

# Reactions of acylpolysilanes with silyl Lewis acids

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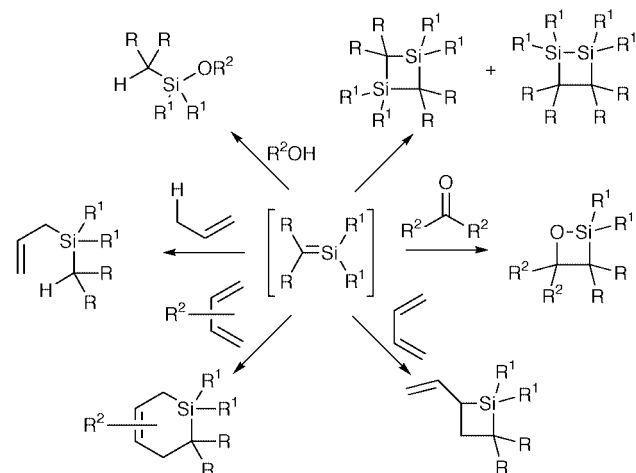
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The reaction of acylpolysilanes with TMSOT and TMS(NTf<sub>2</sub>) proceed *via* a series of 1,2 silyl and silyoxy shifts to afford the silanol products **5** and **6** respectively. A unified mechanistic pathway involving the formation of transient silonium ion complexes and silenes which rationalises these products is proposed. The structural assignment of the products is supported by X-ray structures for the phenyl **6a** and trifluoromethylphenyl **6b** substituted silanols.

## Introduction

Silenes, compounds containing a silicon–carbon double bond have been the object of some interest since their first recorded preparation in 1967.<sup>1,2</sup> Owing to their high reactivity, and in most cases transient existence, much of this effort has been focused on structural and bonding aspects with a particular emphasis on the preparation of stable isolable silenes.<sup>3,4</sup> In many cases evidence for the formation of silenes is obtained from the isolation of adducts from reactions with compounds of different functionalities including alcohols, alkenes and carbonyl compounds (Scheme 1).<sup>5</sup> However, despite this broad

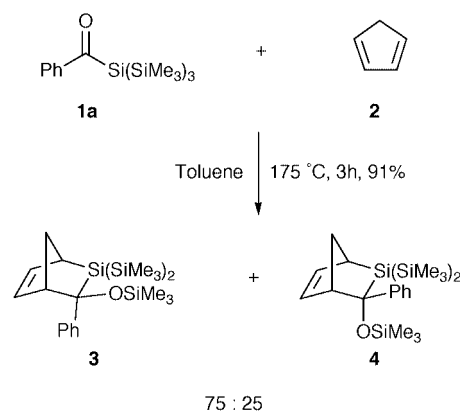


Scheme 1 Typical reactions of silenes.

repertoire of chemistry there has been little effort to exploit the unique reactivity of these species in organic synthesis. With this objective in mind we have initiated a programme to explore this aspect of silene chemistry.

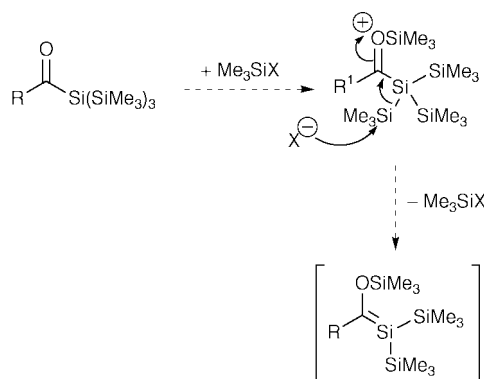
In the first instance we elected to examine the diastereoselectivity of the Diels–Alder reaction of the relatively stable alkoxy-silenes with a range of dienes. Brook has demonstrated that these silenes can be readily generated by either a thermal or photochemical mediated 1,3 silyl rearrangement of acylpolysilanes.<sup>6</sup> Using the former method it proved possible to generate the desired cycloadducts in good yields and with moderate diastereoselectivity (Scheme 2).<sup>7</sup>

However, the high temperatures needed (~180–200 °C) limit the variation of functionality in both reaction partners, require the use of specialised apparatus (Carius tube facility) and,



Scheme 2 Thermal reaction of acylpolysilanes with dienes.

potentially, account for the less than ideal diastereoselectivity. Similar problems of scale, apparatus and limitation of compatibility of ancillary functionality affect the photochemical generation of these alkoxy-silenes. Consequently, we sought alternative methods for silene generation and postulated that the treatment of the acylpolysilane with a silyl Lewis acid would lead, in a low temperature process, to a transient siloxysilene which could be trapped *in situ* by an appropriate diene (Scheme 3). In this paper we report the full

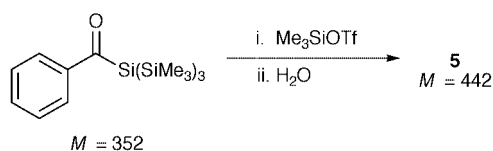


Scheme 3 Proposed reaction of acylpolysilanes with TMSOTf.

details of our studies of the reactions of acylpolysilanes and silyl Lewis acids and the transformations of the resultant products.<sup>8</sup>

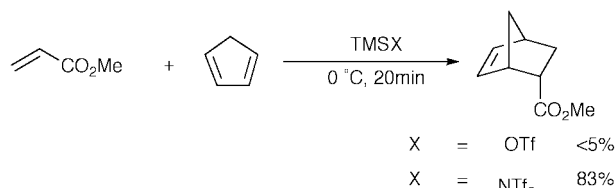
## Results and discussion

In view of our goal of generating siloxysilene cycloadducts from the reaction of acylpolysilane and silyl Lewis acid in the presence of a diene we required ready access to acylpolysilanes. These are readily accessible through the reaction of the corresponding acid chloride with tris(trimethylsilyl)silyllithium following established literature protocols. Treatment of a mixture of benzoylpolysilane **1a** and piperylene (penta-1,3-diene) with, either a stoichiometric or catalytic amount of, trimethylsilyl triflate ( $\text{Me}_3\text{SiOTf}$ , TMSOTf) afforded a complex mixture of products dominated by polymerised diene. In order to ascertain that silene formation had occurred we then carried out the reaction in the absence of the diene with a view to isolating the corresponding silene dimer. Under these conditions, whilst no evidence for silene dimers could be detected, a single new component **5** was obtained of molecular mass 442 and containing five discrete silicon atoms ( $^{29}\text{Si}$  NMR). However, a structure could not be unequivocally assigned at this stage, *vide infra* (Scheme 4).



