

## A novel route to pentacoordinated organylsilanes and -germanes

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### Abstract

New convenient methods of sila- and germatranes synthesis from ethoxy- and tetraorganylsilanes and -germanes have been elaborated. The reaction of ethoxysilanes with boratrane in the presence of catalytic amounts of metal alcoholates has been investigated. Dimethylformamide (DMF) as a solvent and NaOEt as a catalyst used instead of xylene and  $\text{Al}(\text{O}^i\text{-Pr})_3$  were found to give better yields. The possibility of using alkoxy-, aminosilanes, tetraethoxygermane and even tetraorganylsilanes in this reaction leading to the corresponding atranes with good yields has been demonstrated. Triethanolamine in the presence of catalytic amounts of base or CsF easily substitutes furyl-, dihydrofuryl-, dihydropyranyl- and thienyl groups in tris- and tetraheterylsilanes, leading to organylsilatranes with good to excellent yields. © 1997 Elsevier Science S.A.

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### 1. Introduction

Silatranes as a class of pentacoordinated silicon compounds are known for more than three decades; however, their specific biological [1–5] physico-chemical [6–9] and structural [10–18] properties still attract research interests. Although the investigation results were published in many papers [19–28], most of them deal solely with the intriguing properties study of these compounds.

The most popular methods for the silatranes synthesis are the reactions of halo-, hydro- and alkoxy silanes with triethanolamine or its derivatives [29]. The original way of silatranes synthesis from ethoxysilanes and boratrane in the presence of  $\text{Al}(\text{O}^i\text{-Pr})_3$  or  $\text{Al}_2\text{Cl}_6$  has also

been described [30–32]. Convenience and advantages of this method allows us to extend its scope and limitation.

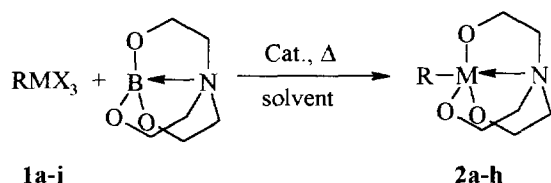
Recently, investigating the possible application of tetraorganylsilanes in organic synthesis, we have found that furyl, dihydrofuryl and dihydropyranyl groups are good leaving groups in the reactions of tetraorganylsilanes with H- [33,34], C- [35], O- and N-nucleophiles [36]. The cleavage of the Si–C bond in (2-furyl)- and (2-thienyl)trialkylsilanes by NaOMe in MeOH has also been documented [37]. The results obtained prompted us to test the reactivity of heterylsilanes and germanes in the reactions with triethanolamine and boratrane.

### 2. Results and discussion

We have found that methyl- (**1d**), chloromethyl- (**1e**), vinyl- (**1c**), phenyl- (**1a**), 2-furyl- (**1f**) and 2-thienyltriethoxysilane (**1g**), tetraethoxysilane (**1h**), tetraethoxygermane (**1i**) and even tris(dimethyl-amino)phenylsilane (**1b**) react with boratrane to give the

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corresponding alkyl-, alkoxy-, alkenyl-, aryl- and heterylsilatranes **2a–g** and germatrane **2h** (Table 1):



	M	R	X		M	R
a)	Si	Ph	OEt	a)	Si	Ph
b)	Si	Ph	NMe <sub>2</sub>	b)	Si	Vy
c)	Si	Vy	OEt	c)	Si	Me
d)	Si	Me	OEt	d)	Si	ClCH <sub>2</sub>
e)	Si	ClCH <sub>2</sub>	OEt	e)	Si	2-furyl
f)	Si	2-furyl	OEt	f)	Si	2-thienyl
g)	Si	2-thienyl	OEt	g)	Si	OEt
h)	Si	OEt	OEt	h)	Ge	OEt
i)	Ge	OEt	OEt			

In the trial series for these reactions, the best yields were found using LiOEt and NaOEt as catalysts. Corresponding reactions of phenyltriethoxysilane (**1a**) at 80°C/1 h yielded 88% and 95% of phenylsilatrane (**2a**), respectively. K, Na and Li hydroxides have been found to be weaker catalysts for this reaction, yielding 28%, 25% and 22% of **2a**, respectively. Yield of phenylsilatrane (**2a**) was low with AlCl<sub>3</sub> (18%) Al(O<sup>*i*</sup>Pr)<sub>3</sub> (16%) and BuLi (11%) as well. However, in the case of ZrCl<sub>4</sub> phenylsilatrane (**2a**) was formed with 43% yield.

