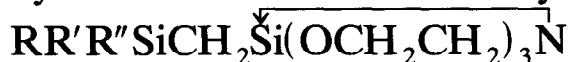


Synthesis and structure of silylmethylsilatrane



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Abstract

New alkoxy-silylmethylsilatrane $\text{MePhROSiCH}_2\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ have been obtained from the reaction of silylmethylsilatrane $\text{MePhHSiCH}_2\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ with alcohols in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. Methylphenylsilylmethylsilatrane (1) reacted with H_2O in the presence of Pd to give methylphenyl(silatranylmethyl)silanol (6) which was converted to siloxane (7) and germoxane (8). The molecular structures of the silatrane 1 and silanol 6 have been determined by an X-ray diffraction study which revealed the presence of intramolecular $\text{OH} \cdots \text{O}$ bond in the latter.

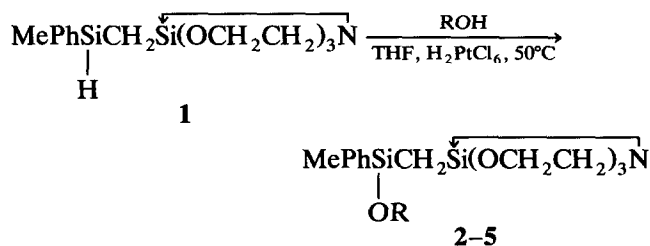
Key words: Germanium; Silicon; Silatrane; Crystal structure; Hydrogen bonding

1. Introduction

We have shown previously that chloromethylsilatrane readily reacts (65°C; tetrahydrofuran THF, 1–3 h) with chlorosilanes under Barbier reaction conditions (in the presence of magnesium in THF) to give silatranylmethylsilanes with good yields [1]. We now report some chemical, physical and structural properties of this type of compound.

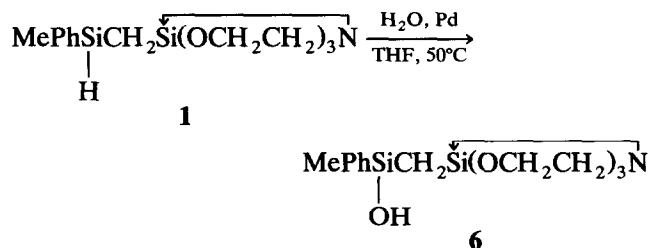
2. Results and discussion

We found that methylphenyl(silatranylmethyl)silane (1) readily reacts with alcohols in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in THF to give (silatranylmethyl)alkoxysilanes (2–5) in good yields (77%–95% by GLC)

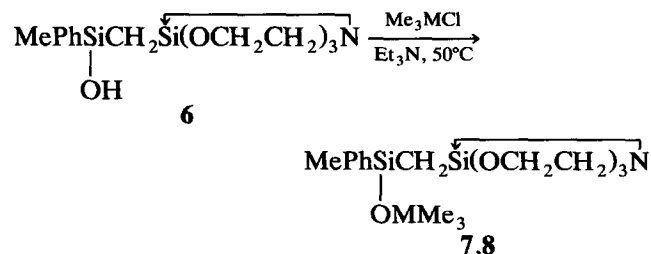


where: R = Me(2); Et(3); ⁱPr(4); ^tBu(5).

Methylphenyl(silatranylmethyl)silanol (6) was obtained in quantitative yield by reaction of methylphenyl(silatranylmethyl)silane (1) with H_2O in THF in the presence of Pd (black):



The silanol 6 reacted with trimethylchlorosilane and trimethylchlorogermane at 50°C in the presence of Et_3N to give 1,1,1,3-tetramethyl-3-phenyl-3-silatranylmethyl-disiloxane (7) and trimethyl[methylphenyl(silatranylmethyl)siloxy]germane (8)



where: M = Si(7); Ge(8).

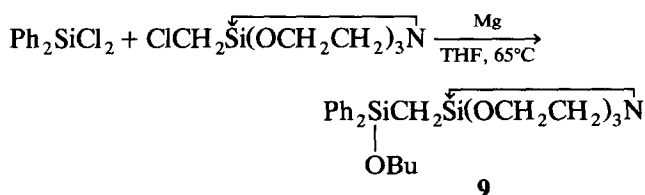
Correspondence to: Prof. E. Lukevics.

