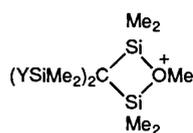


## Comparison of the Reactivities of the Compounds $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})\text{C}(\text{SiMe}_2\text{Cl})$ and $(\text{MeOMe}_2\text{Si})_3\text{C}(\text{SiMe}_2\text{Cl})$ . Crystal Structure of $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$

Franklin I. Aigbirhio, Salih S. Al-Juaid, Colin Eaborn,\* Peter B. Hitchcock and Paul D. Lickiss†  
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

The relative rates of methanolysis of  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CSiMe}_2\text{Cl}$  (**1**),  $(\text{MeOMe}_2\text{Si})_2(\text{Me}_3\text{Si})\text{CSiMe}_2\text{Cl}$  (**2**) and  $(\text{MeOMe}_2\text{Si})_3\text{CSiMe}_2\text{Cl}$  (**3**) in 1:3 v/v MeOH–dioxane at 35 °C have been found to be *ca.* 1:9:160. The smallness of the reactivity increases on introduction of the second and third OMe groups on going from **1**, to **2**, to **3**, compared with the  $>10^6$ -fold increase on going from  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Cl}$  to **1**, is consistent with a mechanism for methanolysis of **1** involving rate-determining intramolecular displacement of  $\text{Cl}^-$  by the OMe group. Possible reasons for the rate enhancements by the second and third OMe groups are discussed. In reaction with KSCN in MeCN, a direct bimolecular nucleophilic displacement, **3** is only 11 times as reactive as **1**. The hydride  $(\text{MeOMe}_2\text{Si})_3\text{CSiMe}_2\text{H}$  reacts more readily than  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CSiMe}_2\text{H}$  with silver salts. The crystal structure of the hydride  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$  has been determined, revealing that one OMe group is in an ideal position to carry out (the notional) backside displacement of  $\text{H}^-$ , and a second such group in a good position to initiate frontside (equatorial) displacement.

It was shown previously that compounds of the type  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{X})$  (*e.g.*,  $\text{X} = \text{Cl}$ ,  $\text{OCOCF}_3$ ,  $\text{NCO}$ ) undergo methanolysis much more rapidly than the related species  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{X}$ ;<sup>1</sup> the chloride  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMe}_2\text{OMe})(\text{SiMe}_2\text{Cl})$  (**1**) being  $>10^6$  times as reactive as  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Cl}$ .<sup>2,3</sup> The high reactivity of the methoxy-substituted compounds was attributed to anchimeric assistance by the MeO group to the departure of  $\text{X}^-$ , with formation of the bridged cation **1b**.<sup>1–3</sup> If this explanation is correct then replacement of further  $\text{Me}_3\text{Si}$  groups by  $\text{MeOMe}_2\text{Si}$  groups should have relatively little influence, and so we decided to examine the reactivity of the trimethoxy compound **3**. We were also able to obtain some information on the reactivity of the dimethoxy compound **2**.



**1a** Y = Me  
**1b** Y = OMe

- 1**  $(\text{MeOMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{CSiMe}_2\text{Cl}$   
**2**  $(\text{MeOMe}_2\text{Si})_2(\text{Me}_3\text{Si})\text{CSiMe}_2\text{Cl}$   
**3**  $(\text{MeOMe}_2\text{Si})_3\text{CSiMe}_2\text{Cl}$   
**4**  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$

In order to throw light on the favoured disposition of the MeO groups in the trimethoxy compounds the crystal structure of the diphenyl derivative  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$  was determined.

### Results and Discussion

The preparation of **3** and **2** (contaminated with *ca.* 5% of **3**) will be described elsewhere.<sup>4</sup>

The solvolyses of compounds **1–3** were found to proceed at a convenient rate in 1:3 MeOH–dioxane at 35 °C. The rates were determined by <sup>1</sup>H NMR spectroscopy. The presence of a little **3** in the sample of **2** did not give rise to significant difficulty, especially since **3** reacted some 18 times as rapidly as **2**.

**Table 1** Rates of methanolysis of the chlorides **1–3** in 1:3 v/v MeOH–dioxane at 35 ± 0.5 °C

Chloride	Additive and concentration/ mol dm <sup>-3</sup>	<i>k</i> /10 <sup>4</sup> s <sup>-1</sup>	Relative rate
<b>1</b>	—	0.081	1
<b>2</b>	—	0.72	9
<b>3</b>	—	13	160
<b>3</b>	NaOMe; 0.10	11	—
<b>3</b>	NaOMe; 0.60	9	—
<b>3</b>	HCl; 0.05	9	—

\* Initially *ca.* 0.02–0.04 mol dm<sup>-3</sup>. A little CCl<sub>4</sub> was also present (see Experimental section).