The reactivity of RSi(OEt)<sub>3</sub> decreases in the following order: R = Ph ≫ 2-furyl > Vy > Me ~ 2-thienyl > chloromethyl (Table 1).

Phenyltriethoxysilane (**1a**) easily reacts with boratrane in the presence of NaOEt to give phenylsilatrane

(**2a**) with 95% yield (Table 1, entry 1). This reaction proceeds even without a catalyst at 80°C/3 h with 93% yield of **2a** (Table 1, entry 2).

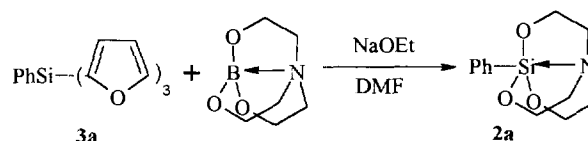
Amino groups in **1b** appear to be good leaving groups as well, leading to the good yield of phenylsilatrane in xylene solution; however, in DMF there was no reaction with boratrane.

(2-Furyl)triethoxysilane (**1f**) is actually more reactive than (2-thienyl)triethoxysilane (**1g**), yielding 71% of corresponding silatrane after 8 h (Table 1, entries 7 and 8).

Tetraethoxygermane (**1i**) readily reacts with boratrane in xylene/Al(O<sup>*i*</sup>Pr)<sub>3</sub> conditions. It is worthy to note that **1i** is more reactive than the corresponding silane **1h** (Table 1, entry 10).

Chloromethyltriethoxysilane (**1e**) was found to be the worst substrate for this reaction and after 75 h at 140°C, only 10% of chloromethylsilatrane (**2d**) was detected (Table 1, entry 6).

It was found that boratrane is able to cleave even Si–C<sub>furyl</sub> bonds in tris(2-furyl)phenylsilane (**3a**) in the presence of catalytic amounts (20 mol%) of NaOEt, giving phenylsilatrane (**2a**) in good yield (65%):



Tris(2-furyl)phenylsilane (**3a**) was quantitatively converted into corresponding silatrane by reaction with triethanolamine in the presence of 5 mol% of 1 M solution of NaOEt in EtOH [38] (Table 2). Under the same conditions, triethanolamine readily reacts with

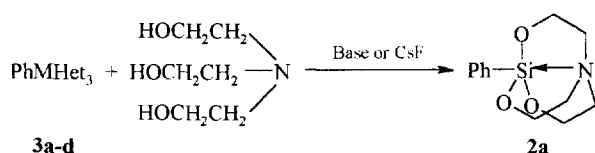
Table 1

Reaction of organyltriethoxysilanes **1a–h** and -germane **1h** with boratrane (0.1 M solution, [1a–i]:[B(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N] = 1:1.5)

Entry	M	R	X	Solvent	Catalyst (5 M%)	Temperature (°C)	Time (h)	Isolated yield of atrane (%)
1	<b>1a</b>	Si	Ph	OEt	DMF	NaOEt	2	<b>2a</b> 95
2	<b>1a</b>	Si	Ph	OEt	DMF	–	3	<b>2a</b> 93
3	<b>1b</b>	Si	Ph	NMe <sub>2</sub>	Xylene	Al(O <sup><i>i</i></sup> Pr) <sub>3</sub>	10	<b>2a</b> 60
4	<b>1c</b>	Si	Vy	OEt	DMF	NaOEt	20	<b>2b</b> 68
5	<b>1d</b>	Si	Me	OEt	DMF	NaOEt	22	<b>2c</b> 50
6	<b>1e</b>	Si	ClCH <sub>2</sub>	OEt	DMF	NaOEt	75	<b>2d</b> 10
7	<b>1f</b>	Si	2-Furyl	OEt	DMF	NaOEt	8	<b>2e</b> 71
8	<b>1g</b>	Si	2-Thienyl	OEt	DMF	NaOEt	28	<b>2f</b> 66
9	<b>1h</b>	Si	OEt	OEt	Xylene	Al(O <sup><i>i</i></sup> Pr) <sub>3</sub>	3	<b>2g</b> 80
10	<b>1i</b>	Ge	OEt	OEt	Xylene	Al(O <sup><i>i</i></sup> Pr) <sub>3</sub>	1.5	<b>2h</b> 87
11	<b>3a</b>	Si	Ph	2-Furyl	DMF	NaOEt <sup>a</sup>	3	<b>2a</b> 65