Scheme 4 Reaction of benzoylpolysilane with TMSOTf.

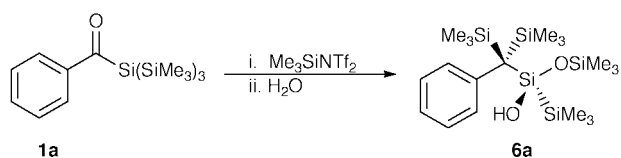
At this point in time, we became aware of a report by Mathieu and Ghosez *et al.* which advocated the use of trimethylsilylbis(triflimide) ( $\text{TMSNTf}_2$ ,  $\text{Me}_3\text{SiN}(\text{CF}_3\text{SO}_2)_2$ ) as an extremely powerful Lewis acid which does not cause the problems of alkene polymerisation frequently observed with TMSOTf (Scheme 5).<sup>9</sup> This reagent is readily prepared through



Scheme 5 Comparison of TMSOTf and TMSNTf<sub>2</sub>.

the reaction of allyltrimethylsilane with bis(trifluoromethylsulfonyl)imide followed by vacuum distillation.

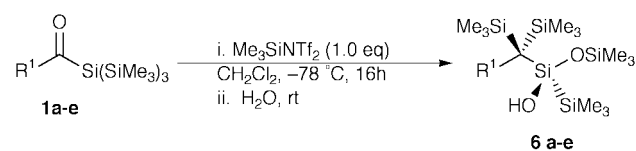
However, application of this reagent with benzoylpolysilane in the presence of piperylene proved to be no more successful with respect to diene degradation. In the absence of a diene the addition of a stoichiometric quantity of bistriflimide to a solution of benzoylpolysilane **1** in dichloromethane at  $-78\text{ }^\circ\text{C}$  afforded a deep red solution which on aqueous work up and purification by flash chromatography afforded a single colourless crystalline product in near quantitative yield (Scheme 6).



Scheme 6 Reaction of benzoylpolysilane with TMSNTf<sub>2</sub>.

This material was isomeric with that obtained from the reaction with TMSOTf with mass spectrometry indicating a molecular ion at 442 corresponding to the starting material plus  $\text{Me}_3\text{SiOH}$ . Elemental analysis confirmed this formula whilst infra-red spectroscopy revealed the presence of an OH group.

Table 1 Reaction of acylpolysilanes with trimethylsilylbistriflimides



Entry	<b>1</b>	R <sup>1</sup>	Product	Yield (%) <sup>a</sup>
1	<b>1a</b>	Ph	<b>6a</b>	93
2	<b>1a</b>	Ph	<b>6a</b>	9 <sup>b</sup>
5	<b>1b</b>	<i>p</i> -CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	<b>6b</b>	82
6	<b>1c</b>	<i>p</i> -MeO-C <sub>6</sub> H <sub>4</sub>	<b>6c</b>	<sup>c</sup>
7	<b>1d</b>	Me	<b>6d</b>	77
8	<b>1e</b>	<sup>t</sup> Bu	<b>6e</b>	n.r.

<sup>a</sup> Yields refer to purified isolated compounds. <sup>b</sup> 10 mol% of TMSNTf<sub>2</sub> was used. <sup>c</sup> Product decomposed on attempted isolation.

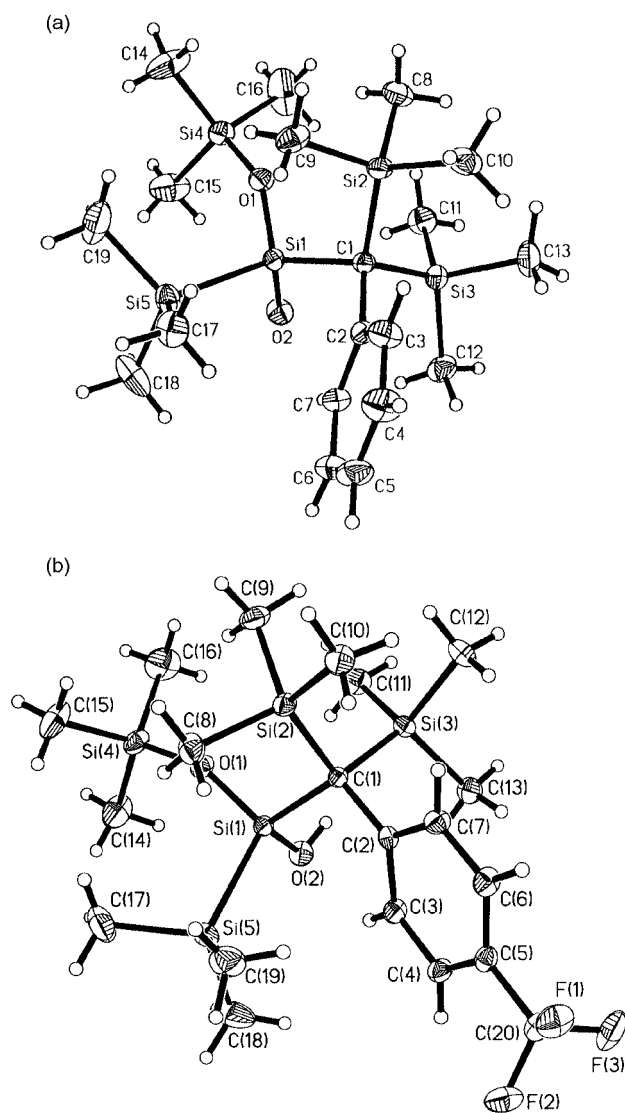
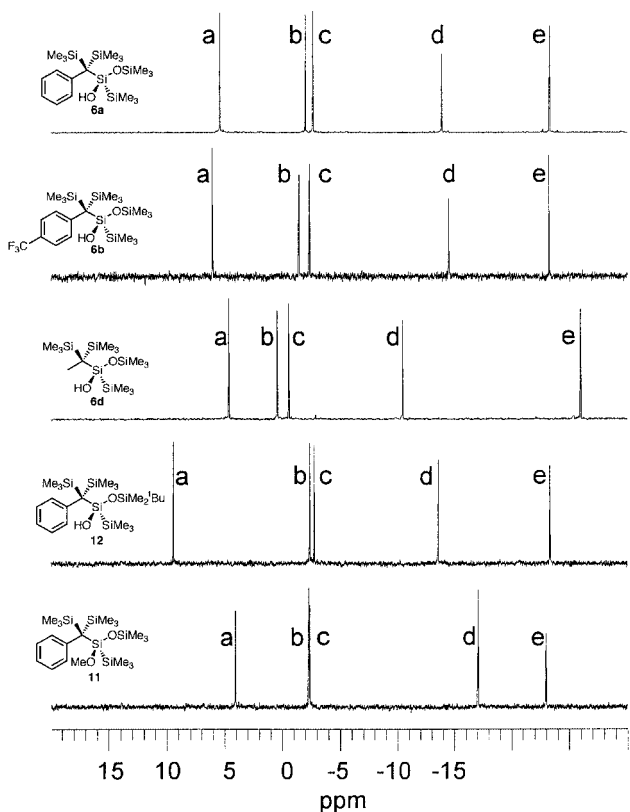


