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Preparation and X-ray crystal structure of a carbamylsilane

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Abstract

The first air-stable, crystalline carbamylsilane, $(Me_3Si)_3SiC(O)NMe_2$ has been prepared and characterized by an X-ray crystallographic study. Photolysis of the carbamylsilane does not give rise to an *N*-substituted silene.

Introduction

The preparation of the first thermally stable carbamylsilane, $Me_3SiC(O)NEt_2$, was reported in 1969 [1] but since then no other report appears to have been published on this class of compounds. The related silyl carbamates $R_3SiOC(O)NHR'$ which have also received very little attention have recently found synthetic use [2]. In the last few years the use of bulky substituents at silicon has enabled stable compounds containing unusual functional groups on silicon to be prepared. For example the cyanate, thiocyanate, and formyl groups have been attached to silicon in $(Me_3Si)_3CSiMe_2OCN$ [3], $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2SCN)$ [4] and $(Me_3Si)_3SiCHO$ [5] respectively. These results prompted us to attempt to prepare the stable carbamylsilanes $(Me_3Si)_3SiC(O)NR_2$ (R = Me or Ph).

Experimental

Preparation of $(Me_3Si)_3SiC(O)NMe_2$

A solution of Me_2NCOCl (1.161 g, 0.015 mol) in dry pentane (30 ml) under a blanket of dry nitrogen was cooled to −30 °C and to it was added over 2 h a solution of $(Me_3Si)_3SiLi(thf)_3$ [6] (7.06 g, 0.015 mol) in a mixture of pentane (100

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ml) and THF (10 ml) with the temperature maintained between −20 and −30 °C. The solution was then allowed to warm to room temperature and was stirred for a further 30 min. The reaction mixture was then added to water (100 ml), and the organic layer was separated and washed with water again (2 × 50 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed under vacuum to give a white solid which thin layer chromatography showed to be a mixture of two components, one being $(Me_3Si)_4Si$. The mixture was separated on a "Chromatatron" silica plate with hexane/diethyl ether (1 : 1 v/v) as eluent to give a little $(Me_3Si)_4Si$ and $(Me_3Si)_3SiC(O)NMe_2$ as a white solid, 3.6 g 75%, m.p. 135–136 °C, ^1H NMR ($CDCl_3$, 303 K) 2.87 (s, 6H, NMe_2), 0.15 (s, 27H, $SiMe_3$). On cooling to 253 K the NMe_2 resonance split into two resonances of equal intensity 13.2 Hz apart (at 80 MHz); coalescence occurred at 298 ± 5 K. ^{13}C NMR (C_6D_6) 1.80 ($SiMe_3$), 39.10 and 32.18 (NMe_2), 185.13 (C=O); ^{29}Si NMR ($CDCl_3$ solution) −11.27 ($SiMe_3$), −74.53 ($\mathit{Si}SiMe_3$); ν (C=O) (KBr disc) 1559 cm^{-1}, m/z 304 (30%, $[M-Me]^+$), 246(25, $[M-Me_3Si]^+$), 189(15, $[M-Me_3Si-MeNCO]^+$), 131(20, $[Me_3SiSiMe_2]^+$), 102(50, $[Me_2NMe_2]^+$), 99(20), 73(100, $[Me_3Si]^+$), 59(45, $[HMe_2Si]^+$).

Preparation of $(Me_3Si)_3SiC(O)NPh_2$

A solution of $(Me_3Si)_3SiLi(thf)_3$ (prepared from 3 g $(Me_3Si)_4Si$ and MeLi) in a mixture of anhydrous pentane (25 ml) and anhydrous THF (5 ml) was added over 2 h to a solution of Ph_2NCOCl (2.17 g, 9.37 mmol) in pentane (15 ml) under dry nitrogen at −30 °C. The resulting mixture was allowed to warm to room temperature and was stirred for a further hour. The mixture was then filtered and solvent was removed from the filtrate under reduced pressure to give a sticky white solid which was crystallized from pentane to give $(Me_3Si)_3SiC(O)NPh_2$, (1.5 g, 36%), mp 120–125 °C, ^1H NMR ($CDCl_3$), 0.07 (s, 27H, $SiMe_3$), 6.9–7.3 (m, 10H, NPh_2) ν(C=O) 1596 cm^{-1}, m/z 443(55%, $[M]^+$), 428(5, $[M-Me]^+$), 370(75, $[M-SiMe_3]^+$), 282(10), 147(15, $[Me_3SiOSiMe_2]^+$), 73(100, $[Me_3Si]^+$), 45(12).