<sup>a</sup> 20 M%.

tris[2-(4,5-dihydrofuryl)]- (**3b**), tris[2-(5,6-dihydro-4H-pyranyl)]- (**3c**), tris(2-thienyl)phenylsilane (**3d**):



	Het
a)	2-furyl
b)	2-(4,5-dihydrofuryl)
c)	2-(5,6-dihydro-4H-pyranyl)
d)	2-thienyl

Reactivity of the leaving groups in the mentioned silanes decreases in the following order: 2-furyl > 2-

thienyl > 2-(4,5-dihydrofuryl) > 2-(5,6-dihydro-4H-pyranyl).

We have investigated the influence of a solvent, type and amount of a catalyst, ratio of reactants and concentration of reaction mixture in the reaction of tris(2-furyl)phenylsilane (**3a**) with triethanolamine (Table 2).

In using ethanol as a solvent, only traces of the desired silatrane **2a** were detected (Table 2, entry 4). When boiling the reaction mixture at 80°C, the main process is initial silane **3a** destruction (Table 2, entry 6). The reaction proceeds very slowly in nonpolar benzene and xylene (Table 2, entries 8, 9). During the prolonged stirring of the reaction mixture in HMPA at 140°C, the slow destruction of furylsilane **3a** was detected without formation of the desired product **2a**. In THF, the reaction proceeds only in the presence of 15 mol% of 1 N solution of NaOEt in EtOH and prolonged stirring (150

Table 2  
Reaction of tris(2-furyl)phenylsilane (**3a**) with triethanolamine (TEA) (0.1 M solution)

Entry	Ratio [ <b>3a</b> ]:[TEA]	Solvent	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield of <b>2a</b> (%)	Rec. of <b>3a</b> (%)
1	1:1	THF	NaOEt (5)	20	100	Traces	> 95
2	1:1	THF	NaOEt (5)	60	3	Traces	> 95
3	1:1	THF	NaOEt (15)	80	150	64	6
4	1:1	EtOH	NaOEt (5)	20	100	Traces	> 95
5	1:1	EtOH	NaOEt (5)	60	3	Traces	> 95
6	1:1	EtOH	NaOEt (10)	80	21	18	—
7	1:1	C <sub>6</sub> H <sub>6</sub>	NaOEt (5)	20	100	Traces	> 95
8	1:1	C <sub>6</sub> H <sub>6</sub>	NaOEt (10)	80	150	64	34
9	1:1	Xylene	NaOEt (5)	140	22	40	60
10	1:1	HMPA	NaOEt (5)	20	6	—	> 95
11	1:1	HMPA	NaOEt (5)	140	16	—	40
12	1:1	CH <sub>2</sub> Cl <sub>2</sub>	NaOEt (5)	20	70	Traces	> 95
13	1:1	CH <sub>2</sub> Cl <sub>2</sub>	NaOEt (5)	80	21	38	58
14	1:1	MeCN	NaOEt (5)	20	70	Traces	> 95
15	1:1	MeCN	NaOEt (5)	80	2	89	—
16	1:1	DMF	NaOEt (5)	20	70	77	—
17	1:1	DMF	NaOEt (5)	80	2	90	—
18	1:1	DMF	—	80	3	—	100
19	1:1	DMF	NaOEt (1)	80	3	Traces	> 95
20	1:1	DMF	NaOEt (5)	80	1	95	—
21	1:1	DMF	NaOEt (10)	80	1	90	—
22	1:1	DMF	NaOEt (20)	80	1	86	—
23	1:1.2	DMF	NaOEt (5)	80	1	95	—
24	1:1.5	DMF	NaOEt (5)	80	1	> 95	—
25	1:2	DMF	NaOEt (5)	80	1	> 95	—
26	1:1.5	—	NaOEt (5)	80	1	60	33
27	1:1.5	DMF <sup>a</sup>	NaOEt (5)	80	1	> 95	—
28	1:1.5	DMF <sup>b</sup>	NaOEt (5)	80	1	> 95	—
29	1:1.5	DMF <sup>c</sup>	NaOEt (5)	80	1	> 95	—
30	1:1.5	DMF	LiOEt (5)	80	1	67	10
31	1:1.5	DMF	LiOH (5)	80	1	68	7
32	1:1.5	DMF	NaOH (5)	80	1	> 95	—
33	1:1.5	DMF	KOEt (5)	80	1	> 95	—
34	1:1.5	DMF	KOH (5)	80	1	> 95	—
35	1:1.5	DMF	CsF (5)	20	1	91	—
36	1:1.5	DMF	Bu <sub>4</sub> NF (5)	20	10	57	15
37	1:1.5	DMF	KOH (5)	20	24	20	16
38	1:1.5	DMF	NaOEt (5)	50	2	56	—

