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Synthesis and structure of silylmethylsilatranes $RR'R''SiCH_2\overline{Si(OCH_2CH_2)_3N}$

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Abstract

New alkoxysilylmethylsilatranes $MePhROSiCH_2\overline{Si(OCH_2CH_2)_3N}$ have been obtained from the reaction of silylmethylsilatrane $MePhHSiCH_2\overline{Si(OCH_2CH_2)_3N}$ with alcohols in the presence of $H_2PtCl_6 \cdot 6H_2O$. 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 OH...O bond in the latter.

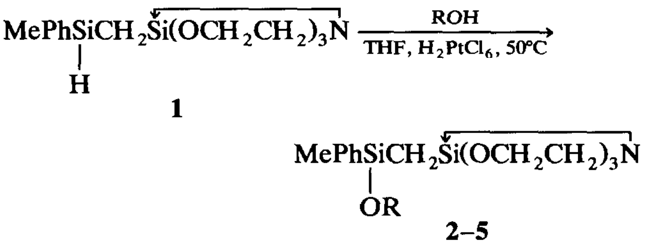
Key words: Germanium; Silicon; Silatrane; Crystal structure; Hydrogen bonding

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

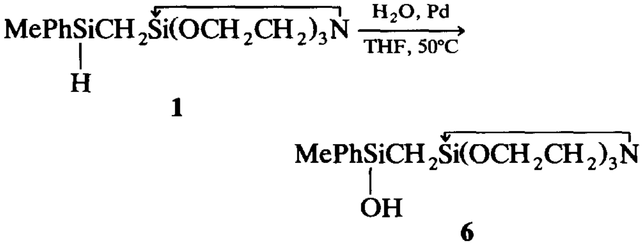
We found that methylphenyl(silatranylmethyl)silane (**1**) readily reacts with alcohols in the presence of $H_2PtCl_6 \cdot 6H_2O$ in THF to give (silatranylmethyl)alkoxysilanes (**2–5**) in good yields (77%–95% by GLC)



$$\underset{\substack{|\\ H}}{MePhSi}CH_2\overline{Si(OCH_2CH_2)_3N}\ (\mathbf{1}) \xrightarrow[\text{THF, } H_2PtCl_6,\ 50°C]{ROH} \underset{\substack{|\\ OR}}{MePhSi}CH_2\overline{Si(OCH_2CH_2)_3N}\ (\mathbf{2–5})$$

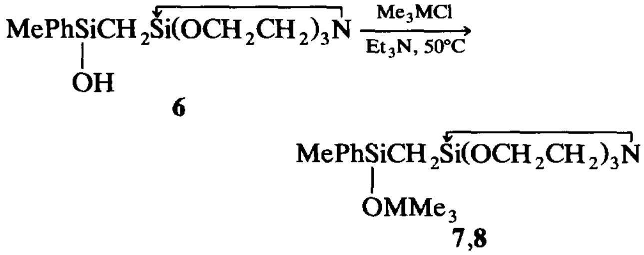
where: R = Me(**2**); Et(**3**); ^iPr(**4**); ^tBu(**5**).

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):



$$\underset{\substack{|\\ H}}{MePhSi}CH_2\overline{Si(OCH_2CH_2)_3N}\ (\mathbf{1}) \xrightarrow[\text{THF, 50°C}]{H_2O,\ Pd} \underset{\substack{|\\ OH}}{MePhSi}CH_2\overline{Si(OCH_2CH_2)_3N}\ (\mathbf{6})$$

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-silatranylmethyldisiloxane (**7**) and trimethyl[methylphenyl(silatranylmethyl)siloxy]germane (**8**)



$$\underset{\substack{|\\ OH}}{MePhSi}CH_2\overline{Si(OCH_2CH_2)_3N}\ (\mathbf{6}) \xrightarrow[Et_3N,\ 50°C]{Me_3MCl} \underset{\substack{|\\ OMMe_3}}{MePhSi}CH_2\overline{Si(OCH_2CH_2)_3N}\ (\mathbf{7,8})$$

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

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TABLE 1. ^1H chemical shifts for silylmethylsilatranes $RR'R''SiCH_2\overset{\leftarrow}{Si}(OCH_2CH_2)_3N$

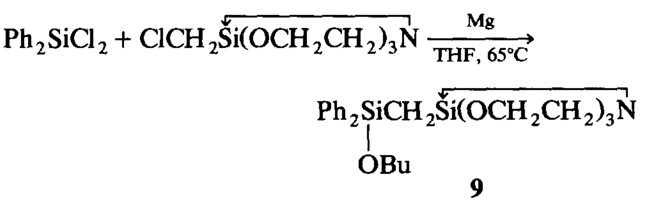
No. of compounds	R	R′	R″	δH [a] (ppm)				
				OCH_2	CH_2N	$SiCH_3$	$SiCH_2Si$	R″
1	CH_3	C_6H_5	H	3.68	2.69	0.37	0.03; −0.05 [b]	4.44
10	CH_3	C_6H_6	CH_3	3.65	3.67	0.30	−0.06	0.30
11	CH_3	C_6H_5	C_6H_5	3.58	2.65	0.60	0.26	7.57; 7.28
6	CH_3	C_6H_5	OH	3.73	2.75	0.39	0.10; 0.00 [b]	10.2
2	CH_3	C_6H_5	OCH_3	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	$OSi(CH_3)_3$	3.67	2.73	0.36	0.05 [c]	0.10
8	CH_3	C_6H_5	$OGe(CH_3)_3$	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(silatranylmethyl)butoxysilane (**9**) was formed with a 58% yield instead of the expected diphenyl(silatranylmethyl)chlorosilane



