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Pentacoordinate silicon compounds. Reactions of silatranes with nucleophiles

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Abstract

The reactions of hydro, organyl and halosilatranes with nucleophiles have been studied. Substitution involving cleavage of equatorial Si–O bonds is always observed. Silatranes exhibit reactivity quite different from that of analogous trialkoxysilanes or anionic pentacoordinate silicon compounds.

Introduction

We have been interested for several years in the reactivity of hypervalent species [1]. We showed recently that catecholates with penta [2] and hexacoordinate [3] silicon centers (species **1** and **2**), though negatively charged, react readily with nucleophiles such as hydrides and Grignard and organolithium reagents.

Silatranes, **3**, [4,5,6] (cyclic organosilicon ethers of tris(2-oxyalkyl)amines) and their derivatives constitute a class of neutral pentacoordinate silicon compounds by virtue of the transannular interaction between the silicon center and the nitrogen group. Many such compounds have been studied in detail by physical methods, but their chemistry has not been extensively explored: the type of reaction that has been most studied is that involving cleavage of the apical bond opposite to the transannular Si←N bond [5–7].

Our study of the reactions of bis(1,2-benzenediolato)allylsilicate **4** and allylsilatrane **5** [8] revealed a large difference between the reactivities of the Si–allyl bonds in these two types of compound; surprisingly the anionic pentacoordinate silicon complex **4** in which the allyl group is in the equatorial position is activated by nucleophiles and reacts with carbonyl compounds [8], whereas the neutral allylsilatrane **5** with the allyl group in the apical position does not react under the same conditions.

Since these results indicated that the reactivity of hypervalent species depends on the overall charge and structure, we decided to explore further the reactivity of

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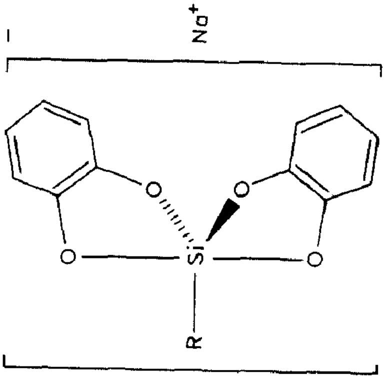

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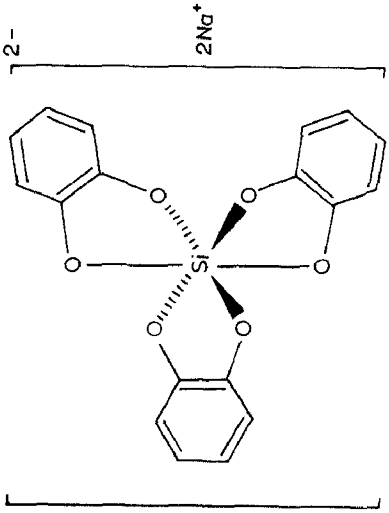

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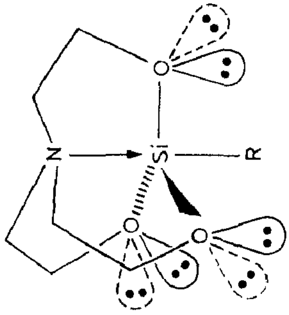

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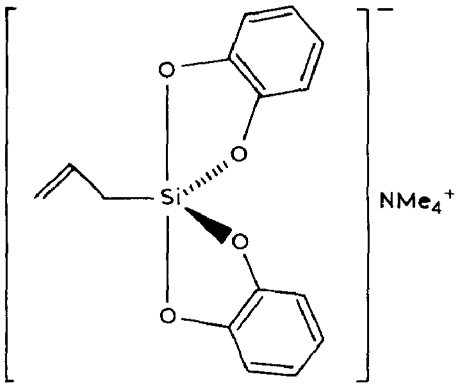

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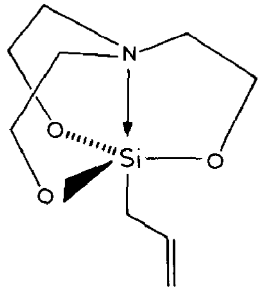

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silatranes. In this paper we report the reactions of hydro-, alkyl-, alkenyl-, bromo-, and chloro-silatranes with organolithium and organomagnesium reagents, as also with metal hydrides.