<sup>a</sup> 0.1 M solution.

<sup>b</sup> 0.5 M solution.

<sup>c</sup> 1 M solution.

h) at 80°C (Table 2, entry 3). The reaction in CH<sub>2</sub>Cl<sub>2</sub> also requires prolonged heating. The most suitable solvents for triethanolamine reaction with tris(2-furyl)phenylsilane (**3a**) appears to be acetonitrile and dimethylformamide.

The best conditions for this reaction are solution in DMF with reactants ratio [**3a**]:[triethanolamine] = 1:1.5 in the presence of 5 mol% of alcoholates or hydroxides of Na and K. The increase of the catalyst amount causes decrease of silatrane **2a** yield (Table 2, entry 22). LiOEt, LiOH and Bu<sub>4</sub>NF are less effective; however, in the presence of CsF, the reaction proceeds at room temperature with 91% yield of phenylsilatrane (**2a**) after 1 h (Table 2, entries 30–31, 35–36).

Other heterylsilanes containing dihydrofuryl, dihydropyranyl and thienyl groups bonded to silicon react with triethanolamine analogously (Table 3).

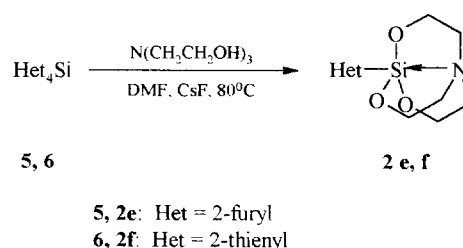
In the presence of the basic catalysts tris[2-(4,5-dihydrofuryl)]phenylsilane (**3b**) was decomposed even at room temperature. The silatrane formation was successful only in the presence of CsF and after 1 h stirring of the reaction mixture at 80°C phenylsilatrane (**2a**) was formed with 68% yield (Table 3, entry 10).

The dihydropyranyl group in **3c** was the worst leaving group among all heteryl groups tested. Thus, the prolonged heating with NaOEt (70 h at 80°C) did not cause any noticeable reaction. Only in the presence of

CsF (18 h at 80°C) we succeeded in the conversion of **3c** into **2a** with 32% yield (Table 3, entry 17).

Thienyl groups of tris(2-thienyl)phenylsilane (**3d**) are also easily replaced by triethanolamine, and phenylsilatrane (**2a**) is obtained with 92% yield after 3 h at 80°C (Table 3, entry 27).

2-Furyl and 2-thienyl groups were found to be the best leaving groups in tetrakis(2-furyl)silane **5** and tetrakis(2-thienyl)silane **6**.



While tetrakis[2-(5,6-dihydro-4H-pyranyl)]silane (**7**) did not react with triethanolamine even at prolonged fusion at 140°C, the silanes **5** and **6** were converted into 2-furyl- (**2e**) and 2-thienylsilatrane (**2f**) in the presence of CsF with 91% and 95% isolated yields, respectively.