Attempted preparation of $(Me_3Si)_3SiC(S)NMe_2$

The procedure used was the same as for $(Me_3Si)_3SiC(O)NPh_2$ but using $Me_2NC(S)Cl$ in place of $Ph_2NC(O)Cl$. After removal of the solvents under reduced pressure a yellow solid remained which had ^1H NMR signals in the aromatic region together with three large and several small signals between 0.1 and 0.3 ppm. Linked GC mass spectral analysis showed the presence of four major components (one of them corresponding to $(Me_3Si)_4Si$) and several minor ones none of which appeared to correspond to $(Me_3Si)_3SiC(S)NPh_2$.

Photolysis of $(Me_3Si)_3SiC(O)NMe_2$

A sample of $(Me_3Si)_3SiC(O)NMe_2$ (ca. 20 mg) was dissolved in dry C_6D_6 (0.5 ml) under nitrogen in a screw-cap 5 mm NMR tube. The tube was placed in a water bath at 10 °C and was irradiated using four 100 W mercury spot lamps (Blak Ray, Ultraviolet Products Inc., $\lambda \geqslant 360$ nm) for 46 h. After this time the ^1H NMR spectrum was that of unchanged started material.

Crystal data: $C_{12}H_{33}NOSi_4$, M 319.747, monoclinic, $a = 30.478(8)$, $b = 17.460(3)$, $c = 16.572(3)$ Å, $\beta = 105.68(2)°$, $V = 8490.8$ Å^3, $Z = 16$, $D_c = 1.00$ g cm^{-3}, $F(000) = 2816$. Monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 2.7$ cm^{-1}.

Space group $C2/c$ from systematic absences of $h0l$ for l odd and successful structure refinement.

A crystal 0.4 × 0.35 × 0.4 mm was used for data collection on an Enraf–Nonius CAD4 diffractometer. Intensities for 4209 $hk \pm l$ reflections with $2 < \theta < 20°$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35 \tan \theta)°$. A rapid pre-scan at $10°$ $\min^{-1}$ in θ was used to determine the scan rate for each reflection, where the reflections with $I/\sigma(I)$ less than 1 were coded as unobserved. The remainder were rescanned subject to a maximum $I/\sigma(I)$ of 50 or maximum recording times of 60 s. Two standard reflections monitored every 30 min showed no significant variation. After correction for Lorentz and polarization effects but not for absorption, equivalent data were averaged to give 4119 unique reflections ($R_{av} = 0.034$) and 2160 reflections with $|F|^2 > \sigma(F)^2$ were used for the structure analysis. The values of $\sigma(F^2)$ were calculated as $[\sigma^2(I) + (0.04\ I)^2]^{1/2}/\mathrm{Lp}$.

The positions of Si atoms were located by direct methods (MULTAN) [7] and a difference map was used to find C, N, and O atoms all of which were refined by full matrix least squares with anisotropic temperature factors. The hydrogen atoms were placed at calculated positions (C–H 0.95 Å) with B_{iso} equal to $1.3 \times B_{eq}$ for the carbon atom to which it is bonded.

Further refinement converged at $R = 0.056$, $R' = 0.063$ with weighting $w = 1/\sigma^2(F)$, 325 variables, and all final shifts to error ratio < 0.018. A final difference map had peaks of up to 0.3 e Å^{-3}.

The structure solution and refinement were carried out on a Microvax computer using the Enraf–Nonius structure determination package. Scattering factors for neutral atoms were taken from ref. 8. Final atom coordinates are listed in Table 1 and lists of temperature factors and structure factors are available from P.B.H.

Table 1

Fractional atomic coordinates ($\times 10^4$) for $(Me_3Si)_3SiC(O)NMe_2$ with estimated standard deviations in parentheses

	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Si(1)	3739.7(7)	1331.0(13)	4441.9(12)	1269.9(7)	1330.4(13)	743.1(12)
Si(2)	3934.1(9)	1070.0(16)	3190.1(14)	1051.8(9)	1113.1(16)	−711.1(14)
Si(3)	4361.6(8)	1059.9(14)	5594.4(14)	1617.1(9)	2537.5(15)	1027.6(15)
Si(4)	3433.1(8)	2569.3(14)	4384.0(15)	646.9(8)	1084.7(14)	1288.4(14)
O(1)	3167(2)	186(3)	3753(3)	1770(2)	82(3)	570(3)
N(1)	3053(2)	489(4)	4988(4)	1937(2)	403(4)	1929(4)
C(1)	3270(3)	594(5)	4390(4)	1703(2)	532(4)	1115(4)
C(2)	3443(4)	1227(6)	2269(5)	834(4)	120(6)	−931(6)
C(3)	4122(3)	55(6)	3198(5)	1545(3)	1242(6)	−1160(5)
C(4)	4414(3)	1674(8)	3069(6)	596(4)	1783(7)	−1261(6)
C(5)	4908(3)	1258(6)	5337(7)	1317(4)	3243(6)	245(7)
C(6)	4363(4)	1617(6)	6551(6)	1624(4)	2951(5)	2090(6)
C(7)	4352(3)	27(5)	5842(5)	2212(3)	2444(6)	1017(7)
C(8)	3406(4)	2976(5)	5425(6)	674(3)	1601(7)	2278(6)
C(9)	3776(3)	3242(6)	3945(7)	109(3)	1349(6)	526(6)
C(10)	2847(3)	2531(6)	3720(8)	629(3)	40(5)	1488(5)
C(11)	3150(3)	909(5)	5749(5)	1878(4)	871(5)	2606(5)
C(12)	2702(3)	−108(6)	4881(6)	2251(3)	−246(6)	2148(6)

