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2-(Alkoxymethyl)phenylsilicon compounds: the search for pentacoordination [1]

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Abstract

The synthesis of 2-(methoxymethyl)phenylsilanes and 2-(isopropoxymethyl)phenylsilanes is described. The coordination behaviour of the ether side chains has been studied by NMR spectroscopy. In 2-(alkoxymethyl)phenylsilicon compounds with methoxy, hydrido or phenyl groups the silicon atom is assumed to be tetracoordinated. Pentacoordination is confirmed in trifluoro-[2-(methoxymethyl)phenyl]-silane (**11**) and trifluoro-[2-(isopropoxymethyl)phenyl]silane (**12**). The free energy of activation for ligand permutation at silicon in trifluoro-[2-(methoxymethyl)phenyl]silane (**11**) is estimated to be below 9 kcal mol^{-1}. The synthesis of phenyl-[2-(methoxymethyl)phenyl]silyl triflate (**13**) is described. In the solid state a short silicon-donor oxygen distance is observed, indicating strong bonding interaction. The structure of **13** in solution is discussed on the basis of NMR data and conductivity measurements.

Keywords: Silicon; 2-(Alkoxymethyl)phenylsilanes; Si-pentacoordination; Crystal structure; Siliconium ion

1. Introduction

The ability of silicon to extend its coordination sphere, induced by a ligand with a suitable donor-functionalized side chain, has been intensively studied in the last decade, predominantly by Corriu and coworkers. For the extension of the coordination sphere mainly aromatic ligands bearing dimethylamino-functionalized side chains were used. The results of these investigations made a major contribution to the understanding of nucleophilic substitution at silicon [1]. Furthermore, they promoted the understanding of systems with Si=X double bonds (X = NR, PR, S, Se, ML_n) as well as of siliconium ions, which have been stabilized by use of such ligands [2–12].

In contrast to the great number of pentacoordinated neutral silicon compounds with amino-functionalized aryl groups, only a few species with other donor elements in the side chain have been described [13–19]. In this context, we are interested in silicon compounds substituted with alkoxy-, thioalkoxy- and phosphino-functionalized phenyl groups (Scheme 1). Our investigations concentrate on the coordination behaviour of such donors with respect to hard and soft silicon centres, following Pearson's classification.

In this paper we report on phenylsilanes with side chain substituents involving oxygen donor atoms. The synthesis of 2-methoxymethylphenylsilanes with methoxy, hydrido, phenyl or fluoro substituents is described. In order to study steric influences, the analogous 2-(isopropoxymethyl)phenylsilanes were also investigated. Furthermore, we report on the synthesis of phenyl-[2-(methoxymethyl)phenyl]silyl triflate (**13**). The coordination behaviour in **13** is discussed on the basis of NMR data and X-ray structure analysis.

2. Results and discussion

2.1. Syntheses

1-Bromo-2-(methoxymethyl)benzene (**1**) and the analogous 1-bromo-2-(isopropoxymethyl)benzene (**2**) were synthesized in a two-step sequence in high yields using standard organic reactions. The side chain-functionalized aryl systems can be readily attached to silicon by reaction of the corresponding aryllithium compounds with silanes bearing suitable leaving groups, e.g.

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[1] Dedicated to Professor R. Corriu in recognition of his outstanding contributions to organosilicon chemistry.

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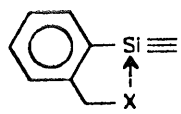


X=NMe_2, PR_2, OR, SR

Scheme 1.

methoxy or hydrido [20]. Thus, lithium halide exchange of the aryl bromide **1** with n-butyllithium and subsequent reaction with tetramethoxysilane at −20°C gave trimethoxy-[2-(methoxymethyl)phenyl]silane (**5**). The corresponding 2-(isopropoxymethyl)phenyl compound **6** was synthesized analogously. Compounds **5** and **6** were isolated as colourless air-stable oils.