Results and discussion

Reactivity of hydrosilatranes

Several reactions of hydrosilatranes are known [5,6]. Some of them have provided the basis for the synthesis of various Si-substituted silatranes [9,10], as shown in eqs. 1–4:

$$HSi(OCH_2CH_2)_3N + ROH \xrightarrow{RO^-} ROSi(OCH_2CH_2)_3N + H_2 \quad (1)$$

$$HSi(OCH_2CH_2)_3N + RCO_2H \xrightarrow{ZnCl_2} RCO_2Si(OCH_2CH_2)_3N + H_2 \quad (2)$$

$$HSi[OCH(CH_3)CH_2]_3N + X_2 \rightarrow XSi[OCH(CH_3)CH_2]_3N + HX \quad (3)$$

$$HSi[OCH(CH_3)CH_2]_3N + HX \rightarrow XSi[OCH(CH_3)CH_2]_3N + H_2 \quad (4)$$

Equation 4 illustrates the enhanced hydridic character of the Si–H bond. Nevertheless the hydrosilatrane behaves as a reducing agent only under drastic conditions for some reactive organic compounds [11]. The Si–H bond, in the apical position in the silatrane is less reactive than the Si–H in the equatorial position in the pentacoordinate anionic silicon compounds [12].

We first studied the reaction of hydrosilatrane with ^{n}BuLi (in hexane solution). ^{n}BuLi in excess (5 molar equivalents) reacts readily with hydrosilatrane at room temperature to give a mixture of $^{n}Bu_3SiH$ (66%) and $^{n}Bu_4Si$ (22%) (Table 1, entry 1). A higher yield of $^{n}Bu_3SiH$ is obtained when 3.2 molar equivalents of ^{n}BuLi are used (entries 2 and 3, Table 1). The influence of the hydrosilatrane/^{n}BuLi ratio was studied in order to investigate the degree of selectivity of the reaction. After addition of one or two molar equivalents of ^{n}BuLi to the hydrosilatrane, the reaction mixture was treated with $LiAlH_4$ to remove any remaining Si–O bonds, a process which would result in formation of $^{n}Bu_2SiH_2$. As can be seen from entries 4 and 5 in Table 1, the reaction of ^{n}BuLi on hydrosilatrane appears to proceed mainly

Table 1

Reactions of hydrosilatrane with organometallic compounds in THF

Entry	Reagent (molar equivalent)	Temp. (°C)	Time (h)	Yields (%) [a]	
				R_3SiH	R_4Si
1	^nBuLi (5)	20	1	66	22
2	^nBuLi (3,2)	20	1	90	10
3	^nBuLi (3,2)	0	24	62 [b]	–
4	^nBuLi (2)	20	24	34 [c]	–
5	^nBuLi (1)	20	24	24 [c]	–
6	^nBuLi/12-crown-4 (3.2)	–50	1	87	–
7	^nBuLi/12-crown-4 (3.2)	–78	24	84	2
8	^nBuMgBr (3,2)	20	24	78	–
9	$^nBu_2Mg$ (3,2)	20	24	81	–
10	PhLi (5)	20	20	–	68 [b]
11	PhMgBr (5)	20	20	96 [b]	–

[a] Yields were determined by GC with biphenyl as internal standard. [b] Isolated yields. [c] The reaction mixture was treated with $LiAlH_4$ for 2.5 h at 50 °C.

by cleavage of the three Si–O bonds whatever the ratio hydrosilatrane/^nBuLi, only traces of $^nBu_2SiH_2$ being detected.

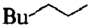
The reactions of hydrosilatrane with other nucleophilic reagents were then examined, namely ^nBuLi/12-crown-4, ^nBuMgBr, $^nBu_2Mg$ (entries 6–9 in Table 1). In all cases a good yield of $^nBu_3SiH$ was obtained. The order of reactivity of these nucleophilic reagents is $^nBuLi/12\text{-crown-4} \gg {}^nBuLi > {}^nBu_2Mg \simeq {}^nBuMgBr$. Whatever the nucleophilic reagent, cleavage of the equatorial Si–O bonds occurs more readily than that of the apical Si–H bond.