TABLE 1. ^1H chemical shifts for silylmethylsilatranes $\text{RR}'\text{R}''\text{SiCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$

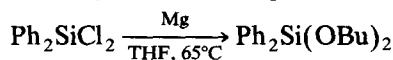
No. of compounds	R	R'	R''	δH^a (ppm)				
				OCH_2	CH_2N	SiCH_3	SiCH_2Si	R''
1	CH_3	C_6H_5	H	3.68	2.69	0.37	0.03; -0.05^b	4.44
10	CH_3	C_6H_5	CH_3	3.65	3.67	0.30	-0.06	0.30
11	CH_3	C_6H_5	C_6H_5	3.58	2.65	0.60	0.26	7.57; 7.28
6	CH_3	C_6H_5	OH	3.73	2.75	0.39	0.10; 0.00^b	10.2
2	CH_3	C_6H_5	OCH_3	3.67	2.71	0.41	0.13; 0.08^b	3.45
3	CH_3	C_6H_5	OEt	3.68	2.74	0.41	0.15; 0.11^b	3.69; 1.18
4	CH_3	C_6H_5	O^iPr	3.65	2.71	0.41	0.12	4.06; 1.16 1.11
5	CH_3	C_6H_5	O^tBu	3.64	2.71	0.44	0.15; 0.12^b	1.25
7	CH_3	C_6H_5	$\text{OSi}(\text{CH}_3)_3$	3.67	2.73	0.36	0.05^c	0.10
8	CH_3	C_6H_5	$\text{OGe}(\text{CH}_3)_3$	3.68	2.74	0.35	0.06^c	0.36
12	CH_3	CH_3	CH_3	3.73	2.78	0.02	-0.32	0.02
13	CH_3	CH_3	H	3.75	2.79	0.10	-0.25	3.95
9	C_6H_5	C_6H_5	OBu	3.56	2.67	—	0.39	3.71; 1.50

^a Protons of phenyl groups give multiplets 7.28–7.32 and 7.58–7.68 ppm.^b Geminal couplings, 13.7–13.8 Hz.^c At 240 K, methylene protons give AB signals (0.03 ppm and $J = 14.0$ Hz).

When a mixture of chloromethylsilatrane with diphenyldichlorosilane in THF was refluxed in the presence of magnesium for 6 h, diphenyl(silatranyl-methyl)butoxysilane (**9**) was formed with a 58% yield instead of the expected diphenyl(silatranyl-methyl)chlorosilane



Diphenyldichlorosilane was shown to react with THF under similar conditions (65°C , 10 h) to give diphenyldibutoxysilane with a quantitative yield



The substitution of Si–Cl proceeds stepwise, and after 5 h the reaction mixture contained 33% diphenylchlorobutoxysilane and 45% diphenyldibutoxysilane (as indicated by GLC).

The formation of the butoxysilane **9** in the reaction of chloromethylsilatrane with diphenyldichlorosilane could involve either of two routes. (a) The cleavage of

TABLE 2. ^{13}C and ^{29}Si chemical shifts for silylmethylsilatranes $\text{RR}'\text{R}''\text{SiCH}_2\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$

No. of compounds	R	R'	R''	δC^a (ppm)					δSi (ppm)	
				OCH_2	CH_2N	SiCSi	SiCH_3	R''	SiC	Si _{atr}
1	CH_3	C_6H_5	H	57.58	50.83	-1.09	-3.27	—	-35.32	-64.44
10	CH_3	C_6H_5	CH_3	57.82	51.10	1.13	-0.55	-0.55	-3.69	-62.32
11	CH_3	C_6H_5	C_6H_5	57.79	51.19	-0.19	-1.91	^a	-7.27	-63.56
6	CH_3	C_6H_5	OH	57.61	50.83	3.20	0.62	—	6.99	-65.67
2	CH_3	C_6H_5	OCH_3	57.69	51.00	3.18	0.85	18.34	9.88	-68.44
3	CH_3	C_6H_5	OEt	58.53	51.83	1.82	-0.48	58.90; 19.01	7.53	-64.13
4	CH_3	C_6H_5	O^iPr	57.81	51.13	1.70	-0.74	64.46; 25.55; 25.49	5.34	-63.71
5	CH_3	C_6H_5	O^tBu	58.01	51.15	4.53	1.70	31.99; 29.53; 1.70	-2.03	-62.85
7	CH_3	C_6H_5	$\text{OSi}(\text{CH}_3)_3$	57.92	51.15	4.21	1.37	1.96	-2.45^b	-63.26
8	CH_3	C_6H_5	$\text{OGe}(\text{CH}_3)_3$	58.72	51.91	5.18	2.67	3.59	-1.08	-62.11
12	CH_3	CH_3	CH_3	58.81	52.05	2.95	1.46	1.46	0.20	-60.84
13	CH_3	CH_3	H	57.80	51.05	-0.10	-1.93	—	-14.66	-62.86
9	C_6H_5	C_6H_5	OBu	57.68	50.98	1.86	—	—	-3.10	-63.81