Good first-order plots were obtained, and the observed rate constants are shown in Table 1. Rate constants were reproducible to within *ca.* ±7%, but the spectrometric technique was rather imprecise, and the uncertainty in the values in these and the other rate measurements described below could possibly be as large as ±20%, but this would not affect the validity of the discussion, in which, in the main, only large effects are considered. Relative values of the rate constants for a given compound under different conditions, *e.g.* for methanolysis of **3** in the presence or absence of NaOMe or HCl, are probably more reliable than the absolute values of the individual rate constants.

It can be seen that the introduction of a second MeO group on going from **1** to **2** causes a nine-fold rate increase, and there is a further 18-fold increase on introduction of the third MeO group on going to **3**. These factors are sizeable, but insignificant in comparison with the reactivity increase of  $>10^6$  on going from  $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Cl}$  to the mono-methoxy compound **1**.

In the presence of low concentrations of NaOMe the rate of reaction of **3** was slightly, but probably significantly, lower. A similar effect was observed previously for the methanolysis of **1**. Rather surprisingly the presence of 0.05 mol dm<sup>-3</sup> HCl also appeared to lead to a slightly lower rate. These small influences of added acid and base could arise from the general medium effects associated with disruption of the solvent structure by the additives.

† Present address: Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK.

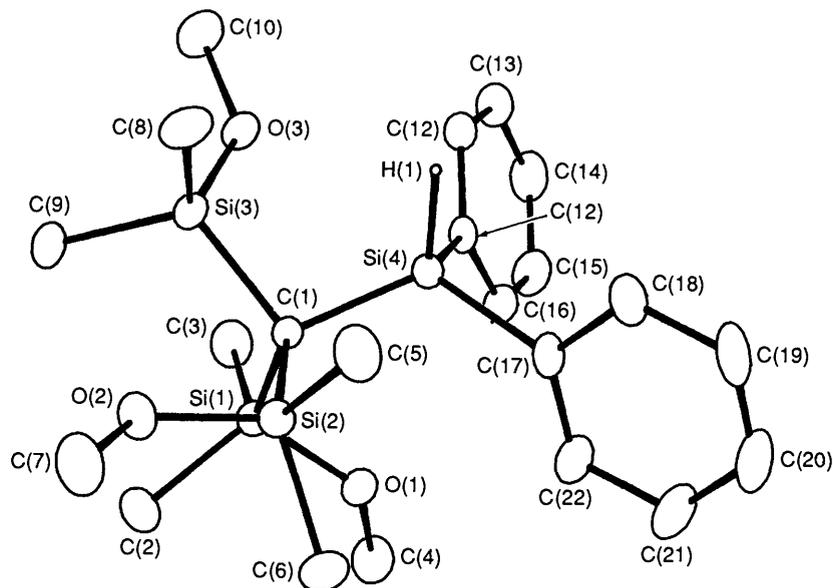


Fig. 1 Molecular structure of  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$  with atom numbering. Only the hydrogen atom attached to silicon is shown.

The small effect of the introduction of the second and third MeO groups on going from 1 to 2 to 3 is consistent with the view that only one such group can be directly involved in the rate determining step if the mechanism proposed<sup>1-3</sup> for the solvolysis of 1 applies. The reactivity by this mechanism would be expected to rise on introduction of the additional MeO groups simply because there is a greater chance at any one instant that one such group is in the best position to carry out the intramolecular nucleophilic attack on the functional silicon atom, and the proportion of molecules in favourable orientations could well rise more rapidly than the number of MeO groups.\* Furthermore, because of the possibility of rotation about the Si-OMe bond to minimize steric interactions involving the Me group, the effective bulk of the  $\text{MeOMe}_2\text{Si}$  group is probably smaller than that of the  $\text{Me}_3\text{Si}$  group, with the consequence that there is less steric hindrance to solvation of, for example, cation **1b** than of cation **1a**. In addition there is the possibility of 'internal solvation' of the forming cation by the additional MeO groups, described below.