Fig. 1 Crystal structure of (a) silanol **6a** and (b) silanol **6b**.

However, it proved difficult to reconcile this data with the NMR spectra which showed four  $\text{SiMe}_3$  units and five different silicon signals. Fortunately it proved possible to grow crystals suitable for X-ray diffraction which revealed the structure as the silanol **6a** (Fig. 1a).

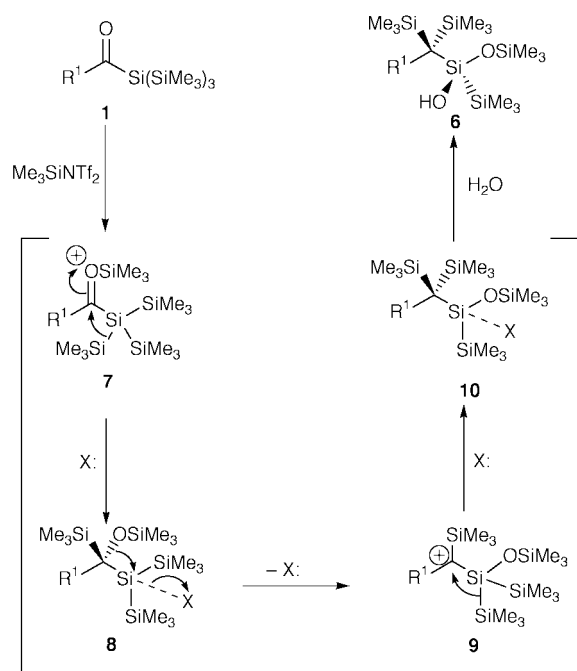
Repeating the reaction with other acylpolysilanes demonstrated that this is a general pathway (Table 1). With the exception of the pivaloyl derivative all polysilanes react to give the



**Fig. 2**  $^{29}\text{Si}$  NMR spectra of  $\text{TMSNTf}_2$  rearrangement products. a,  $\text{OSiR}_3$ ; b,  $\text{Me}_3\text{SiC}(\text{SiMe}_3)_2$ ; c,  $\text{Me}_2\text{SiC}(\text{SiMe}_3)_2$ ; d,  $\text{O-Si-O}$ ; e,  $\text{Si-SiMe}_3$ .

analogous product in good to excellent yields although the 4-methoxyphenyl derivative underwent decomposition upon attempted isolation. In all cases these compounds could be characterised by a range of analytical techniques including  $^{29}\text{Si}$  NMR which showed five distinctive signals (Fig. 2). Confirmation that these related to the same series was obtained by a second crystal structure using the 4-trifluoromethylphenyl derivative **6b** (Fig. 1b).

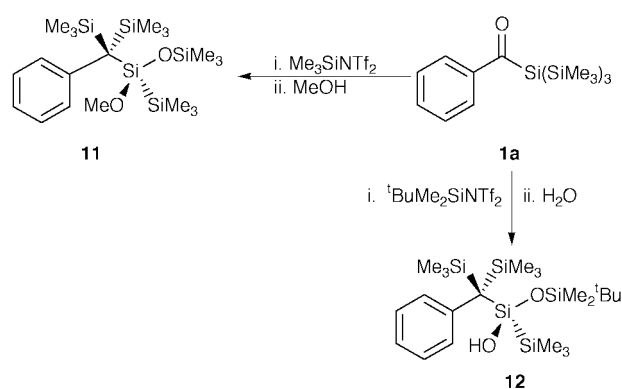
To account for these observations we suggest that the reaction follows the pathway outlined in Scheme 7. Initial activation of the carbonyl group by the Lewis acid generates the