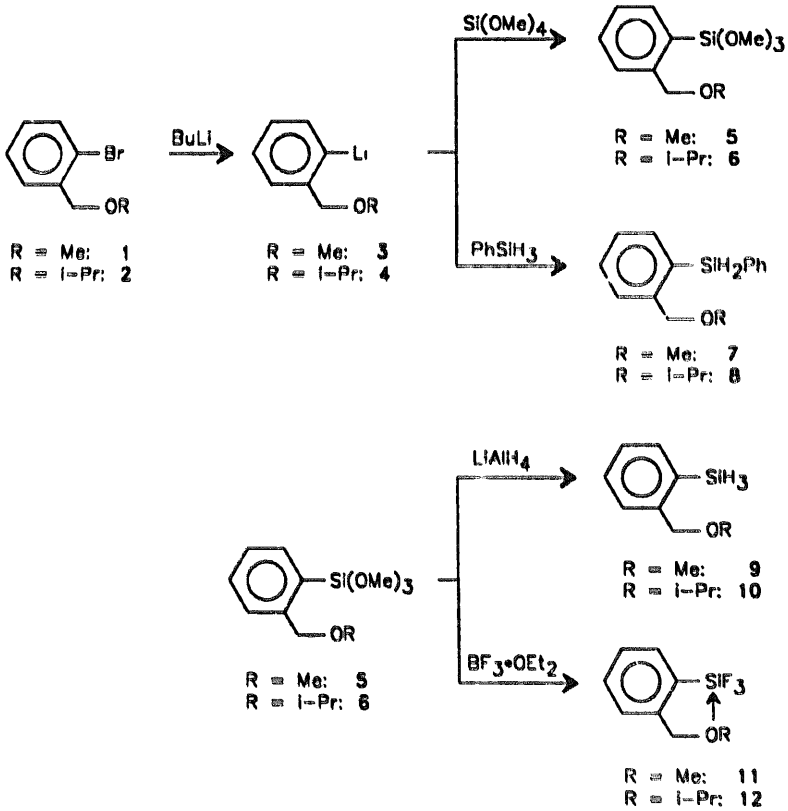
The phenyl-[2-(alkoxymethyl)phenyl]silanes **7** and **8** were obtained by reaction of the aryllithium compounds **2** and **3** with phenylsilane. Both silanes were isolated as viscous oils stable to air and moisture.

The trimethoxy compounds were used as starting materials for the synthesis of the corresponding trifluoro and trihydrido species. Thus, reaction of **5** and **6** with lithium aluminium hydride at 0°C yielded the 2-(alkoxymethyl)phenylsilanes **9** and **10**. Both compounds were obtained as air-stable, colourless liquids.

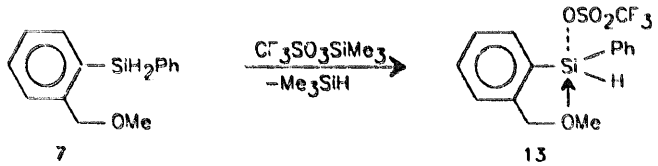
The trifluorosilanes **11** and **12** were synthesized by replacement of the methoxy groups with fluoro groups in **5** and **6** by use of boron trifluoride etherate. Compounds **11** and **12** were isolated as colourless oils. Both compounds are air-sensitive; they hydrolyze rapidly to give siloxanes [21].

2.2. Coordination behaviour

Pentacoordination at silicon can be demonstrated by ^{29}Si NMR spectroscopy [22]. Relative to those for analogous tetracoordinated compounds, the ^{29}Si resonances of the hypercoordinated species are shifted towards higher field. Furthermore, the coupling to adjacent nu-



Scheme 2.



Scheme 3.

Table 1
^{29}Si NMR data for 2-(alkoxymethyl)phenylsilanes

Compound	δ (ppm)	Compound	δ (ppm) J (Hz)	Compound	δ (ppm) J (Hz)	Compound	δ (ppm) J (Hz)
$PhSi(OMe)_3$ [24]	−57.5	Ph_2SiH_2 [24]	−33.2 J_{SiH} = 198 Hz	$PhSiH_3$ [24]	−60.1 J_{SiH} = 200 Hz	$PhSiF_3$ [24]	−73.2 J_{SiH} = 268 Hz
$L_1Si(OMe)_3$	−53.9	L_1SiH_2Ph	−36.2	L_1SiH_3	−61.8	L_1SiF_3	−88.0
5	$\Delta\delta$ = +3.6	**7**	J_{SiH} = 200 Hz $\Delta\delta$ = −3.0	**9**	J_{SiH} = 197 Hz $\Delta\delta$ = −1.7	**11**	J_{SiF} = 240 Hz $\Delta\delta$ = −14.8
$L_2Si(OMe)_3$	−53.6	L_2SiH_2Ph	−36.8	L_2SiH_3	−61.1	L_2SiF_3	−82.2
6	$\Delta\delta$ = +3.9	**8**	J_{SiH} = 198 Hz $\Delta\delta$ = −3.6	**10**	J_{SiH} = 202 Hz $\Delta\delta$ = −1.0	**12**	J_{SiF} = 245 Hz $\Delta\delta$ = −9.0

L_1 = 2-(methoxymethyl)phenyl; L_2 = 2-(isopropoxymethyl)phenyl.
$\Delta\delta$ = shift compared to $PhSiR_3$.

clei (F, H) is influenced by pentacoordination [23]. We used these spectroscopic tools to assess the hypervalency in 2-(alkoxymethyl)phenyl-substituted silanes. The ^{29}Si NMR data of the compounds described above and those of the analogous phenylsilanes without donor functionality are presented in Table 1.