It is possible to synthesize silatranes **2e** and **2f** by the traditional methods using transesterification of (2-furyl)-

Table 3

Reaction of trisheterylphenylsilanes Het<sub>3</sub>SiPh **3b–d** with triethanolamine (TEA) (0.1 M solution; [**3 b–d**]:[TEA] = 1:1.5)

Entry	Het	Solvent	Catalyst (mol%)	Temperature (°C)	Time (h)	Yield of <b>2a</b> (%)	
1	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	KOH (5)	20	24	25
2	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	NaOEt (5)	50	2	7
3	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	NaOEt (5)	80	1	14
4	<b>3b</b>	2-(4,5-dihydrofuryl)	–	NaOEt (5)	80	3	Traces
5	<b>3b</b>	2-(4,5-dihydrofuryl)	Xylene	NaOEt (10)	100	48	–
6	<b>3b</b>	2-(4,5-dihydrofuryl)	CH <sub>2</sub> Cl <sub>2</sub>	NaOEt (5)	80	20	–
7	<b>3b</b>	2-(4,5-dihydrofuryl)	MeCN	NaOEt (5)	80	3	Traces
8	<b>3b</b>	2-(4,5-dihydrofuryl)	THF	NaOEt (5)	80	3	Traces
9	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	CsF (5)	20	10	34
10	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	CsF (5)	80	1	68
11	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	Bu <sub>4</sub> NF (5)	20	1	Traces
12	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	Bu <sub>4</sub> NF (10)	80	2	10
13	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	Bu <sub>4</sub> NF (10)	100	20	30
14	<b>3b</b>	2-(4,5-dihydrofuryl)	DMF	NaOEt (5)	80	3	Traces
15	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	NaOEt (10)	150	44	Traces
16	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	CsF (10)	20	18	20
17	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	CsF (5)	80	18	32
18	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	Bu <sub>4</sub> NF (10)	20	1	–
19	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	Bu <sub>4</sub> NF (15)	80	70	10
20	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	Bu <sub>4</sub> NF (15)	100	20	Traces
21	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	–	NaOEt (5)	80	20	Traces
22	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	NaOEt (5)	100	20	10
23	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	NaOEt (5)	150	24	10
24	<b>3c</b>	2-(5,6-dihydro-4H-pyranyl)	DMF	NaOEt (20)	100	24	Traces
25	<b>3d</b>	2-thienyl	DMF	KOH (5)	20	24	36
26	<b>3d</b>	2-thienyl	DMF	NaOEt (5)	50	2	64
27	<b>3d</b>	2-thienyl	DMF	NaOEt (5)	80	3	92
28	<b>3d</b>	2-thienyl	DMF	Bu <sub>4</sub> NF (5)	20	10	32

Table 4

Yields of silatranes **2a–d**, **2f**, **2g** obtained by boratrane or triethanolamine method

Silatrane	Boratrane method	Triethanolamine method (reference)
<b>2a</b> (R = Ph)	95	83 [42]
<b>2b</b> (R = Vy)	68	92 [42]
<b>2c</b> (R = Me)	50	90 [42]
<b>2d</b> (R = ClMe)	10	95 [43]
<b>2e</b> (R = 2-furyl)	71	88 [44]
<b>2f</b> (R = 2-thienyl)	66	86 [45]
<b>2g</b> (R = OEt)	80	90 [46]

or (2-thienyl)triethoxysilanes with triethanolamine [39]. However, the starting (2-furyl)- or (2-thienyl)triethoxysilanes can be obtained only by complicated synthesis with 9.6% and 22.4% yield, respectively [40]. In this case, the total yield of 2-furylsilatrane (**2e**) is < 10% (based on furan) and 2-thienylsilatrane (**2f**), 20% (based on 2-bromothiophene). The method of synthesis presented here allows to increase the total yield of silatranes **2e** and **2f** to more than 50% (on furan and 2-bromothiophene, respectively).

### 3. Conclusions

The boratrane method is quite promising synthetically, since it is more 'neutral' than commonly used triethanolamine way for the preparation of atranes. In some cases, like the synthesis of 1-hydrosilatranes, it is the only possible method [32] because the Si–H bond instability in trichloro-, triacetoxy- and trialkoxysilanes leads to very low yields or only to the formation of Si-substituted silatranes [41]. Although the boratrane method generally did not show the considerable difference in yields of ordinary silatranes in comparison with transesterification method (Table 4), it was ascertained to be an original complementary way for obtaining silatranes.

