ($CDCl_3$) δ 0.12 (s, 6H, CH_3Si), 1.95 (s, 6H, CH_3), 3.07 (s, 3H, CH_3N), 6.99 (d, *J* = 8.2 Hz, 1H, *m*-H), 6.99 (d, *J* = 6.9 Hz, 1H, *m*-H), 7.13 (dd, *J* = 8.2, 6.9 Hz, 1H, *p*-H), 7.22–7.37 (m, 5H, PhSi); ^{13}C NMR ($CDCl_3$) δ −3.1 (CH_3Si), 17.6 (CH_3), 32.9 (CH_3N), 127.6 (*m*-C of PhSi), 128.5 (*p*-C of Ph), 128.6 (*m*-C of Ph), 129.3 (*p*-C of PhSi), 134.0 (*o*-C of PhSi), 135.2 (*i*-C of PhSi), 137.6 (*o*-C of Ph), 140.5 (*i*-C of Ph), 186.5 (C=O, J_{C-Si} = 76.8 Hz); ^{29}Si NMR ($CDCl_3$) δ −15.7; IR (KBr) 1596 (Ph), 1562 (C=O) cm^{-1}; MS *m/z* (relative intensity) 298 (11), 297 (M^+, 38), 296 (100). Anal. Calcd for $C_{18}H_{23}NOSi$: C, 72.68; H, 7.79; N, 4.71. Found: C, 72.93; H, 7.95; N, 4.64.

((2,6-Diethylphenyl)methylcarbamoyl)trimethylsilane (9c): 27% yield; pale greenish yellow oil; ^1H NMR ($CDCl_3$) δ −0.17 (s, 9H, CH_3Si), 1.23 (t, *J* = 7.6 Hz, 6H, CH_3CH_2), 2.51 (dq, *J* = 18.6, 7.6 Hz, 2H, CH_3CH_2), 2.57 (dq, *J* = 18.6, 7.6 Hz, 2H, CH_3CH_2), 3.13 (s, 3H, CH_3N), 7.17 (d, *J* = 8.4 Hz, 1H, *m*-H), 7.17 (d, *J* = 6.8 Hz, 1H, *m*-H), 7.30 (dd, *J* = 8.4, 6.8 Hz, 1H, *p*-H); ^{13}C NMR ($CDCl_3$) δ −1.8 (CH_3Si), 14.6 (CH_3CH_2), 23.7 (CH_3CH_2), 34.4 (CH_3N), 126.3 (*m*-C), 128.7 (*p*-C), 139.8 (*i*-C), 142.6 (*o*-C), 188.6 (C=O); IR (neat) 1596 (Ph), 1576 (C=O) cm^{-1}; MS *m/z* (relative intensity) 263 (M^+, 100). Anal. Calcd for $C_{15}H_{25}NOSi$: 68.39; H, 9.57; N, 5.32. Found: C, 68.40; H, 9.70; N, 5.42.

((2,6-Diethylphenyl)methylcarbamoyl)dimethylphenylsilane (9d): 17% yield; pale greenish yellow oil; ^1H NMR ($CDCl_3$) δ 0.07 (s, 6H, CH_3Si), 1.08 (t, *J* = 7.6 Hz, 6H, CH_3CH_2), 2.21 (dp, *J* = 15.7, 7.6 Hz, 2H, CH_3CH_2), 2.38 (dq, *J* = 15.7, 7.6 Hz, 2H, CH_3CH_2), 3.10 (s, 3H, CH_3N), 7.06 (d, *J* = 7.6 Hz, 2H, *m*-H), 7.21–7.35 (m, 6H, *p*-H, PhSi); ^{13}C NMR ($CDCl_3$) δ −3.0 (CH_3Si), 14.4 (CH_3CH_2), 23.7 (CH_3CH_2), 34.6 (CH_3N), 126.2 (*m*-C of Ph), 127.5 (*m*-C of PhSi), 128.9 (*p*-C of Ph), 129.2 (*p*-C of PhSi), 133.9 (*o*-C of PhSi), 135.2 (*i*-C of PhSi), 139.5 (*i*-C of Ph), 142.9 (*o*-C of Ph), 186.9 (C=O); IR (neat) 1596 (Ph), 1574 (C=O) cm^{-1}; MS *m/z* (relative intensity) 326 (24), 325 (M^+, 76), 135 (100); HRMS calcd for $C_{20}H_{27}NOSi$ (M^+) 325.1862, found 325.1873.