**Scheme 7** Mechanistic pathway for the reaction of acylpolysilanes **1** with trialkylsilylbistriflimides.

oxocarbenium ion **7** which is stabilised by three  $\beta\text{-Me}_3\text{Si}$  units and the alkyl or aryl substituent,  $\text{R}^1$ . In the situation in which the acylpolysilane substituent provides little stabilisation for a neighbouring cationic centre there is no reaction (*e.g.*  $\text{R} = \text{'Bu}$ ). A 1,2 migration of a trimethylsilyl group from silicon to carbon then occurs, followed by a 1,2 shift of a trimethylsilyloxy group from carbon to silicon and a second silicon to carbon trimethylsilyl group migration. Related migrations of trimethylsilyl groups from silicon to an adjacent cationic centre are precedented.<sup>10–13</sup> The precise order of these events is not clear and these may be either concerted or stepwise pathways. Whilst a silyl cation may be invoked as an intermediate in this process we have obtained no evidence for this and Lewis base co-ordinated species **8** and **10** ( $\text{X} = \text{NTf}_2^-$  or  $\text{RCOSiR}'_3$ ) are equally plausible. The resultant “selenium ion” complex **10** is then hydrolysed by water on aqueous workup to produce the observed silanol.

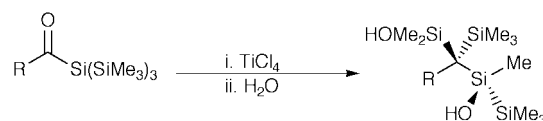
To corroborate this pathway we then explored several variations including the use of substoichiometric quantities of bistriflimide and activating the reaction using *tert*-butyldimethylsilylbistriflimide ( $\text{TBDMSNTf}_2$ ) (Scheme 8), prepared



**Scheme 8**

in an analogous fashion from *tert*-butyldimethylallylsilane and bis(trifluoromethylsulfonyl)imide. These reactions provided definitive evidence for the direct involvement of the silylbistriflimide in the reaction with the yield and degree of conversion being comparable to the stoichiometry (Table 1, run 2) and the incorporation of the TBDMS group into the product at the silyloxy position as confirmed by  $^{29}\text{Si}$  NMR spectroscopy (**12**  $\text{OSi}^t\text{BuMe}_2$ ,  $\delta = 9.48$ , **6a**  $\text{OSiMe}_3$ ,  $\delta = 5.44$ , Fig. 2). Finally, use of methanol to quench the reaction generated the corresponding methyl ether **11** consistent with the formation of a selenium ion complex as the final intermediate on the pathway.

Related structures have been reported by Brook *et al.* in the reaction of tertiary alkyl acylpolysilanes ( $\text{R} = \text{'Bu}$ , adamantyl and 2,2,2-bicyclooctyl) with titanium tetrachloride (Scheme 9).<sup>12</sup> This was accounted for by a similar mechanistic pathway

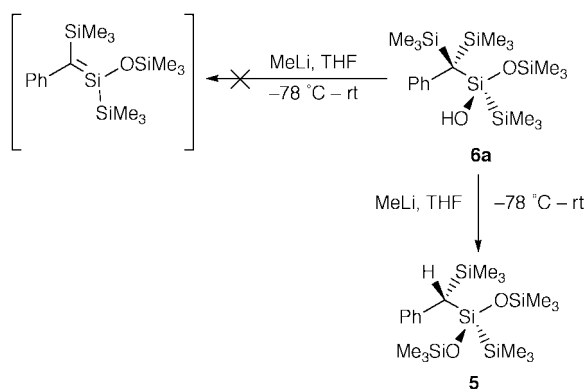


**Scheme 9** Reaction of acylpolysilanes with  $\text{TiCl}_4$ .

although, in this latter case, a 1,3 methyl shift from one of the trimethylsilyl groups to the “selenium ion” also occurs. Reasons for this difference between the titanium tetrachloride and the bistriflimide promoted pathways are not obvious at the present time.

Although this rearrangement did not afford the desired silene dimer it occurred to us that the presence of  $\alpha,\beta$ -hydroxysilane within this product might allow these silanols to function as convenient silene precursors through a Peterson type elimin-

ation. This method of silene generation has been exploited by Oehme and co-workers in the generation of transient alkyl substituted silenes.<sup>14</sup> Consequently, treatment of the silanols with MeLi was undertaken. In no case could any evidence for silene dimers or cycloadducts be observed. However, reaction of silanol **6a** with MeLi afforded the identical material to that obtained from the reaction of benzoylpolysilane with TMSOTf (Scheme 10). Subsequent NMR studies, using 2D H-C corre-



Scheme 10 Reaction of silanol **6a** with MeLi.

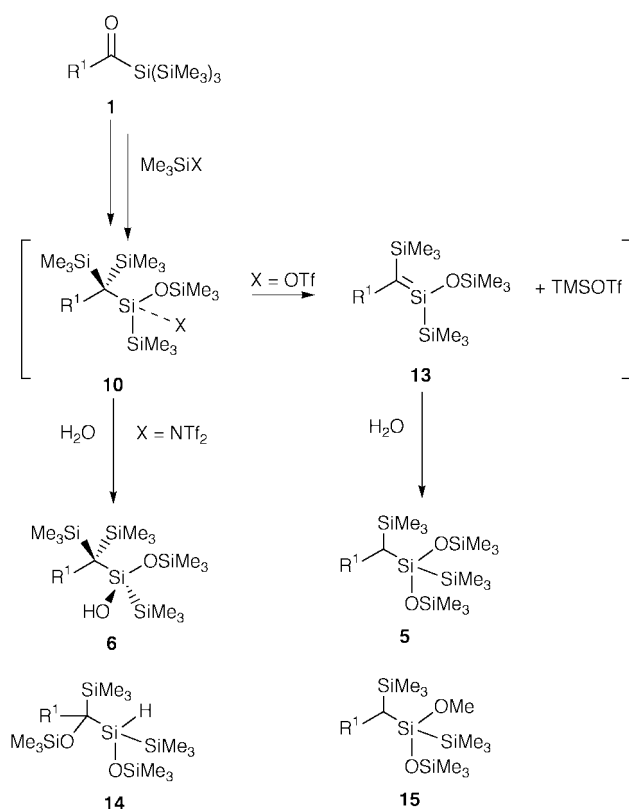
lation experiments, allowed the assignment of structure as that shown in Scheme 10. Similar anionic Brook-type migrations of silyl groups to proximal oxy-anions have been observed in related systems using a number of different bases (MeLi, KH, NaH).<sup>10</sup> Attempts to achieve the Peterson elimination under acidic conditions (HF, HBF<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>) failed, all variations merely returning unchanged silanol.