$$Ph_2SiCl_2 + ClCH_2\overset{\leftarrow}{Si}(OCH_2CH_2)_3N \xrightarrow[\text{THF, 65°C}]{\text{Mg}} \underset{\text{OBu}}{Ph_2SiCH_2\overset{\leftarrow}{Si}(OCH_2CH_2)_3N}$$

9

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

$$Ph_2SiCl_2 \xrightarrow[\text{THF, 65°C}]{\text{Mg}} Ph_2Si(OBu)_2$$

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 $RR'R''SiCH_2\overset{\leftarrow}{Si}(OCH_2CH_2)_3N$

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	$OSi(CH_3)_3$	57.92	51.15	4.21	1.37	1.96	−2.45 [b]	−63.26
8	CH_3	C_6H_5	$OGe(CH_3)_3$	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.

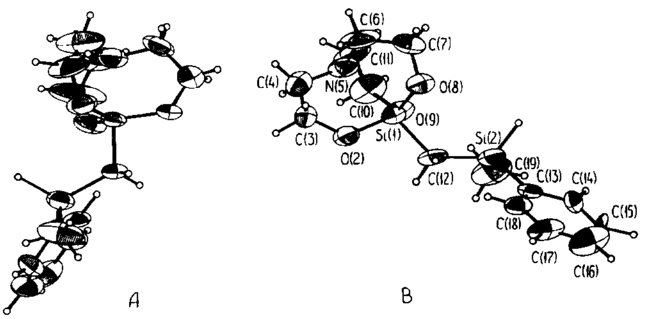


Fig. 1. Methylphenyl(silatranylmethyl)silane (1).

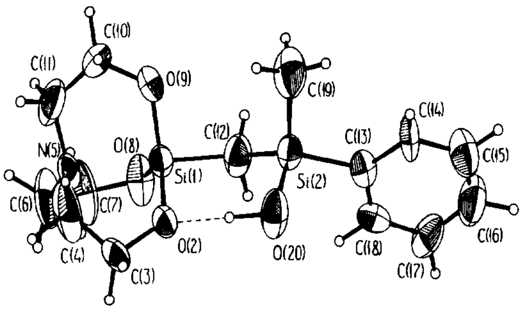


Fig. 2. Methylphenyl(silatranylmethyl)silanol (6).

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 $MePh_2SiOCH_2CH_2CH_2CH_2D$, thus excluding siloxybutylmagnesium chloride as a possible intermediate. No reaction was observed when methyldiphenylchlorosilane was treated with THF at 65°C in the absence of magnesium.

The ^1H, ^{13}C and ^{29}Si NMR spectra were studied for the series of silatranylmethylsilanes and the data are listed in Tables 1 and 2.

Different shielding of the protons in the methylene group directly bound to the chiral silicon was expected for **1**–**7** containing an asymmetric centre [2]. Indeed, the methylene protons are inequivalent for **1**–**3**, **5** and **6** at 303 K, and also for **7** and **8** at lower temperatures (270 K). Compound **4** ($R = {}^iPr$) differs from the other –OR derivatives of silylmethylsilatrane in that the chemical shifts of the two methylene protons are equal. However, in this case there is non-equivalence in the ^1H and ^{13}C screening of the methyl groups in the isopropyl group. It follows that the magnetic non-equivalence of the methylene occurs mainly because of the anisotropic influence of the phenyl ring at silicon.

X-Ray diffraction studies were carried out on silatranes **1** and **6**. In the crystal of **1** there are two independent molecules; Fig. 1 shows a perspective view of their structures **1** and the atom names. The structure of **6** is shown in Fig. 2. Tables 3 and 4 give the atomic coordinates for **1** and **6**, and Tables 5 and 6 give the values of bond lengths and angles for **1** and **6**

TABLE 3. Atomic coordinates for non-hydrogen atoms in methylphenyl(silatranylmethyl)silane (**1**)