Results and discussion

The carbamyl silanes are formed readily in fair to good yields in a manner similar to that used in the preparation of a range of acylpolysilanes (see eg. refs. 9 and 10). The reasons for the failure to prepare a sulphur analogue in this work are unknown. Peddle and Walsingham [1] treated $(Me_3Si)_2S$ with $Hg[C(O)NEt_2]_2$ to give $Me_3SiC(O)NEt_2$ which they found to be thermally stable, as are the compounds described above, but sensitive to moisture. The carbamylsilanes described here are much less sensitive to water and survive an aqueous reaction work-up. They are however, decomposed when their solutions in wet tetrahydrofuran are heated under reflux for 3 h, to give a complicated mixture of products which does not seem to contain any of the expected $(Me_3Si)_3SiOH$. This relatively greater chemical stability is presumably due to the steric hindrance afforded by the $(Me_3Si)_3Si$ group towards attack at the functional group.

It was expected that photolysis of a carbamylsilane $(Me_3Si)_3SiC(O)NR_2$ would lead to formation of an *N*-substituted silene, $(Me_3Si)_2Si{=}C(OSiMe_3)NR_2$ in a manner similar to the formation of silenes $(Me_3Si)RSi{=}C(OSiMe_3)R'$ from the photolysis of acylpolysilanes $(Me_3Si)_2RSiC(O)R'$ (R = Me, t-Bu, Ph, Me_3Si; R' = t-Bu, adamantyl, bicyclooctyl, mesityl or CEt_3 etc.) [9,10]. Unfortunately, even on prolonged photolysis of $(Me_3Si)_3SiC(O)NMe_2$ no rearrangement occurred. It is unclear why no rearrangement takes place but it should be noted that neither $(Me_3Si)_3SiC(O)OR$ (R = Me, Me_3Si, or $(Me_3Si)_3Si$) [11] nor $(Me_3Si)_3GeC(O)C_{10}H_{15}$ [12] rearrange under similar conditions, and it thus seems that electronic factors play a dominant rôle in such rearrangements.

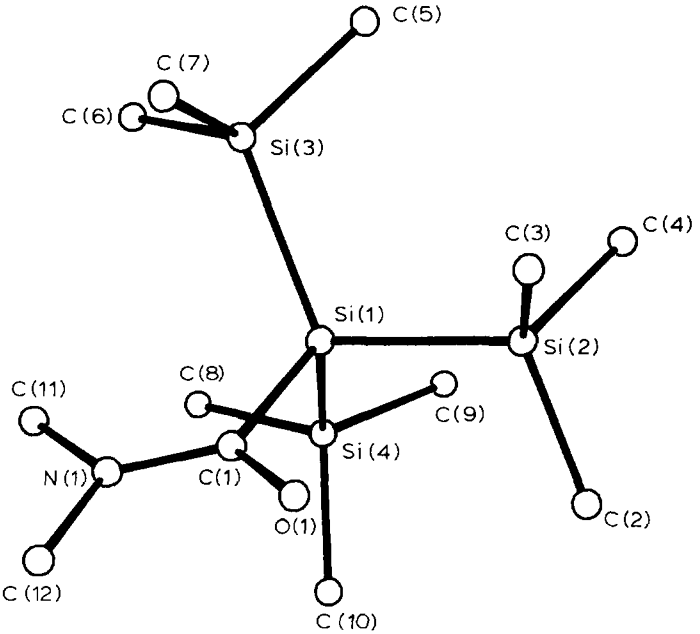

Fig. 1. An ORTEP [15] drawing and atom numbering scheme for $(Me_3Si)_3SiC(O)NMe_2$. The two independent molecules are numbered in the same way, equivalent data for both are given Tables 1 and 2.