To account for these observations we suggest that the reaction of acylpolysilanes with silyl Lewis acids is initiated by activation of the carbonyl group followed by the 1,2 migrations as described above to afford silenium ion complex **10**. The more nucleophilic triflate anion then displaces a neighbouring trimethylsilyl group to generate a transient silene **13** which on addition of water undergoes nucleophilic attack by trimethylsilanol generated by hydrolysis of the residual TMSOTf. The less nucleophilic bistriflimide anion is not sufficiently active to promote the elimination to the silene and the hydrolysis product, silanol **6**, of intermediate complex **10** is isolated upon addition of water. Further evidence for this hypothesis is obtained through variation of the time and temperature of the TMSOTf mediated reaction. If the reaction mixture is maintained at  $-78^{\circ}\text{C}$  and quenched after a shorter period of time then both silanol **6** and bis(silyloxy)acetal **5** can be isolated. Larger scale versions of this reaction allow the isolation of small amounts (5–20% by NMR using <sup>29</sup>Si-<sup>1</sup>H satellites) of the alternative regioisomer **14** by nucleophilic addition of trimethylsilanol to the silene **13**. Finally, quenching the reaction mixture with methanol leads to the corresponding methyl silyl ether **15** (Scheme 11).

In conclusion, a rearrangement involving a series of 1,2 shifts of silyl and silyloxy groups occur on treatment of acylpolysilanes with silyl Lewis acids. Silene intermediates can be invoked when the silyl counter ion is sufficiently nucleophilic (X = OTf) although all attempts to trap these species have, to date, proved unsuccessful. Current work is focused on circumventing these difficulties and exploring alternative mild methods of silene generation. These will be reported in due course.

## Experimental

All reactions were undertaken in an inert gas atmosphere of dry nitrogen or argon in pre-dried glassware. Nuclear magnetic resonance (NMR) spectra were obtained on Varian Inova 500



Scheme 11 Overall mechanistic pathway for the reaction of acylpolysilanes with silyl Lewis acids.

(<sup>29</sup>Si at 99.325 MHz), VXR-400 (<sup>1</sup>H at 399.952 MHz, <sup>13</sup>C at 100.577 MHz), Unity-300 (<sup>1</sup>H at 299.910 MHz, <sup>13</sup>C at 75.420 MHz) and Mercury-200 (<sup>1</sup>H at 199.993 MHz, <sup>13</sup>C at 50.293 MHz) spectrometers with CDCl<sub>3</sub> as solvent ( $\delta = 7.26$ ) and are recorded in ppm ( $\delta$  units) downfield of tetramethylsilane ( $\delta = 0$ ) with coupling constants quoted in Hertz (Hz). Infra-red (IR) spectra were recorded on a Perkin Elmer FT-IR 1720X spectrometer. Low-resolution mass spectra were recorded on VG Analytical 7070E and VG Autospec organic mass spectrometers, and gas chromatography–mass spectra (GC-MS) were recorded using a Hewlett Packard 5890 Series II gas chromatograph connected to a VG mass Lab trio 1000. Flash column chromatography was performed on silica (60–240 mesh). Melting points were determined using Gallenkamp melting point apparatus and are uncorrected. All solvents were distilled prior to use following standard protocols.<sup>15</sup> Petroleum ethers refer to the fraction boiling in the 40–60 °C range unless otherwise stated. Acylpolysilanes were prepared from the corresponding acid chloride following literature procedures.<sup>6</sup>

## General procedure for reaction of acylpolysilanes with silylbistriflimides

A solution of acylpolysilane in dichloromethane (~0.3 M) was cooled to  $-78^{\circ}\text{C}$ . Silylbistriflimide (1 eq.) was then added. The solution became dark red in colour and was stirred at  $-78^{\circ}\text{C}$  for approximately 16 hours when saturated NaHCO<sub>3</sub> solution was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether. The combined organic layers were then dried over MgSO<sub>4</sub>, filtered, and concentrated to give the crude product which was purified as described below.

**1-Hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane 6a.** A solution of benzoyl-tris(trimethylsilyl)silane (1.11 g, 3.30 mmol) was treated with trimethylsilylbistriflimide (1.12 g, 3.29 mmol) as described above to give an off-white solid. Recrystallisation from ethanol gave pure **6a** as colourless crystals (1.35 g, 93%); mp 92–93 °C

(Found: C, 50.27; H, 9.61.  $C_{19}H_{42}O_2Si_5$  requires C, 51.52; H, 9.56%);  $\nu_{\max}$  (KBr disc)/ $cm^{-1}$  3629, 3552 (br, -OH), 3055, 1945, 1686, 1593, 1497, 1439, 1403, 1264, 1150;  $\delta_H$  (300 MHz) 7.52–7.01 (5H, m, Ar-H), 2.20 (1H, s, -OH), 0.23, 0.22, 0.21 (each 9H, s,  $2 \times C-Si(CH_3)_3$ ,  $1 \times O-Si(CH_3)_3$ ), -0.15 (9H, s, Si-Si( $CH_3$ )<sub>3</sub>);  $\delta_C$  (75 MHz) 141.5, 131.7, 127.9, 123.8, 28.8, 3.87, 3.86, 2.8, -0.5;  $\delta_{Si}$  5.4, -2.0, -2.7, -13.9, -23.3;  $m/z$  ( $EI^+$ ) 442 (14%,  $M^+$ ), 427 (22,  $M^+ - CH_3$ ), 411 (17), 369 (81,  $M^+ - SiMe_3$ ), 353 (46,  $M^+ - OSiMe_3$ ), 337 (44), 279 (48), 264 (40), 207 (33), 147 (47), 135 (31), 73 (100).