The reaction of tetraheterylsilanes with triethanolamine is preferable for the synthesis of heterylsilatranes. The starting tetraheterylsilanes can be obtained more easily, and they are more stable than the corresponding heteryl trihalo-, trialkoxy-, triacyloxy- or trihydrosilanes. The reaction proceeds smoothly and gives higher yields of heterylsilatranes than those obtained by the traditional methods.

### 4. Experimental

<sup>1</sup>H NMR spectra were recorded on Bruker WH-90/DS spectrometer in CDCl<sub>3</sub>. Mass spectra were obtained with a Kratos MS-25GC-MS instrument (70 eV). GLC analysis was carried out with a CHROM-5 appara-

tus equipped with a flame ionisation 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<sup>-1</sup>) as carrier gas.

THF was dried with sodium benzophenone ketyl. Xylene was dried with Na, dimethylformamide was dried by fractional distillation with benzene followed by keeping over molecular sieves.

<sup>n</sup>BuLi (4–5 N) was prepared by modified literature procedure [47]. 2-Furyllithium and 2-thienyllithium were prepared by the addition of 4–5N <sup>n</sup>BuLi solution in hexane to a solution of furan or thiophene in tetrahydrofuran (THF/hexane, 2:1) at –30°C with subsequent stirring for 30 min. The temperature of the reaction was raised to boiling, and the reaction mixture was stirred for 30 min at this temperature. [2-(4,5-Dihydrofuryl)]lithium and [2-(5,6-dihydro-4H-pyran)]lithium were prepared as described in Ref. [34].

Tris(2-furyl)phenylsilane (**3a**) [48], tetra(2-furyl)silane (**5**) [39], tetra(2-thienyl)silane (**6**) [49] were prepared according to published data.

The physico-chemical constants of phenylsilatrane (**2a**) [50], vinylsilatrane (**2b**) [51], methylsilatrane (**2c**) [52], chloromethylsilatrane (**2d**) [51], 2-furylsilatrane (**2e**) [40], 2-thienylsilatrane (**2f**) [40], ethoxysilatrane (**2g**) [52] and ethoxygermatrane (**2h**) [53] obtained in reactions of heterylsilanes with triethanolamine correspond to published data.

Boratrane was prepared as described [54] from H<sub>3</sub>BO<sub>3</sub> and N(C<sub>2</sub>H<sub>4</sub>OH)<sub>3</sub> with 86% isolated yield.

Al(O<sup>i</sup>-Pr)<sub>3</sub> was prepared from Al and <sup>i</sup>-PrOH using HgCl<sub>2</sub> as a catalyst [55] with 92% isolated yield. Commercially available CsF was dried at 250°C for 3 h. NaOEt was used as a 1 N solution of Na in dry EtOH.

#### 4.1. Reaction of organylsilanes and -germane with boratrane (general procedure)

0.1 M solution of boratrane and the relevant substrate (silane or germane), [silane]:[boratrane] = 1:1.5, were heated with stirring with 5 mol% of catalyst until the disappearance of the initial substrate. The process was controlled using GC analysis. Then, successive evaporation of the solvent, filtration through a small amount of dried neutral Al<sub>2</sub>O<sub>3</sub> using CHCl<sub>3</sub> as an eluent, and extraction in system CHCl<sub>3</sub>/H<sub>2</sub>O were done. In the case of carrying the reaction in xylene, filtration and crystallisation from xylene were used.

#### 4.2. Synthesis of heterylsilanes (general procedure)

Chlorosilane was added to the solution of heteryllithium in THF/hexane at –30°C. The mixture was stirred for 30 min and the temperature of the reaction was raised to ambient temperature followed by stirring

for 1 h. After 12 h, the reaction mixture was filtered, evaporated, and the product obtained was isolated by crystallization.

#### 4.3. *Tris*[2-(4,5-dihydrofuryl)]phenylsilane (**3b**)

**3b** (1.1 g, yield 34%) was obtained from a mixture of phenyltrichlorosilane (2.1 g, 0.01 mol) and dihydrofuryllithium (0.03 mol). The product was crystallized from hexane. m.p. 72°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 2.66 (dt, 6H, *J* = 9.5, 2.7 Hz); 4.28 (t, 6H, *J* = 9.5 Hz); 5.56 (t, 3H, *J* = 2.7 Hz); 7.27–7.84 (m, 5H).