The substantial difference in reactivity between ^nBuLi/12-crown-4 and ^nBuLi implies that there is no coordination between RLi and the nitrogen atom; i.e. the reaction involves direct nucleophilic attack at silicon.

PhLi and PhMgBr also react readily with hydrosilatrane (entries 10 and 11 in Table 1). With PhLi the major product results from tetrasubstitution of the silatrane (68% yield of Ph_4Si).

Table 2

Reactions of organylsilatranes **6** with an excess of an organometallic reagent (3.5 molar equivalents) in THF

Entry	R	Reagent	Temp (°C)	Time (h)	Products [a]	Yields (%)
1	nBu	MgBr	30	4	$^nBuSi($$)_3$	70
2	nBu	^nBuLi	20	4	$^nBu_4Si$	70
3	CH_2	^nBuLi	20	0,5	Si^nBu_3	61
4	CH_2=CH	^nBuLi	20	0,5	^nBu$Si(OCH_2CH_2)_3N$ ^nBuSi^nBu_3	17 30
5	CH_2=CH	^tBuLi	–78 °C	2,5	^tBu$Si(OCH_2CH_2)_3N$	81
6	Ph–CH_2	^nBuLi	20	4	Ph–$CH_2Si^nBu_3$	75
7	Ph–CH_2CH_2	^nBuLi	20	4	Ph–$CH_2CH_2Si^nBu_3$	92

[a] Yields refer to isolated products

Reactivity of organylsilatranes

Very few reactions resulting in cleavage of the silatrane ring in organylsilatranes are known [6], except from those involving hydrolysis [6,13].

The reactions of some organylsilatranes with lithium aluminium hydride were investigated. As shown in eqn. 5, the organylsilatrane **6** is reduced to the corresponding primary silane occurs when R is an aromatic group, but the reaction is much slower than that of the anionic pentacoordinate bis(1,2-benzenediolato)phenyl or 1-naphthylsilicates **1** (R = phenyl or 1-naphthyl) [2] under the same conditions. When R is an alkyl group no reduction occurs.

$$\begin{array}{llll} \text{RSi(OCH}_2\text{CH}_2)_3\text{N} \xrightarrow[\text{Et}_2\text{O}]{\text{LiAlH}_4} & \text{RSiH}_3 & & (5)\\ \quad(\mathbf{6}) & (\text{R}=\text{Ph} & (32\%)(20\text{ h}, 35\,^\circ\text{C}); & \\ & \text{R}=1\text{-Np} & (65\%)(24\text{ h}, 20\,^\circ\text{C}); & \\ & \text{R}=\text{PhCH}_2\text{CH}_2 & (0\%)(48\text{ h}, 35\,^\circ\text{C})) & \end{array}$$

The reactions of various organylsilatranes with ^{n}BuLi (in hexane solution) were studied (Table 2). In all cases a fairly high yield of tetraorganosilane was obtained. With vinylsilatrane there was simultaneous substitution of the Si–O bonds and addition of ^{n}BuLi to the C=C bond (entry 4), while ^{t}BuLi involves only addition to the C=C bond at −78 °C, with no attack on the silatrane ring (entry 5). Additions to the C=C bond have been observed previously for vinylsilatrane [14].

Reactivity of halosilatranes

The halosilatranes are normally considered to be the most interesting members of this family of pentacoordinate silicon compounds because of their remarkable solvolytic stability, as observed by Frye [15]. It is possible to recrystallize these halides from alcoholic solvents with little or no solvolysis [5] of the Si–X bonds. In spite of this surprising observation, the reactions of halosilatranes have not been explored [15], except that very recently, Voronkov [7] has examined some electrophilic reactions of iodosilatranes.