^a Carbon atoms of the phenyl groups gave signals in the range 139.86–144.59 (*ipso*-C), 133.06–134.92 (*ortho*- or *meta*-C), 127.57–128.99 (*para*-C) and 126.70–127.66 ppm (*ortho*- or *meta*-C).^b The ^{29}Si shift for silicon in the substituent was $+6.33$ ppm.

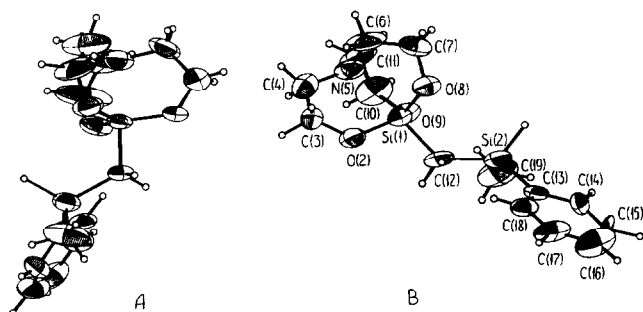


Fig. 1. Methylphenyl(silatranylmethyl)silane (1).

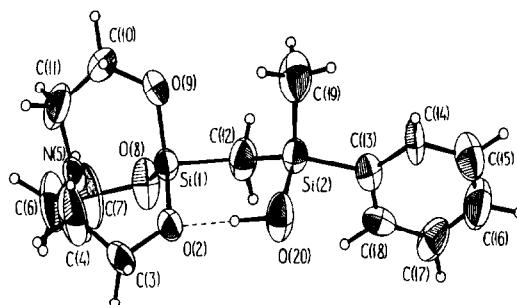


Fig. 2. Methylphenyl(silatranylmethyl)silanol (6).

THF by diphenyldichlorosilane with formation of diphenylchlorobutoxysilane which reacts with chloromethylsilatrane; or (b) the cleavage of THF by the intermediate diphenyl (silatranylmethyl)chlorosilane.

Methyldiphenylchlorosilane reacts with THF in the presence of magnesium in a similar manner to give methyldiphenylbutoxysilane. Treatment of the reaction mixture with deuterium oxide did not give the deuterated butoxysilane $\text{MePh}_2\text{SiO$

TABLE 4. Atomic coordinates for non-hydrogen atoms in methylphenyl(silatranyl)methylsilanol (**6**)

Atom	x	y	z
Si1	0.2814(3)	0.2055(2)	0.1174(2)
Si2	0.4894(4)	0.0579(2)	0.1518(2)
O2	0.1572(9)	0.1336(4)	0.1104(3)
O8	0.3105(9)	0.2627(5)	0.0590(4)
O9	0.3122(10)	0.2402(5)	0.1854(4)
O20	0.3306(9)	0.0053(5)	0.1421(4)
N5	0.0622(10)	0.2721(5)	0.1246(4)
C3	−0.0110(14)	0.1428(8)	0.1059(6)
C4	−0.052(2)	0.2159(9)	0.1309(11)
C6	0.060(2)	0.3153(10)	0.0706(8)
C7	0.206(2)	0.3204(9)	0.0398(8)
C10	0.199(2)	0.2865(7)	0.2172(7)
C11	0.087(2)	0.3179(9)	0.1787(7)
C12	0.464(2)	0.1485(7)	0.1086(7)
C13	0.6576(13)	−0.0001(6)	0.1208(5)
C14	0.7494(14)	−0.0447(7)	0.1582(7)
C15	0.868(2)	−0.0905(9)	0.1342(8)
C16	0.891(2)	−0.0931(9)	0.0732(9)
C17	0.797(2)	−0.0526(8)	0.0331(6)
C18	0.6826(14)	−0.0056(7)	0.0585(6)
C19	0.519(2)	0.0705(9)	0.2336(6)

respectively. Tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

In **1** the N → Si transannular bond lengths are 2.208(9) Å (molecule A) and 2.240(9) Å (molecule B); in **6** the corresponding distance is 2.214(9) Å. These values are to those of other silatranes (see for example refs. 3 and 4). The deviation of the Si(1) atoms from the 02.08.09 planes are 0.222(3), for molecule A in **1**, 0.241(3) for molecule B in **1**, and 0.218(3) Å for **6**. These values are also typical for other silatranes in most cases.