((2,6-Diisopropylphenyl)methylcarbamoyl)trimethylsilane (9e): 40% yield from 30 atm CO, 31% yield from 1 atm CO; white solid, mp 57–59 °C; ^1H NMR ($CDCl_3$) δ −0.14 (s, 9H, CH_3Si), 1.18 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2CH$), 1.26 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2CH$), 3.01 (hept, *J* = 6.8 Hz, 2H, $(CH_3)_2CH$), 7.19 (d, *J* = 8.5 Hz, 1H, *m*-H), 7.19 (d, *J* = 6.9 Hz, 1H, *m*-H), 7.35 (dd, *J* = 8.5, 6.9 Hz, 1H, *p*-H); ^{13}C NMR ($CDCl_3$) δ −1.5 (CH_3Si), 23.2 (CH_3CH), 25.7 ($C'H_3CH$), 28.0 ($(CH_3)_2CH$), 35.8 (CH_3N), 124.1 (*m*-C), 129.2 (*p*-C), 138.6 (*i*-C), 147.4 (*o*-C), 189.3 (C=O); IR (KBr) 1594 (Ph), 1566 (C=O) cm^{-1}; MS *m/z* (relative intensity) 292 (27), 291 (M^+, 100); HRMS calcd for $C_{17}H_{29}NOSi$(M^+) 291.2010, found 291.2003.

((2,6-Diisopropylphenyl)methylcarbamoyl)dimethylphenylsilane (9f): 17% yield; pale yellow oil; ^1H NMR ($CDCl_3$) δ −0.02 (s, 6H, CH_3Si), 1.09 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2CH$), 1.13 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2CH$), 2.94 (hept, *J* = 6.8 Hz, 2H, $(CH_3)_2CH$), 3.18 (s, 3H, CH_3N), 7.18 (d, *J* = 7.8 Hz, 2H, *m*-H), 7.28–7.38 (m, 4H, *p*-H, PhSi), 7.58–7.61 (m, 2H, PhSi); ^{13}C NMR ($CDCl_3$) δ −2.5 (CH_3Si), 22.7 (CH_3CH), 25.6 ($C'H_3CH$), 27.9

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($(CH_3)_2CH$), 35.9 (CH_3N), 123.9 (*m*-C of Ph), 127.5 (*m*-C of PhSi), 129.1 (*p*-C of Ph, *p*-C of PhSi), 134.0 (*o*-C of PhSi), 135.2 (*i*-C of PhSi), 138.2 (*i*-C of aniline), 147.3 (*o*-C of aniline), 187.0 (C=O); IR (neat) 1594 (Ph), 1570 (C=O) cm^{-1}; MS *m/z* (relative intensity) 354 (23), 353 (M^+, 73), 135 (100); HRMS calcd for $C_{22}H_{29}NOSi$ (M^+) 353.2175, found 353.2162.

Synthesis of Carbamoylsilane under an Ambient Pressure of Carbon Monoxide. A 30-mL round-bottomed flask equipped with a magnetic stirrer bar, a three-way stopcock, and a nitrogen line was flame-dried under a stream of nitrogen. The lithium silylamide was prepared in situ according to the procedure as described above. The three-way stopcock was then connected to a vacuum line and a balloon filled with carbon monoxide through a glass column packed with soda lime and anhydrous $CaSO_4$. After two cycles of evacuation of nitrogen and filling with carbon monoxide, the reaction mixture was stirred under the atmosphere of carbon monoxide for 8 h. To the reaction mixture was added dropwise 3.1 mL (30 mmol) of methyl iodide at −78 °C, and the temperature was raised gradually to 20 °C. The workup described above was followed.