Chloro- and bromosilatranes were found to react with ^{n}BuLi to give, after reduction with $LiAlH_4$, tri-n-butylsilane as the major product even when an excess of ^{n}BuLi was used (Table 3). We confirmed that the reaction of chlorosilatrane with ^{n}BuLi did not give any $^{n}Bu_3SiCl$ before reduction (see Experimental Section). Moreover since only a poor yield of $^{n}Bu_4Si$ was obtained from reaction of an excess of ^{n}BuLi on chlorosilatrane after prolonged reaction (Table 3, entry 3) it can be concluded that the n-butylsilatrane is not formed during the reaction since an excess

Table 3

Reactions of halosilatranes $XSi(OCH_2CH_2)_3N$ with ^{n}BuLi in THF followed by $LiAlH_4$ reduction

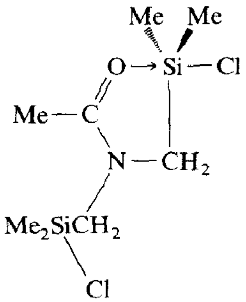
Entry	X	Reagent (molar equivalents)	Temp. (°C)	Time (h)	Yield (%) [a]	
					$^{n}Bu_3SiH$	$^{n}Bu_4Si$
1	Cl	^{n}BuLi (1)	20	24	6	<1
2	Cl	^{n}BuLi (3.2)	20	24	56.4 [b]	2.5
3	Cl	^{n}BuLi (5.5)	20	48	74	10
4	Br	^{n}BuLi (3.2)	20	24	44	2.5

[a] Yields were determined by GC with biphenyl as internal standard. [b] Isolated yields.

of ^{n}BuLi reacts with n-butyl silatrane to give $^{n}Bu_4Si$ (Table 2, entry 2). This means that the initial substitution involves cleavage of an Si–O bond rather than an Si–Cl bond as would be usual for a tetracoordinated chloroalkoxysilane, as illustrated in the eq. 6:

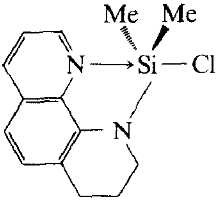
$$ClSi(OCH_3)_3 \xrightarrow[\text{ether} \ -78°\text{C}, \ 30']{^{n}\text{BuLi (1 equiv.)}} \underset{(31.4\%)}{^{n}BuSi(OCH_3)_3} + \underset{(32.6\%)}{^{n}Bu_2Si(OCH_3)_2} \qquad (6)$$

The unusual reactivity of chlorosilatrane is connected with its very unusual geometry, chlorosilatrane being the only pentacoordinate chlorosilane which has two short bonds in the two apical positions. In general the close approach of the incoming lone pair (of nitrogen) is reflected in a long opposite bond (Si–Cl) and vice versa. The structure of chlorosilatrane has been established by X-ray diffraction [6], which showed that the silicon atom and the N and Cl atoms in axial positions are in an almost perfect trigonal bipyramidal disposition. The length of the transannular coordinate Si←N bond is 2.023 Å, the shortest bond between Si and N atoms found in silatranes (which range from ca. 2.0–2.4 Å) [6]. Furthermore this Si←N length is close to the normal length in tetracoordinated silicon compounds (1.72 Å) (16). The Si–Cl bond (2.12 Å) is short compared with axial Si–Cl bonds in other pentacoordinate silicon derivatives **7** [17], **8** [18] and **9** [19].



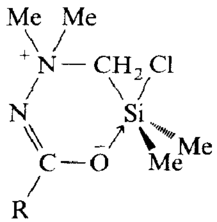
(**7**)

(Si–Cl$_{ax}$ 2.35 Å)



(**8**)

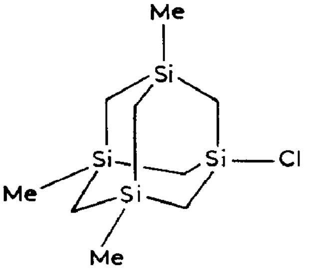
(Si–N 2.02; Si–Cl$_{ax}$ 2.26 Å)



(**9**)

(R = 4′-MeOC$_6$H$_4$; Si–Cl 2.62 Å)