#### 4.4. *Tris*[2-(5,6-dihydro-4H-pyranyl)]phenylsilane (**3c**)

**3c** (0.84 g, yield 24%) was obtained from a mixture of phenyltrichlorosilane (2.1 g, 0.01 mol) and dihydropyranyllithium (0.03 mol). The product was crystallized from hexane. m.p. 160°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.57–2.02 (m, 12H); 3.98 (t, 6H, *J* = 4.8 Hz), 5.33 (t, 3H, *J* = 3.9 Hz); 7.28–7.82 (m, 5H). MS *m/e* (rel. intensity, %): 354 (M<sup>+</sup>, 35), 139 (100).

#### 4.5. *Tris*(2-thienyl)phenylsilane (**3d**)

**3d** (1.91 g, yield 54%) was obtained from a mixture of phenyltrichlorosilane (2.1 g, 0.01 mol) and thienyllithium (0.03 mol). The product was crystallized from benzene. m.p. 142°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.15–7.80 (m, 14H); MS *m/e* (rel. intensity, %): 354 (M<sup>+</sup>, 35).

#### 4.6. *Tetrakis*[2-(5,6-dihydro-4H-pyranyl)]silane (**7**)

**7** (2.2 g, yield 61%) was obtained from a mixture of tetrachlorosilane (1.7 g, 0.01 mol) and dihydropyranyllithium (0.04 mol). The product was crystallized from hexane. m.p. 160°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 1.67–2.22 (m, 16H); 3.82 (t, 8H, *J* = 4.9 Hz), 5.42 (t, 4H, *J* = 3.4 Hz); MS *m/e* (rel. intensity, %): 360 (M<sup>+</sup>, 100).

#### 4.7. Reaction of heterylsilanes and -germanes with triethanolamine (general procedure)

The mixture of triethanolamine, solvent and catalyst was stirred in Pierce reaction-vials for 10–15 min and heterylsilane (-germane) was added. The reaction products were analysed by GLC with alkane C<sub>26</sub> as an internal standard. The temperature and time of reaction, solvent, catalyst, yield of products are presented in Tables 1 and 2.

#### 4.8. Reaction of *tris*(2-furyl)phenylsilane (**3a**) with triethanolamine

The mixture of triethanolamine (223.5 mg, 1.5 mmol), furylsilane **3a** (312 mg, 1 mmol) and KOH (50 μl 1 N

KOH in EtOH, 5 mol%) in 10 ml of *N,N*-dimethylformamide was heated for 1 h at 80°C. It was then diluted with 30 ml of CHCl<sub>3</sub> and treated with saturated aqueous solution of NH<sub>4</sub>Cl, water and brine. The organic extract was dried with Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed by evaporation. Phenylsilatrane (**2a**) (237.4 mg, yield 95%) was crystallized from xylene.

#### 4.9. Reaction of *tetra*(2-furyl)silane (**5**) with triethanolamine

The mixture of triethanolamine (59.6 mg, 0.4 mmol), *tetra*(2-furyl)silane (**5**) (79 mg, 0.27 mmol) and NaOH (13.5 μl 1 N NaOH in EtOH, 5 mol%) in 2.7 ml *N,N*-dimethylformamide was heated 3 h at 80°C. (2-Furyl)silatrane (**2e**) (59.4 mg, yield 91%) was isolated by column chromatography on silica gel with 1:1 hexane: ethyl acetate as eluent.

#### 4.10. Reaction of *tetra*(2-thienyl)silane (**6**) with triethanolamine

The mixture of triethanolamine (223.5 mg, 1.5 mmol), thienylsilane **6** (360 mg, 1 mmol) and NaOH (50 μl 1 N NaOH in EtOH, 5 mol%) in 10 ml *N,N*-dimethylformamide was heated 8 h at 80°C. (2-Thienyl)silatrane (**2f**) (244.7 mg, yield 95%) was isolated by column chromatography on silica gel with 1:1 hexane: ethyl acetate as eluent.

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