Desilylation of Carbamoylsilane 9a to Formamide 10. To a suspension of NaOH/EtOH (from 1.1 mmol of NaH and 5 mL of EtOH) was added 0.235 g (1.0 mmol) of **9a** at 20 °C. After 12 h, 10 mL of saturated NH_4Cl(aq) and 10 mL of Et_2O were added. From the dried and concentrated organic layer, 0.149 g (91% yield) of *N*-methyl-*N*-(2,6-dimethylphenyl)formamide (**10**)[22] was obtained after column chromatography (SiO_2, CH_2Cl_2–MeOH).

Reaction of Carbamoylsilane 9a with Bu_4NF. Treatment of **9a** (0.9 mmol) with Bu_4NF (2.7 mmol) in THF (8 mL) at 20 °C for 5 h followed by workup with Et_2O (10 mL × 3) and H_2O (10 mL) gave, after column chromatography (SiO_2, 100:1 CH_2Cl_2–MeOH), **10** (0.077 g, 52% yield) and *N*-methyl-2,6-dimethylaniline (**11**;[23] 0.031 g, 26% yield).

Reduction of 9a to Silylmethylamine 12. $LiAlH_4$ (0.114 g, 3.0 mmol) was added to a suspension of $AlCl_3$ (0.400 g, 3.0 mmol) in Et_2O (5 mL), and the mixture was heated to reflux for 30 min.[20] To this suspension was added **9a** (0.212 g, 0.9 mmol) at 0 °C. After the mixture was heated to reflux for 2 h, Et_2O (10 mL) and saturated $NaHCO_3$(aq) (10 mL) were added at 0 °C to the mixture, which was then filtered through Celite. The organic layer was separated, dried, concentrated, and subjected to SiO_2 column chromatography (10:1 hexane–CH_2Cl_2) to give pure *N*-methyl-*N*-((trimethylsilyl)methyl)-2,6-dimethylaniline (**12**; 0.165 g, 83% yield). **12**: bp 111 °C/17 Torr; ^1H NMR ($CDCl_3$) δ −0.01 (s, 9H, CH_3Si), 2.31 (s, 6H, CH_3), 2.65 (s, 2H, NCH_2Si), 2.77 (s, 3H, CH_3N), 6.92 (dd, *J* = 4.3, 9.5 Hz, 1H, *p*-H), 6.96 (d, *J* = 4.3 Hz, 1H, *m*-H), 6.97 (d, *J* = 9.5 Hz, 1H, *m*-H); ^{13}C NMR ($CDCl_3$) δ −1.5 (CH_3Si), 19.3 (*o*-CH_3), 43.6 (NCH_2Si), 47.3 (CH_3N), 124.7 (*p*-C), 128.9 (*m*-C), 137.1 (*o*-C), 151.0 (*i*-C); IR (neat) 1596 (Ph) cm^{-1}; MS *m/z* (relative intensity); 221 (M^+, 13), 148 (100). Anal. Calcd for $C_{13}H_{23}NSi$: C, 70.52; H, 10.47; N, 6.33. Found: C, 70.64; H, 10.28; N, 6.49.

Synthesis of Isocyanides 15a,b under a 30-atm Pressure of Carbon Monoxide. The lithium silylamide was prepared in situ in a 30-mL one-neck reaction flask as described above and allowed to react with a 30-atm pressure of carbon monoxide for 30 min. The autoclave was then heated to 100 °C for 1 h and cooled gradually to 20 °C. After evacuation of carbon monoxide, the vessel was taken out. To the reaction mixture was added 5 mL of saturated aqueous NH_4Cl solution at 0 °C. The usual aqueous workup and purification with column chromatography (SiO_2) gave the known isocyanides 2,6-diethylphenyl isocyanide (**15a**;[24] 77%) and 2,6-diisopropylphenyl isocyanide (**15b**;[25] 80%).

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