The association of a short Si–Cl bond with a short Si–N bond in chlorosilatrane could originate from the antiperiplanar stereoelectronic effects arising from the three oxygen atoms [20] (see **3**), which are in a rigid position that allows good stereoelectronic overlap with the antiperiplanar Si←N coordinative bond. This stereoelectronic effect favors the overlap of the lone pair at nitrogen with silicon, and accounts for the shortness of the Si–N bond without the significant stretching of the Si–Cl bond which is observed in structures which do not allow any stereoelectronic effect (see **7**–**9**). Thus, in our opinion, the low reactivity of the Si–Cl bond of chlorosilatrane is the consequence of the molecular geometry. Reactions at Si–Cl bonds in acyclic compounds with nucleophiles normally occurs with inversion of configuration [21], but retention has been found in the case of extracyclic Si–Cl bonds in highly strained bicyclic derivatives. This has been rationalised in terms of frontier orbital considerations [22]. Calculations [22] show that normal tetrahedral Si–Cl bonds will react preferentially with inversion by backside attack, but that flank attack becomes relatively more favoured as the *s* character of the Si–Cl bond is increased. This can be seen from the reactivities of



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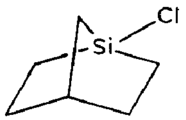

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the chlorosilanes **10** and **11** [23]. Compound **10**, with a regular tetrahedral structure about the silicon atom, reacts only slowly with nucleophiles with necessary retention of configuration, whereas chlorosilane **11**, in which ring strain results in the exocyclic Si–Cl bond having enhanced *s* character, is much more reactive.

In the case of chlorosilatrane, the backside attack is excluded for steric reasons. Furthermore the cleavage of the Si–Cl bond by flank attack is also unfavorable because of the absence of angular strain and because of the length and the Si–Cl bond (2.12 Å), which is very close to that of the Si–Cl bond in tetracoordinate silicon compounds (2.05 Å). Thus cleavage of the Si–O bonds, which may take up a position *trans* to the incoming nucleophile, therefore occurs.

Until now studies of reactions of silatranes have focussed mainly on cleavages [6,7] of the apical bond opposite to the transannular Si←N bond. We have shown here that substitutive cleavage of the equatorial Si–O bonds by strong nucleophiles is also possible, in spite of the unusual geometry of the silatrane ring.

Experimental

Reactions were carried out under nitrogen. All solvents were purified by standard techniques. Silatranes $RSi(OCH_2CH_2)_3N$ were prepared by published procedures (R = H [24], phenethyl [6], benzyl [25], allyl [8], vinyl [26], chloro [5] and bromo [5]. The compounds isolated in this study were characterized by the usual techniques, and their purities confirmed by GC (column SE 30, 10%). NMR spectra were recorded with a Varian EM 360A spectrometer for ^1H, with a Bruker WP 80 for ^{13}C, and with a Bruker WP 200 SY for ^{29}Si. All ^1H, ^{13}C and ^{29}Si chemical shifts reported are in ppm relative to Me_4Si. IR spectra were recorded with a Perkin Elmer 298 spectrophotometer, and mass spectra with a JEOL JMS-DX 300 mass spectrometer.

Preparation of 1-naphthylsilatrane

A solution of 1-naphthyltrimethoxysilane (20 mmol) in 80 ml of xylene was added to one of 20 mmol of triethanolamine in 25 ml of xylene. The mixture was heated under reflux for 3 h, the methanol being continuously removed by distillation. When no more methanol came over the silatrane was precipitated by addition of methanol. The resulting solid was filtered off and recrystallized from $CHCl_3$ to give white crystals of 1-naphthylsilatrane in 76% yield. m.p. 248.5–250 °C, ^1H NMR

($CDCl_3$) 2.82 (6H, distorted t, NCH_2) 3.8 (6H, distorted t, OCH_2) 7.1–8.3 (7H, m, Ar); ^{29}Si ($CDCl_3$) −80.49 ppm; MS *m/e* M^+ 301 (M^+).