**Crystal Structure of  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$  and its Implications.**—To throw light on the favoured dispositions of the MeO groups in a trimethoxy compound we examined the crystal structure of the hydride  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{H}$  (**4**). We chose a diphenyl rather than a dimethyl compound  $(\text{MeOMe}_2\text{Si})_3\text{CSiMe}_2\text{X}$  because the molecules of the latter type approximate to spherical and so, like  $(\text{Me}_3\text{Si})_4\text{C}$ , tend to form plastic crystals, which are not amenable to X-ray diffraction studies. We would have preferred the chloride  $(\text{MeOMe}_2\text{Si})_3\text{CSiPh}_2\text{Cl}$  to the hydride **4** but were unable to make it.

The structure of **4** is shown in Fig. 1, and details of bond lengths and angles are given in Table 2. It can be seen that one of the MeO groups, MeO(1), is well placed to carry out backside nucleophilic attack on the silicon of the Si-H bond; the  $\text{MeO} \cdots \text{Si}(4)\text{-H}$  angle is  $167^\circ$ , i.e. not far from the  $180^\circ$  needed for an ideal five-coordinate transition state with the favoured apical-apical orientation of incoming and leaving group, and

\* For a discussion of the importance of the proximity of the reacting centres in intramolecular reactions see F. M. Menger, *Acc. Chem. Res.*, 1985, **18**, 128. From another viewpoint (A. E. Dorigi and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 3698) the best orientation in the substrate is that giving rise to the least increase in strain on going to the transition state.

Table 2 Intramolecular distances/Å and angles/ $^\circ$  for **4** (esds in parentheses)

Bonds			
Si(1)-O(1)	1.643(2)	Si(1)-C(1)	1.881(3)
Si(1)-C(2)	1.859(4)	Si(1)-C(3)	1.857(4)
Si(2)-O(2)	1.640(2)	Si(2)-C(1)	1.878(3)
Si(2)-C(5)	1.851(3)	Si(2)-C(6)	1.863(4)
Si(3)-O(3)	1.637(2)	Si(3)-C(1)	1.888(3)
Si(3)-C(8)	1.866(4)	Si(3)-C(9)	1.861(4)
Si(4)-C(1)	1.891(3)	Si(4)-C(11)	1.885(3)
Si(4)-C(17)	1.885(3)	O(1)-C(4)	1.403(4)
O(2)-C(7)	1.415(4)	O(3)-C(10)	1.398(5)
C(11)-C(12)	1.385(4)	C(11)-C(16)	1.386(4)
C(12)-C(13)	1.387(5)	C(13)-C(14)	1.358(6)
C(14)-C(15)	1.363(5)	C(15)-C(16)	1.378(5)
C(17)-C(18)	1.398(4)	C(17)-C(22)	1.378(4)
C(18)-C(19)	1.391(5)	C(19)-C(20)	1.355(5)
C(20)-C(21)	1.359(5)	C(21)-C(22)	1.384(5)
Si(4)-H(1)	1.39(2)		
Angles			
O(1)-Si(1)-C(1)	102.5(1)	O(1)-Si(1)-C(2)	108.9(1)
O(1)-Si(1)-C(3)	108.5(2)	C(1)-Si(1)-C(2)	114.7(1)
C(1)-Si(1)-C(3)	114.2(1)	C(2)-Si(1)-C(3)	107.7(2)
O(2)-Si(2)-C(1)	102.8(1)	O(2)-Si(2)-C(5)	108.4(1)
O(2)-Si(2)-C(6)	109.2(1)	C(1)-Si(2)-C(5)	113.9(1)
C(1)-Si(2)-C(6)	115.9(1)	C(5)-Si(2)-C(6)	106.4(2)
O(3)-Si(3)-C(1)	103.0(1)	O(3)-Si(3)-C(8)	108.2(2)
O(3)-Si(3)-C(9)	108.6(2)	C(1)-Si(3)-C(8)	114.1(1)
C(1)-Si(3)-C(9)	114.9(1)	C(8)-Si(3)-C(9)	107.7(2)
C(1)-Si(4)-C(11)	117.9(1)	C(1)-Si(4)-C(17)	116.4(1)
C(11)-Si(4)-C(17)	105.5(1)	Si(1)-O(1)-C(4)	126.3(2)
Si(2)-O(2)-C(7)	123.6(2)	Si(3)-O(3)-C(10)	127.4(2)
Si(1)-C(1)-Si(2)	110.2(1)	Si(1)-C(1)-Si(3)	110.3(1)
Si(1)-C(1)-Si(4)	110.7(1)	Si(2)-C(1)-Si(3)	108.5(1)
Si(2)-C(1)-Si(4)	110.7(1)	Si(3)-C(1)-Si(4)	106.3(1)
Si(4)-C(11)-C(12)	119.6(2)	Si(4)-C(11)-C(16)	122.7(2)
C(12)-C(11)-C(16)	117.4(3)	C(11)-C(12)-C(13)	121.1(3)
C(12)-C(13)-C(14)	119.9(3)	C(13)-C(14)-C(15)	120.2(4)
C(14)-C(15)-C(16)	120.1(3)	C(11)-C(16)-C(15)	121.2(3)
Si(4)-C(17)-C(18)	117.3(2)	Si(4)-C(17)-C(22)	125.6(2)
C(18)-C(17)-C(22)	116.7(3)	C(17)-C(18)-C(19)	121.1(3)
C(18)-C(19)-C(20)	120.3(3)	C(19)-C(20)-C(21)	119.7(3)
C(20)-C(21)-C(22)	120.6(3)	C(17)-C(22)-C(21)	121.5(3)
H(1)-Si(4)-C(11)	103(1)	H(1)-Si(4)-C(17)	104(1)
H(1)-Si(4)-C(1)	108(1)		