As shown in Table 1, the ^{29}Si chemical shifts for the compounds **5–10** are very similar to those observed for the corresponding non-functionalized species. In addition, the $^1J_{SiH}$ coupling constants are very close to those for the parent compounds. Thus, pentacoordination can be excluded in **5–10** [22].

Another situation is encountered for the trifluoro compounds **11** and **12**. Relative to those for phenyltrifluorosilane, the ^{29}Si resonances are shifted to higher field by 14.8 and 9.0 ppm respectively. In addition, the values of the $^1J_{SiH}$ coupling for **11** and **12** are smaller than those found for the non-functionalized species. These findings are in accord with pentacoordination at silicon. The NMR data obtained for **12** show that the interaction between the oxygen donor and the silicon atom is not as effective as that in the analogous trifluorosilane **11**, even though the isopropyl substituent should increase the basicity of the oxygen donor. The weaker donation of the oxygen atom in this derivative seems to be a consequence of the steric demand of the isopropyl group.

Temperature-dependent NMR investigations can give further information about the strength of the donor–silicon interaction. In order to determine the activation energy for the ligand permutation at silicon, we recorded the ^{19}F NMR spectra of the trifluoro compound **11** at low temperatures. At room temperature only one signal for the axial and the equatorial fluoro substituents is observed, at −140.4 ppm. Lowering the temperature leads only to a broadening of the signal. Even at −80°C the signals of the axial and equatorial fluoro ligands are not completely separated. Thus, the free energy of activation for the pseudo-rotation can only estimated to be below 9 kcal mol^{-1}.

2.3. Synthesis and X-ray crystal structure of phenyl-[2-(methoxymethyl)phenyl]silyl triflate (13)

As described above, phenyl groups bearing side chain amino substituents can be used to stabilize ionic silicon species [9–12]. We were interested in examining the potential of 2-(alkoxymethyl)phenyl ligands in this respect. Thus, we treated phenyl-[2-(methoxymethyl) phenyl]silane (**7**) with trimethylsilyl triflate in ether at −20°C. After removal of all volatile components in vacuo we obtained phenyl-[2-(methoxymethyl)phenyl)] silyl triflate (**13**) in excellent yield as an air-sensitive colourless viscous oil, which crystallized slowly at room

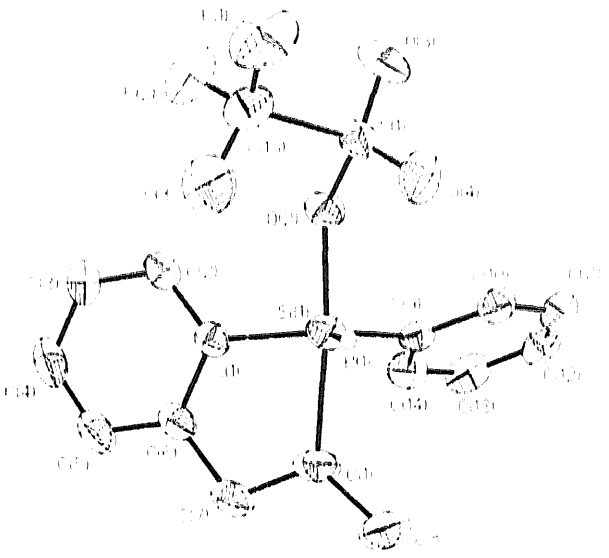


Fig. 1. ORTEP drawing of phenyl-[2-(methoxymethyl)phenyl]silyl triflate (**13**) [25]. The ellipsoids are drawn at the 50% probability level. Selected bond lengths (pm) and angles (°): Si(1)–C(1) 186.4(5), Si(1)–C(9) 185.5(5), Si(1)–H(1) 135(4), Si(1)–O(1) 203.3(3), Si(1)–O(2) 185.7(3), S(1)–O(2) 149.0(3), S(1)–O(3) 141.8(3), S(1)–O(4) 142.0(3); O(1)–Si(1)–O(2) 174.6(2), C(1)–Si(1)–C(9) 121.9(2), C(1)–Si(1)–H(1) 122(2), C(9)–Si(1)–H(1) 115(2), C(1)–Si(1)–O(1) 81.4(2), C(1)–Si(1)–O(2) 94.4(2), C(9)–Si(1)–O(1) 89.4(2), C(9)–Si(1)–O(2) 95.7, O(1)–Si(1)–H(1) 88(2), O(2)–Si(1)–H(1) 91(2), C(2)–C(1)–Si(1) 126.1(3), C(6)–C(1)–Si(1) 117.1(4), C(1)–C(6)–C(7) 116.8(4), C(5)–C(6)–C(7) 122.0(4).

temperature. The X-ray structure of the triflate **13** is shown in Fig. 1. Structural data are given in Tables 2 and 3.