Preparation of 1-butylsilatrane

A mixture of 35 mmol of 1-butyltrimethoxysilane, 35 mmol of triethanolamine and a catalytic amount of KOH (no solvent) was kept at 50 ° C for 1 h, during which a white solid was formed. Methanol is removed under vacuum, and the residue recrystallized from pentane/ether to give white crystals of 1-butylsilatrane (89%), m.p. 90–91° C. ^1H NMR (CCl_4) 0.7–1.5 (9H, m); 2.6 (6H, t, NCH_2); 3.6 (6H, t, OCH_2); ^{29}Si -64.8 ppm; MS *m/e* 231 (M^+) 174 (100%).

General procedure for reactions of silatranes with organometallic reagents

(a) Use of an internal standard. In a typical procedure, 11 ml of 2.5 *M* solution of n-butyllithium in hexane (24.7 mmol) were added at room temperature to a solution of hydrosilatrane (1.5 g, 8.5 mmol) and biphenyl (1.32 g, 8.5 mmol) in 50 ml of THF. The progress of the reaction was monitored by GC with biphenyl as internal standard, and the products were identified by comparison with authentic samples.

(b) Isolation of products. In a typical procedure, 36.5 ml of a 2.5 M solution of n-butyllithium in hexane (91.4 mmol) were added at 0 ° C to a suspension of 28.5 mmol of hydrosilatrane (5.0 g) in 80ml of dry THF. The mixture was stirred at 0 ° C for 24 h then diluted with 100 ml of ether and treated carefully with 20% aqueous HCl. The organic layer was dried over $MgSO_4$, and the residue distilled to give 3.6g of tri-1-butylsilane (62% yield) b.p. 96–104° C/15 Torr (lit. 27: 215–220 ° C).

The following were obtained similarly:

- Tetraphenylsilane (Table 1, entry 10) 68% m.p. 238.4–244°C (lit. 28: 236.5–237 ° C).
- Triphenylsilane (Table 1, entry 11) 96% m.p. 46–47 ° C (lit. 29: 40–43° C).
- 1-Butyltrivinylsilane (Table 2, entry 1) 70% b.p. 61–65 ° C/10–12 Torr; ^1H NMR ($CDCl_3$) 0.6–1.6 (m, 9H, ^nBu) 5.78–6.18 (m, 9H, $CH_2{=}CH$); MS *m/e* 166 (M^+).
- Tetra-1-butylsilane (Table 2, entry 2) 70% b.p. 120–124°C/16 Torr (lit 30: 156–157 ° C/22 Torr).
- Allyltri-1-butylsilane (Table 2, entry 3) 61% b.p. 104–106°C/5 Torr (lit 31: 252–253° C/750 Torr).
- Benzyltri-1-butylsilane (Table 2, entry 6) 75% b.p. 136–138°C/2 Torr (lit 32: 160–165 ° C/1 Torr).
- Tri-1-butylphenethylsilane (Table 2, entry 7) 92% b.p. 120–124°C/1 Torr; ^1H NMR ($CDCl_3$) 0.8–1.66 (m, 29H, $^nBu + CH_2$) 2.30–2.50 (t, 2H, $PhCH_2$) 7.08 (s, 5H, Ph); MS *m/e* 304 (M^+).

Reduction of organylsilatranes

In a typical procedure, a solution of 5 g of 1-naphthylsilatrane (0.0166 mol) in 50 ml of anhydrous ether were added to one of $LiAlH_4$ (1.89 g) in 50 ml of ether. The mixture was stirred for 24 h then treated with aqueous 4 *M* HCl and extracted with ether. The extracts were washed with water, dried over $MgSO_4$, and concentrated. Distillation gave 1.7 g of 1-naphthylsilane (65%), b.p.: 115 ° C/20 Torr (lit. 33: 49.5 ° C/0.025 Torr).