The phenyl ring is planar. The torsion angles C(12)–Si(2)–C(13)–C(14) are 150.9(9), 166.6(8) and 147(1)° for molecule A in **1**, for molecule B in **1** and for molecule **6**, respectively.

In the crystal structures of **1** and **6** all intermolecular contacts correspond to the sums of the van der Waals radii [5].

In **6** there is an intramolecular hydrogen bond between the OH- group and the O(2) atom. There is thought to be an intramolecular hydrogen bond between a silanol group and the carbonyl-oxygen bond in (Me₃Si)₃CSi(OH)₂(OCOCF₃) with an O–H...O distance of 2.41(6) Å and an O–H...O angle of 161(6)° [6]. A six-membered ring is formed in (3-piperidinopropyl)diphenylsilanol by an intramolecular hydrogen bond between the silanol group and the nitrogen atom (O...N distance 2.685 Å; O–H...N angle = 173.2° [7]. In **6** the length of the hydrogen bond O–H...O is 2.79(1) Å (H...O(2) = 1.68 Å, O(20)–H...O(2) angle

= 171°) and somewhat greater than mean statistical value of 2.72 Å [8].

Owing to the intramolecular hydrogen bond, the

TABLE 5. Bond lengths (Å) and bond angles (°) for methylphenyl(silatranyl)methylsilane (**1**)

	Molecule A	Molecule B
<i>Bond lengths</i>		
O(2)–Si(1)	1.632(8)	1.650(7)
O(8)–Si(1)	1.649(8)	1.638(7)
O(9)–Si(1)	1.632(7)	1.639(7)
C(12)–Si(1)	1.864(10)	1.869(10)
C(12)–Si(2)	1.847(10)	1.838(10)
C(13)–Si(2)	1.833(10)	1.888(10)
C(19)–Si(2)	1.865(15)	1.842(15)
C(3)–O(2)	1.423(14)	1.386(12)
C(4)–C(3)	1.416(22)	1.473(17)
N(5)–C(4)	1.391(17)	1.437(15)
C(6)–N(5)	1.395(21)	1.464(17)
C(11)–N(5)	1.422(17)	1.469(17)
C(7)–C(6)	1.435(24)	1.443(22)
O(8)–C(7)	1.409(14)	1.409(13)
C(10)–O(9)	1.363(18)	1.429(16)
C(11)–C(10)	1.404(26)	1.484(21)
C(14)–C(13)	1.414(14)	1.414(15)
C(18)–C(13)	1.386(14)	1.380(15)
C(15)–C(14)	1.369(20)	1.440(21)
C(16)–C(15)	1.355(22)	1.307(25)
C(17)–C(16)	1.386(19)	1.379(23)
C(18)–C(17)	1.392(15)	1.359(16)
<i>Bond angles</i>		
Si(1)–O(2)–C(3)	124.7(7)	125.0(6)
O(2)–Si(1)–O(8)	117.8(4)	118.3(4)
O(2)–Si(1)–O(9)	117.2(4)	117.1(4)
O(2)–Si(1)–C(12)	97.8(4)	96.4(4)
Si(1)–O(8)–C(7)	124.7(8)	124.1(8)
O(8)–Si(1)–O(9)	119.6(3)	118.2(4)
O(8)–Si(1)–C(12)	98.1(4)	98.7(4)
Si(1)–O(9)–C(10)	125.4(9)	122.7(7)
O(9)–Si(1)–C(12)	97.4(4)	100.2(4)
Si(1)–C(12)–Si(2)	120.6(5)	120.1(5)
C(12)–Si(2)–C(13)	112.6(5)	110.6(4)
C(12)–Si(2)–C(19)	108.8(6)	111.3(6)
Si(2)–C(13)–C(14)	123.1(8)	119.8(8)
Si(2)–C(13)–C(18)	121.5(7)	122.7(7)
C(13)–Si(2)–C(19)	108.0(6)	109.3(6)
O(2)–C(3)–C(4)	110.4(10)	110.4(9)
C(3)–C(4)–N(5)	114.9(13)	108.0(10)
C(4)–N(5)–C(6)	116.4(12)	114.6(10)
C(4)–N(5)–C(11)	116.4(12)	115.9(10)
N(5)–C(6)–C(7)	115.6(14)	109.7(10)
C(6)–N(5)–C(11)	111.9(12)	114.1(10)
N(5)–C(11)–C(10)	115.1(13)	107.6(10)
C(6)–C(7)–O(8)	111.1(13)	109.5(10)
O(9)–C(10)–C(11)	112.9(13)	111.2(9)
C(13)–C(14)–C(15)	120.0(11)	114.5(12)
C(14)–C(13)–C(18)	115.4(9)	117.4(10)
C(13)–C(18)–C(17)	123.4(9)	122.2(10)
C(14)–C(15)–C(16)	124.0(12)	128.9(14)
C(15)–C(16)–C(17)	117.6(13)	113.1(15)
C(16)–C(17)–C(18)	119.4(11)	123.8(12)