the  $\text{MeO}(1) \cdots \text{SiPh}_2\text{H}$  distance is 3.19 Å, i.e. significantly less than the sum (3.6 Å) of the relevant van der Waals radii. A

**Table 3** Rates of reaction of **1** and **3** (*ca.* 0.02 mol dm<sup>-3</sup>) with KSCN (0.10 mol dm<sup>-3</sup>) in MeCN

Chloride	T/°C	k <sup>a</sup> /10 <sup>4</sup> s <sup>-1</sup>	Relative rate
<b>1</b>	60	0.89	1
<b>3</b>	60	9.9	11
<b>3</b>	35	1.2	—

<sup>a</sup> Pseudo first-order rate constant for the first 50% of reaction.

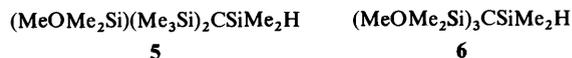
similar disposition of the single MeO group and the Si–Cl bond was found previously in (MeOMe<sub>2</sub>Si)(Me<sub>2</sub>Si)<sub>2</sub>CSiPh<sub>2</sub>Cl, in which the MeO...Si–Cl angle was 168° and the MeO...Si–Ph<sub>2</sub>Cl distance 3.2 Å.<sup>2</sup> The feature of interest in the structure of **4** is that a second MeO group, MeO(3), lies even closer to Si(4) [MeO(3)...Si(4) = 3.04 Å], and would be in a good position to undertake 'flank' attack on the Si–H bond [the angle O(3)...Si–H is 71(1)°], leading to an equatorial-apical orientation of the incoming and leaving group in a five-coordinate transition state or intermediate. It is thus attractive to attribute the high reactivity of the chloride **3** to participation of two MeO groups, in a six-coordinate transition state of the general type suggested by Corriu,<sup>5</sup> with one of the MeO groups in an equatorial position and another such group and the Cl ligand in apical positions; the process would still ultimately lead to the cation **1b**. (Such a transition state would be very crowded but not much more so than the substrate molecule). We cannot rule out this possibility but we note that on the assumption that **3** has a structure analogous to that of **4**, both the MeO(3) and the MeO(2) group would also be well placed to provide 'internal solvation' of the forming cation in a five-coordinate transition state, especially by MeO(3) of any positive charge developed on Si(4) and by MeO(2) of such charge on Si(1) [O(2)...Si(1) = 3.64 Å]. This and the orientational and steric effects considered earlier could suffice to account for the relative reactivities of **3** and **1**.

Other features of the structure of **4** are similar to those noted previously for the structures of the related compounds (MeOMe<sub>2</sub>Si)(Me<sub>3</sub>Si)<sub>2</sub>CSiPh<sub>2</sub>X (X = Cl or OMe).<sup>6</sup> It was found that the C–SiMe<sub>2</sub>OMe bonds in those species were significantly shorter than the C–SiMe<sub>3</sub> bonds, and the lengths of the C–SiMe<sub>2</sub>OMe bonds [mean 1.887(5)] in **4**, are similar to those in the other two compounds. This is consistent with our suggestion above that the effective bulk of MeOMe<sub>2</sub>Si groups is smaller than that of Me<sub>3</sub>Si groups.