Reaction of ^{n}BuLi on vinylsilatrane

15.2 ml of ^{n}BuLi in hexane solution (3.8 mmol) were added at room temperature to a solution of vinylsilatrane (2.15 g, 10 mmol) and biphenyl (1.54 g, 10 mmol) in 80 ml of ether. The mixture was stirred at room temperature for 3 h then directly analysed by GC. This analysis revealed the formation of two products. One (30% yield) was identified as tri-1-butyl-1-hexylsilane by comparison with an authentic sample [34]. The other (17% yield) was shown to be 1-hexylsilatrane from the NMR and mass spectral data for the crude reaction mixture: ^{1}H NMR ($CDCl_3$) 0.6–1.8 (m) 2.70 (t) 3.60 (t, OCH_2); ^{29}Si NMR ($CDCl_3$) 3.00 (^{n}HexSi^{n}Bu$_3$), −65.10 (hexylsilatrane); MS *m/e* 259 (M^+) 174 $(M - nC_6H_{13})^+$.

Reaction of vinylsilatrane with ^{t}BuLi

18 ml of a 1.7 *M* solution of tBuLi in hexane (13.6 mmol) were added at −78° C to a solution of vinylsilatrane (2.5 g, 12 mmol) in ether (80 ml). The mixture was stirred at room temperature for 2.5 h, then allowed to warm to room temperature during 1h. It was then treated with saturated aqueous NH_4Cl and the organic layer was washed with brine and dried over $MgSO_4$. Evaporation of the solvent left a white solid which recrystallized from hexane to give 2.6 g (81%) of pure 3,3-dimethylbutylsilatrane $(CH_3)_3C(CH_2)_2$ $Si(OCH_2CH_2)_3N$, m.p. 159.5–161.4° C; ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 9H $(CH_3)_3C$), 0.70–0.90 (m, 4H, $2xCH_2$); 2.53 (t, *J* 5.8 Hz, 6H, NCH_2); 3.49 (t, *J* 6.0 Hz, 6H, OCH_2); ^{29}Si NMR ($CDCl_3$) −64.54; ^{13}C NMR ($CDCl_3$) 10.3 (t, CH_2Si); 29.0 (q, $(CH_3)_3$); 30.9 (s, $(CH_3)_3C$); 38.8 (t, $(CH_3)_3CCH_2$); 51.4 (t, NCH_2); 57.9 (t, OCH_2); IR (cm^{-1}) 2905, 2865, 1495, 1355, 1280, 1095; MS *m/e* 259 (M^+) 175, 174 $(M - C_6H_{13})^+$ (100%), 130, 89.

Reaction of chlorosilatrane with n-butyllithium

29.6 ml of a 2.5 *M* solution of ^{n}BuLi in hexane (74.4 mmol) were added at room temperature to a solution of chlorosilatrane (5 g, 23.2 mmol) in 80 ml of THF. The mixture was stirred at room temperature for 24 h then a solution of lithium aluminium hydride (1.12 g, 27.9 mmol) in THF (20 ml) was added. The mixture was kept at 50° C for 2.5 h then diluted with 100 ml of ether, cooled, and treated with aqueous 4 *M* HCl. After 3 extractions with ether the organic layer was washed with water, dried over $MgSO_4$, and concentrated and the residue distilled, to give 2.6 g of tri-1-butylsilane (56% yield) (b.p. 98–104° C/15 Torr).

Attempted formation of tri-1-butylchlorosilane by reaction of chlorosilatrane with n-butyllithium

29.6 ml of a 2.5 *M* solution of nBuLi in hexane (74.4 mmol) were added at room temperature to a solution of chlorosilatrane (5 g, 23.2 mmol) in 80 ml of THF. The mixture was stirred at room temperature for 24 h, then distilled. No product was obtained, extensive polymerisation having taken place.

Reaction of chlorotrimethoxysilane with ^{n}BuLi

2.5 ml of a 2.5 *M* solution of ^{n}BuLi in hexane (6.3 mmol) were added slowly at −78° C to a solution of chlorotrimethoxysilane (6.3 mmol) in the presence of bibenzyl (6.3 mmol) used as internal standard. The mixture was stirred at room temperature for 0.5 h then treated with saturated aqueous NH_4Cl. The organic layer was analysed by GC, and the products identified by comparison with authentic sample (1-Butyltrimethoxysilane and di-1-butyldimethoxysilane were prepared by published procedures [35]).

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