TABLE 6. Bond lengths (Å) and bond angles (°) for methylphenyl-(silatranylmethyl)silanol (**6**)

<i>Bond lengths</i>	
O(2)–Si(1)	1.656(8)
O(8)–Si(1)	1.655(10)
O(9)–Si(1)	1.645(10)
C(12)–Si(1)	1.864(16)
C(12)–Si(2)	1.868(14)
C(13)–Si(2)	1.890(11)
C(19)–Si(2)	1.841(14)
O(20)–Si(2)	1.655(9)
C(3)–O(2)	1.450(14)
C(4)–C(3)	1.441(22)
N(5)–C(4)	1.395(19)
C(6)–N(5)	1.415(20)
C(11)–N(5)	1.458(18)
C(7)–C(6)	1.424(24)
O(8)–C(7)	1.416(19)
C(10)–O(9)	1.446(18)
C(11)–C(10)	1.395(23)
C(14)–C(13)	1.383(17)
C(18)–C(13)	1.398(17)
C(15)–C(14)	1.398(21)
C(16)–C(15)	1.365(27)
C(17)–C(16)	1.392(23)
C(18)–C(17)	1.397(20)
<i>Bond angles</i>	
Si(1)–O(2)–C(3)	123.8(7)
O(2)–Si(1)–O(8)	119.0(4)
O(2)–Si(1)–O(9)	118.1(4)
O(2)–Si(1)–C(12)	96.7(5)
Si(1)–O(8)–C(7)	125.0(9)
O(8)–Si(1)–O(9)	117.7(5)
O(8)–Si(1)–C(12)	96.8(6)
Si(1)–O(9)–C(10)	123.1(9)
O(9)–Si(1)–C(12)	99.2(6)
Si(1)–C(12)–Si(2)	120.1(9)
C(12)–Si(2)–C(13)	111.2(6)
C(12)–Si(2)–C(19)	114.6(7)
C(12)–Si(2)–O(20)	108.3(6)
Si(2)–C(13)–C(14)	121.3(9)
Si(2)–C(13)–C(18)	120.7(8)
C(13)–Si(2)–C(19)	108.5(6)
C(13)–Si(2)–O(20)	106.0(5)
C(19)–Si(2)–O(20)	108.0(6)
O(2)–C(3)–C(4)	108.3(11)
C(3)–C(4)–N(5)	114.9(14)
C(4)–N(5)–C(6)	117.0(13)
C(4)–N(5)–C(11)	114.2(13)
N(5)–C(6)–C(7)	115.2(14)
C(6)–N(5)–C(11)	113.6(11)
N(5)–C(11)–C(10)	112.5(13)
C(6)–C(7)–O(8)	111.3(14)
O(9)–C(10)–C(11)	112.6(13)
C(13)–C(14)–C(15)	120.6(14)
C(14)–C(13)–C(18)	117.7(11)
C(13)–C(18)–C(17)	123.0(11)
C(14)–C(15)–C(16)	120.0(15)
C(15)–C(16)–C(17)	122.0(15)
C(16)–C(17)–C(18)	116.7(13)