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Si(1)	0.3020(3)	0.0744(2)	0.7288(1)	0.7924(3)	0.2442(2)	0.0377(1)
Si(2)	0.5476(3)	0.0977(2)	0.8274(1)	1.0354(3)	0.2648(2)	−0.0570(1)
O(2)	0.3197(7)	0.0970(5)	0.6626(3)	0.8170(7)	0.2687(4)	0.1045(3)
O(8)	0.2002(7)	0.1411(5)	0.7662(3)	0.6832(7)	0.3070(4)	−0.0005(3)
O(9)	0.3208(7)	−0.0283(4)	0.7476(3)	0.8084(7)	0.1405(4)	0.0200(3)
N(5)	0.0841(9)	0.0271(6)	0.6986(4)	0.5763(9)	0.1982(6)	0.0706(4)
C(3)	0.2161(14)	0.0731(12)	0.6196(5)	0.7066(12)	0.2702(8)	0.1436(4)
C(4)	0.078(2)	0.0524(12)	0.6427(6)	0.5946(14)	0.2026(9)	0.1304(5)
C(6)	−0.014(2)	0.0690(12)	0.7339(8)	0.4736(12)	0.2631(11)	0.0466(7)
C(7)	0.0448(14)	0.1426(11)	0.7647(7)	0.5292(13)	0.2957(10)	−0.0055(6)
C(10)	0.214(2)	−0.0912(10)	0.7430(9)	0.710(2)	0.0737(7)	0.0386(6)
C(11)	0.093(2)	−0.0648(9)	0.7093(7)	0.5598(13)	0.1095(9)	0.0468(6)
C(12)	0.4870(10)	0.1134(7)	0.7538(4)	0.9737(10)	0.2875(6)	0.0142(4)
C(13)	0.6756(11)	0.0051(6)	0.8364(4)	1.1760(10)	0.3490(7)	−0.0788(4)
C(14)	0.7853(13)	0.0017(9)	0.8794(4)	1.2609(13)	0.3338(9)	−0.1267(5)
C(15)	0.8740(14)	−0.0708(11)	0.8849(6)	1.3633(14)	0.4031(13)	−0.1392(6)
C(16)	0.8662(13)	−0.1416(10)	0.8505(7)	1.385(2)	0.4779(10)	−0.1133(8)
C(17)	0.7637(12)	−0.1392(8)	0.8066(5)	1.3005(13)	0.4871(8)	−0.0665(6)
C(18)	0.6742(10)	−0.0654(7)	0.7996(4)	1.1992(10)	0.4269(7)	−0.0503(4)
C(19)	0.644(2)	0.1994(9)	0.8522(7)	1.116(2)	0.1539(9)	−0.0621(7)

TABLE 4. Atomic coordinates for non-hydrogen atoms in methylphenyl(silatranylmethyl)silanol (**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 transanular 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 (Me$_3$Si)$_3$CSi(OH)$_2$(OCOCF$_3$) 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 that 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(silatranylmethyl)silane (**1**)

	Molecule A	Molecule B
Bond lengths		
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)
Bond angles		
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**)

Bond lengths	
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)
Bond angles	
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 that 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

^{1}H NMR spectra were recorded on a Bruker WH-90/DS spectrometer and ^{13}C and ^{29}Si spectra on a Bruker WM-360 spectrometer in $CDCl_3$. 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, $\beta = 91.37(2)°$; $V = 3294.4$ Å^3, $Z = 8$; $D_{calc} = 1.25$ g cm^{-3}; F(000) = 1328; space group P $2_1/c$. A total of 3093 independent reflections were measured on a Synthex $P2_1$ diffractometer (MoKα 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; $V = 3319.5$ Å^3; $Z = 8$; $D_{calc} = 1.30$ g cm^{-3}; F(000) = 1392; space group, Pbca. A total of 2099 independent reflections were measured on a Syntex $P2_1$ diffractometer (MoKα radiation, $\lambda = 0.71069$ Å, $\mu = 1.3$ cm^{-1}; $\sin\theta/\lambda \leq 0.539$ Å^{-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 $I > 2\sigma_I$ 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 $H_2PtCl_6 \cdot 6H_2O$ (1 M solution in THF; 5 μl 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-silatranylmethyldisiloxane (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).

References

1 V. Gevorgyan, L. Borisova and E. Lukevics, *J. Organomet. Chem.*, *418* (1991) C21.
2 W.B. Jennings, *Chem. Revs.*, *75* (3) (1975) 307.
3 L. Parkanyi, L. Bihatsi and P. Hentsei, *Cryst. Struct. Commun.*, *7* (2) (1978) 335.
4 L. Parkanyi, K. Simon and J. Nagy, *Acta Crystallogr.*, *B30* (10) (1974) 2328.
5 J.V. Zefirov and P.M. Zorkii, *Zh. Strukt. Khim.*, *17* (6) (1976) 994; in Russian.
6 S.S. Al-Juaid, C. Eaborn and P.B. Hitchcock, *J. Organomet. Chem.*, *423* (1992) 5.
7 R. Tacke, M. Strecker, W.S. Sheldrick, E. Heeg, B. Berndt and K.M. Knapstein, *Z. Naturforsch.*, *34B* (9) (1979) 1279.
8 L.N. Kuleshova and P.M. Zorkii, *Acta Crystallogr.*, *B37* (7) (1981) 1363.
9 E. Lukevics, O. Pudova and R. Sturkovich, *Molecular Structure of Organosilicon Compounds*, Ellis Horwood, Chichester, 1989.
10 A.F. Mishnev and S.V. Belyakov, *Kristallografia*, *33* (4) (1988) 835; in Russian.
11 G. Germain, P. Mainand and M.M. Woolfson, *Acta Crystallogr.*, *A27* (3) (1971) 368.
12 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974.