**Relative Reactivities of 1 and 3 towards KSCN in MeCN.**—The trimethoxy compound **3** was also found to be more reactive than the mono-methoxy compound **1** in a reaction involving external nucleophilic attack at the Si–Cl bond in a bimolecular S<sub>N</sub>2 process, namely the reaction with KSCN in MeCN to give (MeOMe<sub>2</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>NCS. Since the reactions were carried out in the presence of a five-fold excess of KSCN satisfactory first-order plots were obtained up to 60% completion of the reaction, and the pseudo-first order rate constants are shown in Table 3. It can be seen that **3** is *ca.* 11 times as reactive as **1**; a similar factor was observed previously between **1** and (Me<sub>3</sub>Si)<sub>2</sub>CSiMe<sub>2</sub>Cl.<sup>1</sup> These relatively small influences of the MeO groups can reasonably be attributed to inductive withdrawal of electrons from the reaction centre (which probably becomes more negatively charged in the transition state) and slightly lower steric hindrance by MeOMe<sub>2</sub>Si than by Me<sub>3</sub>Si groups.

**Relative Reactivities of (MeOMe<sub>2</sub>Si)(Me<sub>3</sub>Si)<sub>2</sub>CSiMe<sub>2</sub>H and (MeOMe<sub>2</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>H towards Silver Salts.**—It was previously noted that, in contrast to the hydride (Me<sub>3</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>H,

which is inert towards silver salts, the related mono-methoxy compound reacts with some such salts, the anchimeric assistance by the MeO group making possible the (rate-determining) abstraction of H<sup>-</sup> by Ag<sup>+</sup> to give the cation **1b**.<sup>1</sup> Since this process is formally analogous to that of the (rate-determining) formation of **1b** in methanolysis of the chloride **1**, we expected that the trimethoxy-substituted hydride **6** would be more reactive than the corresponding monomethoxy compound **5**, and this proved to be the case.



Because of the heterogeneous nature of the reactions it was impracticable to measure rates of reaction of the hydrides separately, and so a mixture of **5** and **6** (0.33 mmol of each) with the silver salt (0.75 mmol) in the chosen solvent (5 cm<sup>3</sup>) was stirred at an appropriate temperature and samples were removed at intervals and analysed by GLC. In the reaction with AgO<sub>2</sub>CCF<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> at 35 °C, all of **6** and roughly half of **5** had reacted within *ca.* 5 min, to give the corresponding trifluoroacetates, and all of **5** had reacted after 15 min. A clearer result was obtained from the reaction with AgOCN in MeCN. After 14 days at 35 °C *ca.* 60% of **6** had reacted, to give (MeOMe<sub>2</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>NCO, but (within the limits of detection) none of **5**, and after 7 days at 50 °C *ca.* 85% of **6** but still none of **5** had reacted. Since reaction of up to 5% of **5** could have escaped detection we can conclude only that **6** is at least 20 times as reactive as **5** (though the actual factor is probably substantially larger), and this is consistent with the results for the methanolysis of the chlorides. In the reaction with AgOCOME in CH<sub>2</sub>Cl<sub>2</sub> at 35 °C, after 14 days *ca.* 40% of **6** had been converted into the corresponding acetate but none of **5** had reacted. There was no reaction of either hydride with AgSCN in MeCN during 14 days at 50 °C or with AgCl in CH<sub>2</sub>Cl<sub>2</sub> during 3 days at 35 °C.

## Experimental

**Materials.**—The preparations of the hydride **4**, the chlorides **1–3**, and the related compounds (MeOMe<sub>2</sub>Si)(Me<sub>3</sub>Si)<sub>2</sub>CSiMe<sub>2</sub>X and (Me<sub>3</sub>OMe<sub>2</sub>Si)<sub>3</sub>CSiMe<sub>2</sub>X (X = H, NCO, OCOF<sub>3</sub>) will be described elsewhere.<sup>4</sup> Methanol was dried by refluxing over and distillation from Mg(OMe)<sub>2</sub>, and stored over molecular sieves (3 Å); MeCN and CH<sub>2</sub>Cl<sub>2</sub> were dried over and distilled from CaH<sub>2</sub> and stored over molecular sieves (4 Å).