silanol **6** forms a six-membered ring with a chair conformation. The atoms Si(1), Si(2), O(2) and O(20) are coplanar; the atom C(12) is shifted to one side of this plane by 47.4° and H(20) to the other by 45.4°. The C(12)–Si–O(20) angle (96.7°) is similar to those in other silatranes (95°–97°) [9]. The C(12)–Si(2)–O(20) angle (108.3°) is similar to those in carbofunctional derivatives of alkyldiphenylsilanol and alkyl(cyclohexyl)phenylsilanol (105°–112°) [9]. The Si(1)–C(12)–Si(2) angle (120.1°) is similar to those in bis(trimethylsilyl)methane (123.2°), but somewhat larger than those in tetra(trimethylsilyl)methane (109°) [9]. The different shielding observed for the methylene protons in silanol **6** (Table 1) may be connected not only with the presence of a chiral silicon centre, but also with the Si–OH...O interaction.

3. Experimental

¹H NMR spectra were recorded on a Bruker WH-90/DS spectrometer and ¹³C and ²⁹Si spectra on a Bruker WM-360 spectrometer in CDCl₃. Mass spectra were obtained with a Kratos MS-25 GC–MS instrument (70 eV). GLC analysis was carried out with a Chrom-5 apparatus equipped with a flame ionization detector. Glass column (1.2 m/3 mm) packed with 5% OV-17/Chromosorb W-AW (60–80 mesh) was used with helium (50 ml min^{−1}) as carrier gas.

The THF was dried with sodium benzophenone ketyl. Dimethyl(silatranylmethyl)silane **13**, methylphenyl(silatranylmethyl)silane (**1**), dimethylphenyl(silatranylmethyl)silane (**10**), methyldiphenyl(silatranylmethyl)silane (**11**) and trimethyl(silatranylmethyl)silane (**12**) were prepared as described [1]. The properties of these compounds were in full agreement with published data. Crystals of **1** and **6** suitable for the X-ray study were obtained from pentane.

3.1. Determination of crystal structures of **1** and **6**

Crystal data for **1**: monoclinic; $a = 9.066(3)$, $b = 15.197(5)$, $c = 23.198(7)$ Å, $\beta = 91.37(2)^\circ$; $V = 3294.4$ Å³, $Z = 8$; $D_{\text{calc}} = 1.25$ g cm^{−3}; $F(000) = 1328$; space group $P 2_1/c$. A total of 3093 independent reflections were measured on a Synthes P2₁ diffractometer (MoK α radiation; $\lambda = 0.71069$ Å, $\mu = 1.2$ cm^{−1}; $\sin \theta/\lambda \leq 0.482$ Å^{−1}; $\theta/2\theta$ scan).

Crystal data for **6**: orthorhombic $a = 8.544(2)$, $b = 17.557(5)$, $c = 22.129(6)$ Å; $V = 3319.5$ Å³; $Z = 8$; $D_{\text{calc}} = 1.30$ g cm^{−3}; $F(000) = 1392$; space group, $Pbca$. A total of 2099 independent reflections were measured

on a Syntex P2₁ diffractometer (MoK α radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu = 1.3 \text{ cm}^{-1}$; $\sin \theta / \lambda \leq 0.539 \text{ \AA}^{-1}$, ω scan).

For solution of the structures, initial phases of ten strong reflections were determined by the maximum determinant method [10]. The phase values obtained were introduced into the starting set of the MULTAN programme [11]. Two variants were calculated, one of them yielding the model. For refinement of structures, 2197 (for **1**) and 1361 (for **6**) independent reflections with $I > 2\sigma_1$ were used. Structures were refined by the full-matrix least-squares method with anisotropic thermal parameters for C, N, O and Si atoms. The weighting scheme was $W^{-1} = \sigma^2 + 0.015F^2$ (for **1** and **6**). The hydrogen atoms of methyl and hydroxy groups were located from difference synthesis. All the other H atom coordinates were placed in the calculated positions. Atomic scattering factors were taken from the *International Tables For X-ray Crystallography* [12]. The final R, R_w and S factors for **1** were 0.0672, 0.0795 and 0.81 respectively; those for **6** were 0.0830, 0.0984 and 0.96 respectively.

3.2. Synthesis of alkoxysilatranes 2–5 (general procedure).

A solution of the silatrane **1** and the relevant alcohol in THF was stirred at 50°C in the presence of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1 M solution in THF; $5 \mu\text{l mmol}^{-1}$). However, for preparation of ethoxysilane **4** the reaction was carried out in ethanol. After complete disappearance of the starting silatrane the mixture was filtered through a small quantity of silica gel and evaporated. The pure products were isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

3.2.1. Methylphenyl(silatranylmethyl)methoxysilane (2)

Compound **2** (> 95% yield by GLC) was obtained by stirring a solution of methylphenyl (silatranylmethyl)silane (**1**) (309 mg, 1 mmol) and methanol (38 mg, 1.2 mmol) in 1 ml of THF for 22 h.