Compound **13** crystallizes in the space group $P2_1/n$. The unit cell contains four molecules. The geometry at silicon is very close to trigonal bipyramidal. The donor-functionalized phenyl ligand, the second phenyl group and the hydrogen atom (H(1)) form the central plane. The axial positions are occupied by the oxygen donor (O(1)) and the triflate ligand (O(2)). The disposition of the axial oxygen atoms and the central silicon is nearly linear (174.6°). The Si–O(1) distance, 203.3 pm, is much shorter than the sum of the van der Waals radii (362 pm) [26], and indicates a substantial bonding interaction. The Si–O(2) distance (185.7 pm) is significantly longer than that of a typical covalent silicon–oxygen bond (161–175 pm) [27]. The sum of the bond angles in the equatorial plane deviates by only 1.1° from the ideal value of 360°. The angles C(1)–Si(1)–C(9) and C(1)–Si(1)–H(1) are slightly widened to 121.9° and 122° respectively, and the angle C(9)–Si(1)–H(1) is reduced to 115°. The silicon is slightly displaced, by about 10 pm, from the trigonal plane towards the axial oxygen O(2) of the triflate. In contrast to the angles around C(9), the angles around C(1) deviate significantly from 120°. Thus, the angle C(2)–C(1)–Si(1) is widened to 126.1°, whereas the angles C(6)–C(1)–Si(1) and C(1)–C(6)–C(7) are narrowed to 117.1° and 116.8° respectively. These geometric factors optimize the interaction between the silicon atom and the oxygen atom O(1) in the side chain. Thus, compound **13** can be regarded as a contact ion pair in the solid state, analogous to the corresponding triflate bearing the 2-(dimethylaminomethyl)phenyl ligand described by Belzner et al. [12].

Table 2
Crystal data and details of structure refinement for **13**

Empirical formula	$C_{15}H_{15}F_3O_4SSi$
Formula weight	376.42
Crystal colour	colourless
Crystal size (mm^3)	0.50 × 0.30 × 0.10
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Space group	$P2_1/n$
Unit cell dimensions (Å)	a = 10.413(3)
	b = 10.361(3)
	c = 16.250(4)
β (deg)	105.96(2)
Volume (Å^3)	1685.5(8)
Z	4
Density (calc.) (Mg m^{-3})	1.483
Absorption coefficient (mm^{-1})	0.310
F(000)	776
θ range for data collection	2.09 to 25.00°
Index ranges	$0 \leq h \leq 12$,
	$0 \leq k \leq 12$, $-19 \leq l \leq 18$
Reflections collected	3151
Independent reflections	2977 (R_{int} = 0.0454)
Absorption correction	none
Data/restraints/parameters	2973/0/222
Goodness-of-fit on F^2	0.987
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0602 for 1777 reflections,
	wR_2 = 0.1181
R indices (all data)	R_1 = 0.1216, wR_2 = 0.1508
Largest and mean Δ/σ	0.000 and 0.000
Largest diff. peak and hole (e Å^{-3})	0.3 and −0.3

Table 3
Atomic coordinates (×10^4) and isotropic displacement parameters U_{iso} of U_{eq} (Å^2 × 10^3) for **13**

Atom	x	y	z	U_{eq}
S(1)	9045(1)	935(1)	6768(1)	35(1)
Si(1)	10532(1)	1628(1)	8626(1)	34(1)
F(1)	7872(3)	−1217(3)	6186(2)	74(1)
F(2)	10001(3)	−1361(3)	6621(2)	66(1)
F(3)	8856(3)	−1236(3)	7531(2)	67(1)
O(1)	10852(4)	1962(4)	9899(2)	58(1)
O(2)	10265(3)	1161(3)	7488(2)	33(1)
O(3)	9278(3)	1259(4)	5974(2)	52(1)
O(4)	7859(3)	1377(3)	6948(2)	49(1)
C(1)	11895(4)	432(4)	9040(3)	30(1)
C(2)	12505(4)	−331(5)	8545(3)	36(1)
C(3)	13486(5)	−1215(5)	8905(3)	42(1)
C(4)	13894(5)	−1371(5)	9785(3)	50(1)
C(5)	13324(5)	−631(5)	10293(3)	47(1)
C(6)	12337(5)	268(4)	9926(3)	36(1)
C(7)	11711(6)	1100(5)	10454(3)	47(1)
C(8)	10044(5)	2802(6)	10259(3)	55(1)
C(9)	10887(4)	3352(5)	8473(3)	31(1)
C(10)	9928(5)	4143(5)	7939(3)	38(1)
C(11)	10168(5)	5434(5)	7837(3)	45(1)
C(12)	11360(5)	5971(5)	8259(3)	47(1)
C(13)	12337(5)	5228(5)	8800(3)	47(1)
C(14)	12095(5)	3928(5)	8906(3)	42(1)
C(15)	8942(5)	−827(5)	6776(3)	46(1)
H(1)	9245(43)	1352(44)	8582(27)	49(14)