Crystal data for **6a** was reported in the preliminary communication.<sup>8</sup>

### 1-Hydroxy-1-[4'-trifluoromethylphenyl]bis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane **6b**

A solution of (4-trifluoromethylbenzoyl)tris(trimethylsilyl)silane (0.89 g, 2.12 mmol) was treated with trimethylsilylbistriflimide (0.76 g, 2.15 mmol) as described above to give an off-white solid. Recrystallisation from ethanol gave pure **6b** as colourless crystals (0.90 g, 82%); mp 68–69 °C (Found: C, 46.82; H, 8.38.  $C_{20}H_{41}F_3O_2Si_5$  requires C, 47.01; H, 8.09%);  $\nu_{\max}$  (KBr disc)/ $cm^{-1}$  3550 (br, OH), 3048, 2933, 2854, 1855, 1550, 1476, 1401, 1245, 1130;  $\delta_H$  (250 MHz) 7.64–7.43 (4H, m, aromatic), 2.20 (1H, br s, -OH), 0.25, 0.22, 0.20 (each 9H, s,  $2 \times C-Si(CH_3)_3$ ,  $1 \times O-Si(CH_3)_3$ ), -0.14 (9H, s, Si-Si( $CH_3$ )<sub>3</sub>);  $\delta_C$  (100 MHz) 146.7, 131.7, 125.8 (q, -CF<sub>3</sub>), 29.8, 3.8, 3.6, 2.8, -0.5;  $\delta_F$  (235 MHz) -62.6;  $\delta_{Si}$  6.1, -1.4, -2.3, -14.5, -23.2;  $m/z$  ( $EI^+$ ) 510 ( $M^+$ , 3.4%), 495 ( $M^+ - CH_3$ , 2), 437 ( $M^+ - SiMe_3$ , 3), 420 ( $M^+ - OSiMe_3$ , 6), 147 (13), 73 (100), 71 (55).

Crystal data for **6b**:  $\dagger C_{20}H_{41}F_3O_2Si_5$ ,  $M = 510.98$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.237(2)$ ,  $b = 10.977(2)$ ,  $c = 13.598(3)$  Å,  $\alpha = 100.67(3)$ ,  $\beta = 109.10(1)$ ,  $\gamma = 90.40(3)^\circ$ ,  $U = 1415.2(5)$  Å<sup>3</sup>,  $F(000) = 548$ ,  $Z = 2$ ,  $D_c = 1.199$  mg m<sup>-3</sup>,  $\mu = 0.286$  mm<sup>-1</sup> (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å),  $T = 120(1)$  K. 15765 reflections ( $1.62 = \theta = 27.48^\circ$ ) were collected on a Bruker SMART-CCD diffractometer ( $\omega$ -scan,  $0.3^\circ$ /frame) yielding 6471 unique data ( $R_{\text{merge}} = 0.023$ ). The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were placed geometrically and refined with a riding model. Final  $wR_2(F^2) = 0.0903$  and  $R(F) = 0.0378$  for all data (284 refined parameters), GOF = 1.042, residuals min = -0.50 e Å<sup>-3</sup> and max = 0.61 e Å<sup>-3</sup>.

### 1-[1',1'-Bis(trimethylsilyl)ethyl]-1-hydroxy-2,2,2-trimethyl-1-trimethylsilyloxydisilane **6d**

A solution of acetyltris(trimethylsilyl)silane (0.73 g, 2.50 mmol) was treated with trimethylsilylbistriflimide (0.88 g, 2.50 mmol) as described above to give a crude oil. Purification by flash column chromatography (eluent: 5% ethyl acetate–petroleum ether) afforded the title disilane **6d** as a colourless oil (0.73 g, 77%) (Found: ( $M + NH_4$ )<sup>+</sup>, 398.2218.  $C_{14}H_{44}O_2NSi_5$  requires  $M$ , 398.2218);  $\nu_{\max}$  (LF)/ $cm^{-1}$  3686, 3500 (broad, OH), 2950, 2904, 2864, 1461, 1406, 1254, 1044;  $\delta_H$  (300 MHz) 1.95–1.80 (1H, br, -OH), 1.10 (3H, s,  $CH_3$ ), 0.16 (18H, s), 0.10 (9H, s) ( $2 \times C-Si(CH_3)_3$ ,  $1 \times O-Si(CH_3)_3$ ), -0.08 (9H, s, Si-Si( $CH_3$ )<sub>3</sub>);  $\delta_C$  (50 MHz) 12.5, 6.3, 2.6, 0.9, 0.7, 0.1;  $\delta_{Si}$  4.7, 0.4, -0.5, -10.4, -25.9;  $m/z$  ( $EI^+$ ) 365 ( $M^+ - CH_3$ , 3%), 349 (6), 307 ( $M^+ - SiMe_3$ , 17), 217 (35), 147 (14), 73 (100%).

### 1-Methoxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane **11**

A solution of benzoyltris(trimethylsilyl)silane (0.85 g, 2.43 mmol) was treated with trimethylsilylbistriflimide (0.86 g, 2.43 mmol) as described above except that the reaction was

quenched by the addition of methanol followed by water. The resultant crude oil was purified by flash column chromatography (eluent: petroleum ether) to afford the title ether **11** as a white solid (0.99 g, 89%); mp 207–208 °C (Found: C, 51.43; H, 10.14.  $C_{20}H_{44}O_2Si_5$  requires C, 51.56; H, 9.70%);  $\nu_{\max}$  (KBr disc)/ $cm^{-1}$  2955, 2899, 2834, 1594, 1497, 1446, 1410, 1255, 1101;  $\delta_H$  (200 MHz) 7.56–7.02 (5H, m, aromatic), 3.64 (3H, s, -OCH<sub>3</sub>), 0.34, 0.29, 0.26 (each 9H, s,  $2 \times C-Si(CH_3)_3$ ,  $1 \times O-Si(CH_3)_3$ ), -0.10 (9H, s, Si-Si( $CH_3$ )<sub>3</sub>);  $\delta_C$  (50 MHz) 141.8, 131.9, 127.8, 123.7, 50.5, 29.0, 4.1, 3.7, 2.9, 0.4;  $\delta_{Si}$  4.1, -2.26, -2.34, -17.0, -22.9;  $m/z$  ( $EI^+$ ) 457 ( $M^+$ , 4%), 441 ( $M^+ - CH_3$ , 8), 383 ( $M^+ - SiMe_3$ , 32), 147 (30), 73 (100).