3.2.2. Methylphenyl(silatranylmethyl)ethoxysilane (3)

Compound **3** (> 90% yield by GLC) was obtained by stirring a solution of methylphenyl (silatranylmethyl)silane (**1**) (309 mg, 1 mmol) in 2 ml of ethanol for 15 h.

3.2.3. Methylphenyl(silatranylmethyl)isopropoxysilane (4)

Compound **4** (> 77% yield by GLC) was obtained by stirring a solution of methylphenyl(silatranylmethyl)

silane (**1**) (309 mg, 1 mmol) and 2-propanol (72 mg, 1.2 mmol) in 1 ml of THF for 64 h.

3.2.4. Methylphenyl(silatranylmethyl)tert-butoxysilane (5)

Compound **5** (> 95% yield by GLC) was obtained by stirring a solution of methylphenyl(silatranylmethyl)silane (**1**) (309 mg, 1 mmol) and *tert*-butanol (88.8 mg, 1.2 mmol) in 1 ml of THF for 24 h.

3.2.5. Methylphenyl(silatranylmethyl)silanol (6)

Compound **6** (2.1 g, > 95% yield) was obtained by stirring a mixture of methylphenyl(silatranylmethyl)silane (**1**) (2 g, 6.5 mmol), distilled water (171 mg, 9.5 mol) and 65 mg of Pd (black) in 13 ml of THF at 50°C. After complete consumption of the silatrane **1** the mixture was filtered and the filtrate evaporated. The silanol **6** was isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

3.2.6. 1,1,1,3-tetramethyl-3-phenyl-3-silatranylmethyl-disiloxane (7)

Compound **7** (90% yield by GLC) was obtained by stirring a mixture of methylphenyl(silatranylmethyl)silanol (**6**) (65 mg, 0.2 mmol), trimethylchlorosilane (32.6 mg, 0.3 mmol) and triethylamine (30.3 mg, 0.3 mmol) in 1 ml of Et_2O and 0.5 ml of THF at room temperature for 15 h. After complete consumption of the silanol **6** the mixture was filtered and the filtrate evaporated. The silatrane **7** was isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

3.2.7. Trimethyl[methylphenyl(silatranylmethyl)siloxy]germane (8)

Compound **8** (90% yield by GLC) was obtained by stirring a mixture of methylphenyl(silatranylmethyl)silanol (**6**) (244 mg, 0.75 mmol), trimethylchlorogermane (153.5 mg, 1.0 mmol) and triethylamine (101 mg, 1.0 mmol) in 1 ml of THF for 15 h at 50°C. After complete consumption of the silanol **6** the mixture was filtered and the filtrate evaporated. The silatrane **8** was isolated by column chromatography on silica gel with 1:1 hexane:ethyl acetate as eluent.

3.2.8. Diphenyl(silatranylmethyl)butoxysilane (9)

A mixture of diphenyldichlorosilane (506 mg, 2 mmol), chloromethylsilatrane (447 mg, 2 mmol) and magnesium (96 mg, 4 mmol, activated by iodine) in 10 ml of THF was boiled under argon for 6 h. It was then treated cautiously with water and the product extracted

into ether, recovered and purified by column chromatography on silica gel with 1 : 1 hexane : ethyl acetate as eluent. Compound **9** was obtained with a 58% yield.

3.2.9. Reaction of diphenyldichlorosilane with tetrahydrofuran in the presence of magnesium

A mixture of diphenyldichlorosilane (127 mg, 0.5 mmol) and magnesium (24 mg, 1 mmol, activated by iodine) in 3 ml of THF was boiled under argon for 10 h. Diphenyldibutoxysilane was obtained with > 95% yield (by GLC data).

3.2.10. Reaction of methyldiphenylchlorosilane with tetrahydrofuran in the presence of magnesium

A mixture of methyldiphenylchlorosilane (116 mg, 0.5 mmol), and magnesium (24 mg, 1 mmol, activated by iodine) in 3 ml of THF was boiled under argon for 6 h. Methyldiphenylbutoxysilane was obtained with > 95% yield (by GLC data).

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