The structure of **13** in solution was investigated by NMR spectroscopy. In the ^{29}Si NMR spectrum a doublet at δ = −48.7 ppm with a $^1J_{SiH}$ coupling constant of 286 Hz was observed. These data are typical for cationic silicon species stabilized by an additional donor ligand [9,10,12,28]. The coupling constant reflects an enhanced s-character of the Si–H bond, and is in accord with an sp^2 hybridized silicon atom. In the ^{1}H NMR spectrum the resonances of the benzylic protons in the side chain show an AB pattern due to the diastereotopic hydrogen atoms. The diastereotopy is a consequence of intramolecular coordination [9,12,20,29,30].

The ionic structure of **13** in solution is confirmed by conductivity measurements. The conductivity of a dichloromethane solution containing silane **7** increases greatly when trimethylsilyl triflate is added; as expected, the starting materials show no significant conductivity.

These results show that the behaviour of **13** in solution is comparable with that observed for nitrogen-donor

stabilized siliconium ions, as described by Corriu, Belzner and coworkers [9,10,12].

3. Conclusion

The results presented in this paper show that alkoxy-functionalized aryl groups are appropriate ligands to induce pentacoordination in neutral organosilicon compounds. Furthermore, the results illustrate that the donor properties of these ligands are sufficient to stabilize siliconium ions. Spectroscopic investigations indicate that the bonding interaction between the donor and the silicon atom in 2-(alkoxymethyl)phenylsilanes is less effective than that in the analogous 2-(dimethylaminomethyl)phenyl-substituted silicon compounds.

4. Experimental section

All reactions were carried out with exclusion of air and moisture under argon using Schlenk techniques. Solvents were dried by standard methods. NMR spectra were recorded on a Bruker AM 300 and a Bruker DRX 500 spectrometer. Mass spectra were recorded on a VG Autospec instrument. Elemental analyses were performed in the microanalytical laboratory of the University of Bielefeld. X-ray structural data were collected on a Siemens P2(1) diffractometer (Mo K α, $\lambda = 0.71073$ Å, graphite monochromator); scan type Wyckoff; programs used Siemens SHELXTL PLUS / SHELXL-93; structure solution by direct methods; structure refinement by full-matrix least-squares on F^2; weighting scheme $w_{calc} = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 2.8928P]$ where $P = (F_o^2 + 2F_c^2)$; H(1) was refined freely and all other protons were held in riding mode.

4.1. 1-Bromo-2-(isopropyloxymethyl)benzene (2)

In a 500 ml Schlenk flask 10.0 g (0.42 mol) of NaH was suspended in 100 ml of THF and 50 ml of isopropanol was added at 0°C. The mixture was stirred for an additional 2 h and 57.5 g (0.27 mol) of 2-bromobenzyl bromide was added at 0°C. After stirring for 20 h at room temperature, the organic solvents were evaporated in vacuo and the residue suspended in hexane. The mixture was filtered and the hexane removed from the solvent in vacuo. Distillation of the remaining oil in vacuo yielded 47.0 g (0.21 mol, 76%) of (2) as a colourless oil, b.p. 92°C (8 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 1.24 (6H, d, $^3J = 6.2$ Hz, $-CH_3$), 3.73 (1H, sept., $^3J = 6.2$ Hz, -CH–), 4.55 (2H, s, $-CH_2-$), 7.11 (1H, m, arom.), 7.29 (1H, m, arom.), 7.50 (2H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) = 22.1 ($-CH_3$), 69.4 (–CH–), 71.7 ($-CH_2-$), 122.5 (arom.), 127.2 (arom.), 128.5 (arom.), 128.9 (arom.), 132.9 (arom.), 138.4 (arom.). *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 230/228 (M^+, 3), 207 (3), 185 (4), 171 (16), 119 (4), 107 (7), 90 (4), 84 (100). *IR:* (liq., CsI-plates) $\tilde{\nu}$ (cm^{-1}) 3066 w, 297 ss, 2930 m, 2871 m, 1569 w, 1466 m, 1441 m, 1379 m, 1335 m, 1128 s, 1086 s, 1027 s. *CHN:* Anal. Found: C, 51.56; H, 5.40. $C_{10}H_{13}BrO$ (229.1) Calc.: C, 52.37; H, 5.67.

4.2. Trimethoxy-[2-(alkoxymethyl)phenyl]silanes

In a 250 ml three-necked flask filled with a dropping funnel, 74.6 mmol of the 2-bromoalkoxymethylbenzene (1 or 2) was dissolved in 50 ml of hexane. The solution was cooled to −20°C and 51.4 ml of n-butyllithium (1.45 M in hexane) was slowly added. The mixture was stirred for an additional 20 h, then warmed to room temperature, transferred to the dropping funnel and added slowly at −20°C to a solution of 13.3 ml (89.5 mmol) of tetramethoxysilane in 50 ml of hexane. The mixture was warmed to room temperature and stirred for 20 h. The solid was filtered off and the hexane evaporated in vacuo. Distillation in vacuo yielded a colourless liquid.