### 1-Hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-(*tert*-butyldimethylsilyloxy)disilane **12**

A solution of benzoyltris(trimethylsilyl)silane (1.03 g, 2.94 mmol) was treated with (*tert*-butyldimethylsilyl)bistriflimide (1.25 g, 3.16 mmol) as described above to give a crude oil. Purification by flash column chromatography (eluent: 5% ethyl acetate–petroleum ether) yielded the title disilane **12** as a clear oil (1.20 g, 84%) (Found:  $M^+$ , 484.2465.  $C_{22}H_{48}O_2Si_5$  requires  $M$ , 484.2501);  $\nu_{\max}$  (LF)/ $cm^{-1}$  3674 (s, -OH), 3054, 2955, 2897, 2858, 1593, 1497, 1472, 1361, 1253, 1151;  $\delta_H$  (300 MHz) 7.55–7.10 (5H, m, aromatic), 2.30 (1H, br s, -OH), 0.96 (9H, s, -C( $CH_3$ )<sub>2</sub>), 0.23, 0.22 (9H each,  $2 \times C-Si(CH_3)_3$ ), 0.18, 0.16 (3H, each, -Si( $CH_3$ )<sub>2</sub><sup>t</sup>Bu, diastereotopic), -0.15 (9H, s, Si-Si( $CH_3$ )<sub>3</sub>);  $\delta_C$  (50 MHz) 141.7, 131.9, 127.9, 123.9, 29.4, 26.5, 18.8, 4.1, 0.0, -1.3, -1.5;  $\delta_{Si}$  9.5, -2.4, -2.7, -13.5, -23.3;  $m/z$  ( $EI^+$ ) 484 ( $M^+$ , 1%), 469 ( $M^+ - CH_3$ , 2.5), 424 ( $M^+ - ^t$ Bu, 1.5), 411 ( $M^+ - SiMe_3$ , 25), 147 (29), 73 (100%).

### 1-[Phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1,1-bis(trimethylsilyloxy)disilane **5**

A solution of 1-hydroxy-1-[phenylbis(trimethylsilyl)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane **6a** (0.10 g, 0.23 mmol) in diethyl ether (5 ml) was cooled to -78 °C. Methyl-lithium (1.6 M solution in diethyl ether, 0.15 ml, 0.23 mmol) was then added. The solution was allowed to warm to 0 °C over 5 h and then stirred for a further 12 h at this temperature. Saturated NH<sub>4</sub>Cl solution was then added, the layers were separated and the aqueous layer extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated to give the crude product. Flash column chromatography (eluent: petrol) gave the product as a white solid (0.075 g, 74%); mp 117–119 °C (Found: C, 51.28; H, 9.66.  $C_{19}H_{42}O_2Si_5$  requires C, 51.49; H, 9.56%);  $\nu_{\max}$  (KBr disc)/ $cm^{-1}$  2957, 2899, 1598, 1494, 1254, 1201, 1074, 1041;  $\delta_H$  (500 MHz) 7.17–7.00 (5H, m, aromatic), 1.58 (1H, s, Ph( $Me_3Si$ )CH), 0.15, 0.12 ( $2 \times 9H$ , s,  $2 \times OSi(CH_3)_3$  diastereotopic), 0.01 (9H, s, CHSi( $Si(CH_3)_3$ )), -0.19 (9H, s, Si-Si( $CH_3$ )<sub>3</sub>);  $\delta_C$  (100 MHz) 140.7, 129.7, 128.0, 123.5, 33.8, 2.5, 2.3, -0.1, -1.4;  $\delta_{Si}$  0.2, -0.8, -5.8, -31.7, -32.7;  $m/z$  ( $EI^+$ ) 442 ( $M^+$ , 0.5%), 427 ( $M^+ - CH_3$ , 3%), 369 ( $M^+ - SiMe_3$ , 7%), 279 (40), 265 (12), 191 (29), 147 (19), 73 (100).

### Reaction of benzoylpolydisilane **1a** with trimethylsilyl trifluoromethylsulfonate: 1-[phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1,1-bis(trimethylsilyloxy)disilane **5** and 1-[phenyl(trimethylsilyl)(trimethylsilyloxy)methyl]-2,2,2-trimethyl-1-trimethylsilyloxydisilane **14**

A solution of benzoyltris(trimethylsilyl)silane **1a** (1.24 g, 3.52 mmol) in dichloromethane (10 ml) was cooled to -20 °C. Trimethylsilyl trifluoromethanesulfonate (3.52 mmol) was then added. The solution was then stirred for approximately 14 h when saturated NaHCO<sub>3</sub> solution was added. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated to give the crude product as an orange oil. Purification by flash column chromatography

<sup>†</sup> CCDC reference number 207/379. See <http://www.rsc.org/suppdata/pl/1999/3645> for crystallographic files in .cif format.