**Methanolysis of 1–3.**—The chloride (*ca.* 5 mg) was dissolved in a drop (*ca.* 0.01 cm<sup>3</sup>) of CCl<sub>4</sub> in an NMR tube and 0.5 cm<sup>3</sup> of a 1:3 methanol–dioxane mixture (containing, if appropriate, NaOMe or HCl), pre-warmed to the reaction temperature, was added. The tube was sealed, placed in a water bath kept at 35.0 ± 0.2 °C and transferred at appropriate intervals to the probe of the NMR spectrometer (which was kept at 35.0 ± 0.5 °C) for recording of the <sup>1</sup>H NMR spectrum. When reaction was complete the solvent was removed under reduced pressure and the residue taken up in CCl<sub>4</sub> for examination by <sup>1</sup>H NMR spectroscopy and linked GLC–mass spectrometry, which confirmed that the products were the expected (MeOMe<sub>2</sub>Si)<sub>2</sub>(Me<sub>3</sub>Si)<sub>2</sub>C, (MeOMe<sub>2</sub>Si)<sub>3</sub>(Me<sub>3</sub>Si)C and (MeOMe<sub>2</sub>Si)<sub>4</sub>C, respectively.

**Reactions of 1 and 3 with KSCN in MeCN.**—The chloride (*ca.* 5 mg) was dissolved in a solution of KSCN (0.5 cm<sup>3</sup>, 0.10 mol dm<sup>-3</sup>) in MeCN, pre-warmed to the reaction temperature and contained in an NMR tube. This was sealed and placed in a water bath kept at the chosen temperature (±0.5 °C). The tube was transferred at appropriate intervals to the probe of the NMR

**Table 4** Fractional atomic coordinates ( $\times 10^4$ )<sup>a</sup> with esds in parentheses

	x	y	z
Si(1)	4621.5(9)	1930.8(7)	6554.1(4)
Si(2)	1722.0(9)	2218.5(7)	7048.6(3)
Si(3)	2138.5(10)	241.9(7)	6284.6(4)
Si(4)	1852.3(8)	2537.7(6)	5775.8(3)
O(1)	4821(2)	3274(2)	6469(1)
O(2)	1919(2)	1137(2)	7464(1)
O(3)	2429(3)	79(2)	5631(1)
H(1)	59(3)	202(2)	556(1)
C(1)	2605(3)	1750(2)	6423(1)
C(2)	5419(4)	1540(3)	7269(2)
C(3)	5650(4)	1193(3)	6047(2)
C(4)	6132(4)	3861(3)	6528(2)
C(5)	-234(4)	2514(3)	6897(1)
C(6)	2540(4)	3459(3)	7422(1)
C(7)	1284(4)	1053(4)	7972(2)
C(8)	210(4)	-111(3)	6349(2)
C(9)	3287(4)	-764(3)	6720(2)
C(10)	2297(5)	-899(3)	5316(2)
C(11)	2967(3)	2580(2)	5166(1)
C(12)	2606(3)	1895(3)	4710(1)
C(13)	3294(4)	1993(3)	4229(1)
C(14)	4349(4)	2764(3)	4202(2)
C(15)	4738(4)	3441(3)	4647(2)
C(16)	4048(3)	3357(3)	5124(1)
C(17)	1284(3)	4018(2)	5884(1)
C(18)	-128(3)	4313(3)	5680(1)
C(19)	-585(4)	5413(3)	5684(1)
C(20)	338(4)	6222(3)	5888(2)
C(21)	1711(4)	5954(3)	6096(2)
C(22)	2180(4)	4863(3)	6096(2)

<sup>a</sup>  $\times 10^3$  for H.

spectrometer (kept at 35 °C) and the spectrum quickly recorded. Although the tube was carried to the spectrometer from the bath at 60 °C to the probe and back in a beaker of water initially at ca. 61 °C, the cooling during readings must have been significant in the case of the reaction of **3** at 60 °C and the rate constant could possibly be too low by up to 20% (though a good first-order plot was obtained) but such an error would have no significant influence on the conclusions. The first-order plots were satisfactorily linear up to >60% completion of the reaction; curvature was to be expected in the later stages because the KSCN was present initially in only five-fold excess. When the reactions were complete the solvent was evaporated off and the organic material extracted from the residue with CCl<sub>4</sub>. Examination of the extract by <sup>1</sup>H NMR spectrometry and MS confirmed that the products were the expected isocyanates (MeOMe<sub>2</sub>Si)(Me<sub>3</sub>Si)<sub>2</sub>CSiMe<sub>2</sub>NCO and (MeOMe<sub>2</sub>-Si)<sub>3</sub>CSiMe<sub>2</sub>NCO.