4.2.1. Trimethoxy-[2-(methoxymethyl)phenyl]silane (5)

Yield 6.74 g (27.9 mmol, 37%), b.p. 62°C (0.2 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 3.40 (3H, s, $-CH_3$), 3.59 (9H, s, Si–O–CH_3), 4.56 (2H, s, $-CH_2-$), 7.25 (1H, m, arom.), 7.45 (2H, m, arom.), 7.72 (1H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 50.4 (Si–O–CH_3), 57.9 ($-CH_3$), 74.2 ($-CH_2-$), 126.5 (arom.), 127.6 (arom.), 127.8 (q-arom.), 130.6 (arom.), 136.2 (arom.), 144.8 (q-arom.). *^{29}Si NMR:* δ −53.9 ppm. *MS:* (CI, 70 eV) *m/z* (rel. int. (%)) 211 (48), 195 (19), 181 (20), 119 (9), 91 (18). *CHN:* Anal. Found: C, 54.50; H, 7.78. $C_{11}H_{18}O_4Si$ (242.4) Calc.: C, 54.52; H, 7.49.

4.2.2. Trimethoxy-[2-(isopropyloxymethyl)phenyl]silane (6)

Yield 7.87 g (29.1 mmol, 39%), b.p. 78°C (0.2 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 1.22 (6H, d, $^3J = 6.1$ Hz, $-CH_3$), 3.59 (9H, s, Si–O–CH_3), 3.71 (1H, sept., $^3J = 6.1$ Hz, –CH–), 4.63 (2H, s, $-CH_2-$), 7.26 (1H, m, arom.), 7.43 (1H, m, arom.), 7.54 (1H, m, arom.), 7.69 (1H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 21.9 ($-CH_3$), 50.3 (Si–O–CH_3), 69.5, 71.0, 126.2 (arom.), 127.2 (arom.), 127.6 (q-arom.), 130.6 (arom.), 136.0 (arom.), 145.7 (q-arom.). *^{29}Si NMR:* δ −53.6 ppm. *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 227 (5), 195 (100), 181 (36), 165 (44), 151 (8), 135 (11), 121 (41), 105 (18), 91 (50), 77 (11), 59 (27), 43 (29). *CHN:* Anal. Found: C, 58.76; H, 8.36. $C_{13}H_{22}O_4Si$ (270.4) Calc.: C, 57.75; H, 8.20.

4.3. Phenyl-[2-(alkoxymethyl)phenyl]silanes

In a 250 ml three-necked flask filled with a dropping funnel, 30.0 mmol of the 2-bromoalkoxymethylbenzene

(**1** or **2**) was dissolved in 40 ml of hexane. The mixture was cooled to −20°C then 20.6 ml of n-butyllithium (1.45 M in hexane) was slowly added. After warming to room temperature the mixture was transferred to the dropping funnel and added slowly to a mixture of 3.70 ml (30.0 mmol) of phenylsilane and 50 ml of hexane at −20°C. The mixture was then allowed to warm to room temperature and stirred for an additional 20 h. The solid was filtered off and the solvent evaporated in vacuo. The remaining oil was distilled.

4.3.1. Phenyl-[2-(methoxymethyl)phenyl]silane (7)

Yellow oil, yield 4.31 g (18.9 mmol, 63%), b.p. 93°C (0.2 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 3.30 (3H, s, $-CH_3$), 4.54 (2H, s, $-CH_2-$), 5.00 (3H, s, Si–H), 7.31–7.47 (6H, m, arom.), 7.64–7.68 (3H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 57.5 ($-CH_3$), 75.0 ($-CH_2-$), 127.2 (arom.), 127.6 (arom.), 127.9 (arom., 2C), 129.5 (arom.), 130.0 (arom.), 131.1 (q-arom.), 132.7 (q-arom), 135.5 (arom., 2C), 137.8 (arom.), 144.7 (q-arom.). *^{29}Si NMR:* δ −36.2 ppm (t, $^1J_{SiH}$ = 200 Hz). *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 228 (M^+, 5), 227 (M^+–H, 24), 195 (4), 181 (5), 165 (16), 165 (67), 105 (50), 59 (100). *CHN:* Anal. Found: C, 73.41; H, 7.27. $C_{14}H_{16}OSi$ (228.4) Calc.: C, 73.63; H, 7.06.