(eluent: petrol) gave the title products (colourless semisolid) as an inseparable mixture (1.25 g, 2.82 mmol, 80%). Both GC and  $^1\text{H}$  NMR analyses indicated a ratio of **5**:**14** of 81:19.  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ )/ $\text{cm}^{-1}$  3060, 2957, 2897, 1596, 1494, 1449, 1405, 1252, 1200;  $\delta_{\text{H}}$  (500 MHz) 7.40–6.96 (5H, m, aromatic, both isomers), 5.26 (1H, s, SiH, minor), 1.59 (1H, s, Ph(Me<sub>3</sub>Si)CH, major), 0.16 (9H, s, OSi(CH<sub>3</sub>)<sub>3</sub>, major and 2 × 9H, s, OSi(CH<sub>3</sub>)<sub>3</sub>, minor), 0.13 (9H, s, OSi(CH<sub>3</sub>)<sub>3</sub>, major), 0.09 (2 × 9H, s, PhC(OSiMe<sub>3</sub>)Si(CH<sub>3</sub>)<sub>3</sub> and Si(SiCH<sub>3</sub>)<sub>3</sub>, both minor), 0.01 (9H, s, PhCHSi(CH<sub>3</sub>)<sub>3</sub>, major), -0.18 (9H, s, Si-Si(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (125 MHz) 141.9, 140.7, 130.9, 129.7, 128.0, 127.6, 123.5, 33.8, 2.5, 2.3, 2.0, 1.7, -0.0, -1.4;  $m/z$  (EI<sup>+</sup>) major: 442 (M<sup>+</sup>, 1%), 369 (M<sup>+</sup> - SiMe<sub>3</sub>, 10%), 279 (51), 265 (19), 191 (40), 147 (34), 73 (100);  $m/z$  (EI<sup>+</sup>) minor: 442 (M<sup>+</sup>, 1%), 427 (M<sup>+</sup> - SiMe<sub>3</sub>, 8%), 368 (20), 280 (23), 265 (20), 147 (20), 135 (10), 73 (100).

#### 1-[Phenyl(trimethylsilyl)methyl]-2,2,2-trimethyl-1-methoxy-1-trimethylsilyloxydisilane **15**

A solution of benzoyltris(trimethylsilyl)silane **1a** (0.51 g, 1.46 mmol) in dichloromethane (10 ml) was cooled to -20 °C. Trimethylsilyl trifluoromethanesulfonate (1.46 mmol) was then added. The solution was stirred for approximately 14 h when methanol was added. After 1 h saturated NaHCO<sub>3</sub> solution was then added. The organic layer was separated, and the aqueous layer extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated to give the crude product as a dark yellow oil. Purification by flash column chromatography (eluting: petrol) gave the title silane **15** as a colourless oil (0.33 g, 58%) (Found: M<sup>+</sup>, 384.1792. C<sub>17</sub>H<sub>36</sub>O<sub>2</sub>Si<sub>4</sub> requires *M*, 384.1792);  $\nu_{\text{max}}$  (thin film)/ $\text{cm}^{-1}$  3020, 2956, 2898, 2835, 1700, 1597, 1493, 1450, 1405, 1287, 1251, 1204;  $\delta_{\text{H}}$  (400 MHz) 7.20–7.00 (5H, m, aromatic), 3.52 (3H, s, OCH<sub>3</sub>), 1.60 (1H, s, Ph(Me<sub>3</sub>Si)CH), 0.16 (9H, s, OSi(CH<sub>3</sub>)<sub>3</sub>), 0.01 (9H, s, PhCHSi(CH<sub>3</sub>)<sub>3</sub>), -0.17 (9H, s, Si-Si(CH<sub>3</sub>)<sub>3</sub>);  $\delta_{\text{C}}$  (100 MHz) 140.4, 129.6, 128.1, 123.6, 50.8, 32.7, 2.4, -0.2, -1.0;  $m/z$  (EI<sup>+</sup>) 384 (M<sup>+</sup>, 2%), 369 (M<sup>+</sup> - CH<sub>3</sub>, 22), 311 (M<sup>+</sup> - SiMe<sub>3</sub>, 17), 265 (20), 221 (100), 117 (44), 73 (76).

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#### References

- 1 L. E. Gusel'nikov and M. C. Flowers, *J. Chem. Soc., Chem. Commun.*, 1967, 864.
- 2 G. Raabe and J. Mischl, in *The Chemistry of Organosilicon Compounds*, ed. S. Patai and Z. Rappoport, J. Wiley and Sons Ltd., Chichester, 1989, pp. 1044–1102.
- 3 N. Wiberg, G. Wagner, J. Riede and G. Muller, *Organometallics*, 1987, **6**, 32.
- 4 A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. M. R. Kallury, Y. C. Poon, Y. M. Chang and W. Wong-Ng, *J. Am. Chem. Soc.*, 1982, **104**, 5667.
- 5 A. G. Brook, S. S. Hu, A. K. Saxena and A. J. Lough, *Organometallics*, 1991, **10**, 2758.
- 6 A. G. Brook, J. W. Harris, J. Lennon and M. El Sheikh, *J. Am. Chem. Soc.*, 1979, **101**, 83.
- 7 A. S. Batsanov, I. M. Clarkson, J. A. K. Howard and P. G. Steel, *Tetrahedron Lett.*, 1996, **37**, 2491.
- 8 M. B. Berry, R. J. Griffiths, D. S. Yufit and P. G. Steel, *Chem. Commun.*, 1998, 2155.
- 9 B. Mathieu and L. Ghosez, *Tetrahedron Lett.*, 1997, **38**, 5497.
- 10 K. Sternberg and H. Oehme, *Eur. J. Inorg. Chem.*, 1998, 177.
- 11 K. Sternberg, M. Michalik and H. Oehme, *J. Organomet. Chem.*, 1997, **533**, 265.
- 12 A. G. Brook, M. Hesse, K. M. Baines, R. Kumarathanan and A. J. Lough, *Organometallics*, 1993, **12**, 4259.
- 13 M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, 1958, **23**, 292.
- 14 C. Krempner, H. Reinke and H. Oehme, *Chem. Ber.*, 1995, **128**, 143.
- 15 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1988.

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