Table 2

Intramolecular distances (Å) and angles (°) for $(Me_3Si)_3SiC(O)NMe_2$ with estimated standard deviations in parentheses

(a) Bonds	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Si(1)–Si(2)	2.351(3)	2.351(3)	Si(1)–Si(3)	2.347(3)	2.348(3)
Si(1)–Si(4)	2.347(3)	2.353(4)	Si(1)–C(1)	1.910(8)	1.905(7)
Si(2)–C(2)	1.846(9)	1.858(11)	Si(2)–C(3)	1.861(10)	1.863(11)
Si(2)–C(4)	1.857(12)	1.855(12)	Si(3)–C(5)	1.859(11)	1.843(11)
Si(3)–C(6)	1.859(10)	1.897(10)	Si(3)–C(7)	1.852(9)	1.826(11)
Si(4)–C(8)	1.888(11)	1.853(11)	Si(4)–C(9)	1.847(12)	1.838(9)
Si(4)–C(10)	1.828(10)	1.858(9)	O(1)–C(1)	1.241(9)	1.253(9)
N(1)–C(1)	1.345(11)	1.363(9)	N(1)–C(11)	1.418(11)	1.438(11)
N(1)–C(12)	1.469(12)	1.464(11)			
(b) Angles	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Si(2)–Si(1)–Si(3)	109.8(1)	109.8(1)	Si(2)–Si(1)–Si(4)	109.6(1)	109.3(1)
Si(2)–Si(1)–C(1)	101.2(3)	101.1(2)	Si(3)–Si(1)–Si(4)	116.4(1)	117.0(1)
Si(3)–Si(1)–C(1)	109.4(2)	110.9(2)	Si(4)–Si(1)–C(1)	109.5(3)	107.7(3)
Si(1)–Si(2)–C(2)	111.1(4)	109.8(3)	Si(1)–Si(2)–C(3)	109.2(3)	110.7(3)
Si(1)–Si(2)–C(4)	112.3(4)	111.6(4)	C(2)–Si(2)–C(3)	109.0(4)	108.6(5)
C(2)–Si(2)–C(4)	108.2(5)	108.1(5)	C(3)–Si(2)–C(4)	107.0(5)	107.8(5)
Si(1)–Si(3)–C(5)	110.6(3)	110.4(4)	Si(1)–Si(3)–C(6)	113.8(3)	114.8(3)
Si(1)–Si(3)–C(7)	108.6(3)	108.2(3)	C(5)–Si(3)–C(6)	107.6(5)	106.1(5)
C(5)–Si(3)–C(7)	107.5(5)	111.0(6)	C(6)–Si(3)–C(7)	108.5(4)	106.3(5)
Si(1)–Si(4)–C(8)	115.1(3)	113.8(4)	Si(1)–Si(4)–C(9)	109.9(4)	110.7(4)
Si(1)–Si(4)–C(10)	107.7(3)	108.2(3)	C(8)–Si(4)–C(9)	106.8(5)	107.7(5)
C(8)–Si(4)–C(10)	106.7(6)	108.5(5)	C(9)–Si(4)–C(10)	110.5(5)	107.8(4)
C(1)–N(1)–C(11)	124.0(7)	122.5(7)	C(1)–N(1)–C(12)	119.6(7)	120.3(7)
C(11)–N(1)–C(12)	116.5(8)	117.2(6)	Si(1)–C(1)–O(1)	116.1(6)	117.3(5)
Si(1)–C(1)–N(1)	124.7(5)	124.9(6)	O(1)–C(1)–N(1)	119.2(7)	117.8(6)

The IR absorption of the carbonyl group in $(Me_3Si)_3SiC(O)NMe_2$ of 1559 cm^{-1} is very similar to that in $Me_3SiC(O)NEt_2$, 1560 [1] which shows a bathochromic shift of about 60 cm^{-1} relative to its carbon analogue $Me_3CC(O)NEt_2$ [1]. The variable temperature NMR spectra of $(Me_3Si)_3SiC(O)NMe_2$ are typical for hindered rotation about an amide C–N bond, the energy barrier to rotation being about 64.5 ± 1.2 kJ mol^{-1}.

The crystal structure revealed that there are two independent molecules in the unit cell. Both molecules have the same conformation and are numbered equivalently. One of the molecules is shown together with the atom numbering scheme in Fig. 1 and intramolecular bond lengths and angles are given in Table 2. The structural details of the molecules are unremarkable. In both molecules the Si–Si–Si angle bisected by the plane of the amide group is opened out (116.4(1) and 117.0(1)°), with the remaining Si–Si–Si angles averaging 109.6(2)°. The Si–Si and Si–Me bond lengths average 2.349(2) and 1.86(2) Å respectively. Corresponding data, for example in $(Me_3Si)_3Si$(9-fluorenyl) are 2.366, 1.856Å, and 109.27° [13]. The Si–C–N, Si–C–O, and O–C–N bond angles average 124.8, 117.7, and 118.5° which compared with average corresponding angles in a range of amides [14] of 115, 124, and 121° show a distinct opening up of the Si–C–N bond and concomitant reduction in the other angles around the amide linkage.

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