4.3.2. Phenyl-[2-(isopropyloxymethyl)phenyl]silane (8)

Colourless oil, yield 3.15 g (7.70 mmol, 41%), b.p. 73°C (0.04 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 1.21 (6H, d, ^3J = 6.1 Hz, $-CH_3$), 3.70 (1H, sept., ^3J = 6.1 Hz, =CH–), 4.61 (2H, s, $-CH_2-$), 5.06 (2H, s, Si–H, $^1J_{SiH}$ = 198 Hz), 7.28–7.33 (1H, m, arom.), 7.39–7.46 (5H, m, arom.), 7.60 (1H, m, arom.), 7.65–7.68 (2H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 21.9 ($-CH_3$), 70.5 ($-CH_2-$), 71.3 (=CH–), 127.0 (arom.), 127.7 (arom.), 127.9 (arom., 2C), 129.5 (arom.), 130.1 (arom.), 130.6 (q-arom.), 132.5 (q-arom.), 135.7 (arom., 2C), 137.5 (arom.), 145.3 (q-arom.). *^{29}Si NMR:* δ −36.8 ppm. *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 256 (M^+, 3), 255 (M^+–H, 15), 229 (7), 213 (35), 195 (50), 179 (33), 169 (46), 135 (100), 105 (34), 43 (39). *CHN:* Anal. Found: C, 70.77; H, 7.98. $C_{16}H_{20}OSi$ (256.4) Calc.: C, 70.54; H, 7.40.

4.4. 2-(Alkoxymethyl)phenylsilanes

In a 250 ml Schlenk flask filled with a dropping funnel, 0.42 g (11.0 mmol) of $LiAlH_4$ was suspended in 50 ml of diethyl ether and a solution of 2.20 g (9.17 mmol) of trimethoxysilane **5** in 10 ml of diethyl ether was added at 0°C. The mixture was stirred for 20 h at room temperature, then the ether evaporated in vacuo and the residue suspended in hexane. The solid suspension was filtered, the solvent removed from the filtrate and the remaining colourless oil distilled in vacuo.

4.4.1. 2-(Methoxymethyl)phenylsilane (9)

Yield 0.60 g (3.99 mmol, 43%), *b.p.* 47°C (2 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 3.41 (3H, s, $-CH_3$), 4.23 (3H, s, SiH, $^1J_{SiH}$ = 197 Hz), 4.56 (2H, s, $-CH_2-$), 7.31 (2H, m, arom.), 7.41 (1H, m, arom.), 7.70 (1H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 57.5 ($-CH_3$), 75.2 ($-CH_2-$), 127.2 (arom., 2C), 130.0 (q-arom.), 129.0 (arom.), 138.0 (arom.), 144.7 (q-arom.). *^{29}Si NMR:* δ −61.8 ppm. *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 152 (M^+, 16), 151 (M^+–H, 100), 135 (5), 121 (70), 105 (65), 95 (6), 91 (61), 77 (15), 65 (15), 59 (56). *CHN:* Anal. Found: C, 64.24; H, 6.26. $C_8H_{12}OSi$ (152.3) Calc.: C, 61.10; H, 7.94.

4.4.2. 2-(Isopropoxymethyl)phenylsilane (10)

Yield 0.80 g (4.40 mmol, 54%), *b.p.* 63°C (4 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 1.25 (6H, d, ^3J = 6.2 Hz, CH_3), 3.75 (1H, d, ^3J = 6.2 Hz, –CH), 4.22 (3H, s, SiH, $^1J_{SiH}$ = 202 Hz), 4.55 (2H, s, $-CH_2-$), 7.26 (2H, m, arom.), 7.37 (1H, t, ^3J = 7.2 Hz, arom.), 7.65 (1H, d, ^3J = 7.2 Hz, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 21.7 ($-CH_3$), 70.6 (–CH), 71.3 ($-CH_2-$), 126.8 (arom.), 127.0 (arom.), 128.1 (q-arom.), 129.7 (arom.), 137.7 (arom.), 145.0 (q-arom.). *^{29}Si NMR:* δ −61.1 ppm. *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 180 (M^+, 21), 179 (M^+–H, 50), 165 (11), 137 (36), 105 (14), 91 (100). *CHN:* Anal. Found: C, 66.60; H, 9.08. $C_{10}H_{16}OSi$ (180.3) Calc.: C, 66.60; H, 8.90.

4.5. Trifluoro-[2-(alkoxymethyl)phenyl]silanes

In a 50 ml Schlenk flask 9.40 mmol of the trimethoxysilane (**5** or **6**) was dissolved in 13 ml of diethyl ether, the solution cooled to −20°C and 1.20 ml (12.2 mmol) of $BF_3{\cdot}Et_2O$ added slowly from a syringe. The reaction mixture was stirred for 20 h. The solvent was evaporated in vacuo and the oily residue distilled to give the silanes as colourless oils.