*Reactions of the Hydrides 5 and 6 with Silver Salts.*—A solution of **5** and **6** (0.33 mmol of each) in the chosen solvent (5 cm<sup>3</sup>) was stirred under nitrogen with the silver salt (0.75 mmol) in a small flask protected from light and kept in a constant temperature ( $\pm 0.5$  °C) bath. Small samples were removed at intervals and analysed by GLC. (Authentic samples of the products were available). When the reaction was complete or discontinued the remaining solution was filtered and

evaporated to dryness under vacuum. The residue was extracted with CCl<sub>4</sub> and the extract examined by linked GLC-MS, to confirm the identities of the products. The relevant results are described in the Results and Discussion section.

*Determination of the Crystal Structure of 4.*—Crystals were obtained by recrystallization from pentane. C<sub>22</sub>H<sub>38</sub>Si<sub>4</sub>O<sub>3</sub>,  $M = 462.9$ , monoclinic,  $a = 9.303(1)$ ,  $b = 12.041(7)$ ,  $c = 24.059(4)$  Å,  $\beta = 96.21(1)^\circ$ ,  $V = 2679.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.15$  g cm<sup>-3</sup>,  $F(000) = 1000$ . Monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 2.3$  cm<sup>-1</sup>. Space group  $P2_1/c$  from systematic absences of  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd.

A crystal ca.  $0.4 \times 0.4 \times 0.4$  mm was used for data collection at 295 K on an Enraf-Nonius CAD4 diffractometer. Intensities for  $+h + k \pm l$  with  $2 < \theta < 25^\circ$  were measured by a  $\theta/2\theta$  scan with a scan width of  $\Delta\theta = (0.8 + 0.35 \tan\theta)^\circ$  and a minimum scan time of 1 min. 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 and 3305 reflections with  $|F^2| > \sigma(F^2)$  were used for the structure analysis. The values of  $\sigma(F^2)$  were calculated as  $[\sigma^2(I) + (0.041I)^2]^{1/2}/Lp$ .

The positions of Si atoms were found by direct methods, and a difference map was used to locate C and O atoms, all of which were refined by full matrix least-squares with anisotropic temperature factors. The hydrogen atoms were found on a difference map and were refined with isotropic temperature factors. Refinement converged at  $R = 0.044$ ,  $R' = 0.054$ , with weighting scheme  $w = 1/\sigma^2(F)$ , and a maximum shift to esd of 6.3. A final difference map had peaks of up to  $0.4 e \text{ \AA}^{-3}$ .

The structure solution and refinement was carried out on a MicroVax computer using the Enraf-Nonius Structure Determination Package.<sup>7</sup> Scattering factors for neutral atoms were taken from ref. 8. The atom coordinates are listed in Table 4. Lists of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC).\*

#### Acknowledgements

We thank the SERC for support, the Royal Society for the award of a 1983 University Research Fellowship to P. D. L., Dr. A. G. Avent for the NMR spectra and Mr. A. Greenway for mass spectra and GLC-MS analyses.

#### References

- 1 C. Eaborn and M. N. Romanelli, *J. Chem. Soc., Perkin Trans. 2*, 1987, 657.
- 2 C. Eaborn, P. D. Lickiss, S. T. Najim and M. N. Romanelli, *J. Chem. Soc., Chem. Commun.*, 1985, 1754.
- 3 C. Eaborn and D. E. Reed, *J. Chem. Soc., Chem. Commun.*, 1983, 495.
- 4 F. I. Aigbirhio, N. H. Buttruss, C. Eaborn, S. Gupta, P. B. Hitchcock, A. C. Sullivan and J. D. Smith, to be published.
- 5 R. J. P. Corriu, *J. Organomet. Chem.*, 1990, **400**, 81.
- 6 N. H. Buttruss, C. Eaborn, P. B. Hitchcock, P. D. Lickiss and S. T. Najim, *J. Chem. Soc., Perkin Trans. 2*, 1987, 891 and 1753.
- 7 G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 260.
- 8 *International Tables for Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Paper 1/01731D

Received 15th April 1991

Accepted 17th May 1991

\* For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.