4.5.1. Trifluoro-[2-(methoxymethyl)phenyl]silane (11)

Yield 1.10 g (5.30 mmol, 56%) of **11**, *b.p.* 42°C (0.3 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 3.66 (3H, s, $-CH_3$), 4.65 (2H, s, $-CH_2-$), 7.19 (1H, d, ^3J = 7.7 Hz, arom.), 7.36 (1H, t, ^3J = 7.6 Hz, arom.), 7.51 (1H, t, ^3J = 7.3 Hz, arom.), 7.93 (1H, d, ^3J = 7.5 Hz, arom.). *^{1}H NMR:* (C_7D_8) δ (ppm) 3.1 (3H, s, $-CH_3$), 3.78 (2H, s, $-CH_2-$), 6.59 (1H, d, arom.), 6.97 (1H, m, arom.), 7.08 (1H, m, arom.), 7.94 (1H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 58.0 ($-CH_3$), 71.8 ($-CH_2-$), 120.4 (q, $^2J_{CF}$ = 21.6 Hz, q-arom., C–Si), 124.0 (arom.), 127.5 (arom.), 132.4 (arom.), 137.5 (arom.), 145.3 (q-arom.). *^{29}Si NMR:* δ −88.0 ppm (q, $^1J_{SiF}$ = 240 Hz). *^{19}F NMR:* δ −140.4 ppm (d, $^1J_{SiF}$ = 240 Hz). *MS:* (Cl, 70 eV) *m/z* (rel. int. (%)) 191 ($M-CH_3$, 4), 179 (3), 105 (2), 91 (2), 63 (8). *CHN:* Anal. Found: C, 46.59; H, 4.46. $C_8H_9F_3OSi$ (206.2) Calc.: C, 46.59; H, 4.40.

4.5.2. *Trifluoro-[2-(isopropyloxymethyl)phenyl]silane (12)*

Yield 1.50 g (6.39 mmol, 68%), *b.p.* 48°C (0.2 mbar). *^{1}H NMR:* ($CDCl_3$) δ (ppm) 1.36 (6H, d, ^3J = 6.8 Hz, $-CH_3$), 4.14 (1H, sept., ^3J = 6.0 Hz, –CH–), 4.65 (2H, s, $-CH_2-$), 7.23 (1H, m, arom.), 7.35 (1H, m, arom.), 7.52 (1H, m, arom.), 7.93 (1H, m, arom.). *^{13}C NMR:* ($CDCl_3$) δ (ppm) 20.6 ($-CH_3$), 66.4, 73.5, 119.7 (q, $^2J_{CF}$ = 21.5 Hz, q-arom., C–Si), 124.9 (arom.), 127.1 (arom.), 132.4 (arom.), 137.3 (arom.), 146.3 (q-arom.). *^{29}Si NMR:* δ −82.2 ppm (q, $^1J_{Si-F}$ = 245 Hz). *^{19}F NMR:* δ −136.5 ppm. *MS:* (CI, 70 eV) *m/z* (rel. int. (%)) 235 ($M+H^+$, 62), 215 (73), 191 (30), 175 (82), 131 (7), 119 (28), 105 (7), 91 (51), 73 (38), 59 (10), 43 (28). *CHN:* Anal. Found: C, 51.14; H, 5.72. $C_{10}H_{13}F_3OSi$ (234.3) Calc.: C, 51.27; H, 5.54.

4.6. *Phenyl-[2-(Methoxymethyl)phenyl]silyl triflate (13)*

In a 100 ml Schlenk flask 0.91 g (3.98 mmol) of silane **7** was dissolved in 20 ml of diethyl ether. The mixture was cooled to −20°C, then 0.72 ml (3.98 mmol) of trimethylsilyl triflate added slowly and the mixture stirred for 48 h at room temperature. The ether was evaporated in vacuo and the remaining oil allowed to crystallize slowly to yield 1.32 g (3.50 mmol, 88%) of **13** as a colourless solid, *m.p.* 81°C. *^{1}H NMR:* (C_6D_6) δ (ppm) 2.30 (3H, s, $-CH_3$), 3.58, 3.62 (2H, AB-system, ^2J = 12.7 Hz, $-CH_2-$), 5.56 (1H, s, Si–H, $^1J_{SiH}$ = 286 Hz), 6.53–6.57 (1H, m, arom.), 7.03–7.12 (5H, m, arom.), 7.43–7.46 (2H, m, arom.). *^{29}Si NMR:* δ −48.7 ppm. *MS:* (EI, 70 eV) *m/z* (rel. int. (%)) 376 (M^+, 4), 375 (M^+–H, 10), 227(M^+–Trifl., 2). *CHN:* Anal. Found: C, 47.51; H, 4.17. $C_{15}H_{15}F_3O_4SSi$ (376.4) Calc.: C, 47.86; H, 4.02.

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