Synthesis and characterization of 2,4,6-tris((dimethylamino)methyl)phenoxysilicon compounds

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Dedicated to Professor O.M. Nefedov on the occasion of his 70th birthday.

Abstract

A series of 2,4,6-tris((dimethylamino)methyl)phenoxysilicon compounds $\Sigma_{4-n}Si(OAr)_n$ (Σ = Cl; $n = 1$ (1), 2 (2); Σ = Me, $n = 1$ (3), 2 (4); Σ = Me$_3$Si, $n = 1$ (5), 2 (6)), PhSiH$_n$(OAr)$_{3-n}$ ($n = 2$ (7), 1 (8)) and H$_n$Si(OAr)$_{4-n}$ ($n = 2$ (9), 1 (10)) has been synthesized by various adapted methods. The compounds were characterized spectroscopically by ^{29}Si-, ^{1}H-, ^{13}C-, ^{15}N-NMR. In solution the extent of Si···N bond formation and coordination in these compounds is determined from the ^{29}Si-NMR (and ^{15}N) chemical shifts and $^1J_{Si-H}$. The silicon center is tetracoordinated in 3–6, pentacoordinated in 1, 2, 7, 8 and hexacoordinated [4 + 2] in 9. The ^{1}H-NMR features are consistent, in all cases, with dynamic coordination mode of the o-NMe$_2$ groups in solution at room temperature. The solid-state structures of the lithium phenolate and of compounds 6 and 9 have been determined by X-ray diffraction. The trimeric structure of ArOLi contains an Li$_3$O$_3$-ring that is almost perfectly planar; the structures of 6 and 9 confirm no N $\rightarrow$ Si contact in 6 and a bicapped tetrahedral silicon in 9. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Hypercoordination; NMR; Crystal structure

1. Introduction

During the past 15 years there has been an explosive growth of research interest into chemistry of intramolecularly coordinated organosilicon compounds; these compounds have a varied chemistry that is significantly different from that of their tetravalent counterparts. Numerous structural types in which Y → Si intramolecular coordination due to a C,Y-chelating ligand (Y = heteroatom-containing substituent) have been developed, particularly ortho-silylated benzyldiorganoamines [1,2], but less attention has been paid to compounds containing O,Y-chelating ligands. The only previously reported such structures, bearing the O–C(R)=N–NMe$_2$ ligand [3], are hexacoordinate bischelates with near-octahedral geometries. We have already demonstrated the interesting potential of a

phenoxy ligand with two ortho-chelating tertiary amine substituents that can, through intramolecular dynamic coordination, stabilize divalent species (ArO)$_2$M and their complexes (ArO)$_2$MM′L$_n$ (ArO = 2,4,6-[(CH$_3$)$_2$NCH$_2$]$_3$C$_6$H$_2$O; M = Ge, Sn, Pb; M′ = Fe, Cr, W) [4]. In the present study we have focused on new silicon compounds with as supporting ligand this phenoxy ligand bearing in 2,4,6 positions (dimethylamino)methyl groups suitable for intramolecular coordination, $\Sigma_{4-n}Si(OAr)_n$ and RSiH$_n$(OAr)$_{3-n}$ (Σ = Cl, Me, Me$_3$Si; R = Ph, ArO; $n = 1$, 2).

2. Results and discussion

2.1. Synthesis

2.1.1. Chlorosilanes Cl$_3$SiOAr (1) and Cl$_2$Si(OAr)$_2$ (2)

We first considered obtaining the trichloro[2,4,6-((dimethylamino)methyl)phenoxy]silane Cl$_3$SiOAr (1) and the dichlorobis[2,4,6-((dimethylaminomethyl)-

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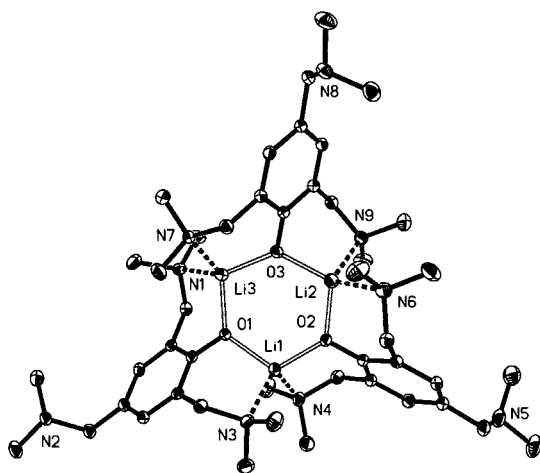*E-mail address:* barrau@chimie.ups-tlse.fr (J. Barrau).

Fig. 1. Solid-state structure of (ArOLi)$_3$.

phenoxy]silane $Cl_2Si(OAr)_2$ (**2**) by the classic method of synthesis of ethers by alcoxylation by achieving the direct action of the 2,4,6-tris((dimethylamino)methyl)-phenolate of lithium on the tetrachlorosilane.

The 2,4,6-tris((dimethylamino)methyl)phenolate of lithium [ArOLi] was obtained by the action of one equivalent of ^{n}BuLi on the corresponding alcohol in ether; ArOLi is soluble in ether and was conveniently purified by crystallization at $-20\,°C$ from ether/pentane solution (50/50). Molecular weight determination (cryoscopy in benzene) showed ArOLi to be trimeric in solution. Its mass spectrum also displays the same cluster structure $(ArO)_3Li_3$ in the gas phase. The electron-impact mass spectrum shows six fragment ions corresponding to $[(ArO)_2Li_3]^+$, $[(ArO)Li_2]^+$, Li^+, $[(ArO)_3Li_3 - NMe_2]^+$, $[(ArO)_2Li_2 - NMe_2]^+$, and $[ArOLi - NMe_2]^+$; the most abundant species is $[(ArO)Li_2]^{+\cdot}$. Thus the fragmentation leads to the related species $Li_x(ArO)_x$, which lose an NMe_2 group.

The solid-state structure of (ArOLi)$_3$ determined by single crystal diffraction is shown in Fig. 1; the interatomic distances and the characteristic angles are reported in Table 1. This study reveals that this compound is also trimeric in the solid state; (ArOLi)$_3$ crystallized in the monoclinic system, space group $P2_1/c$, with parameters: $a = 20.836(4)$, $b = 27.613(8)$, $c = 8.798(2)$ Å; $\alpha = 90°$; $\beta = 97.26(2)°$; $\gamma = 90°$ and $\rho_{calc} = 1.077$ g cm^{-3} for $Z = 4$. The polydendate aryloxy ligand confers to this compound a six-membered practically planar cyclic $(LiO)_3$ structure; every atom of lithium is connected to two aryloxy groups by two oxygen atoms and two nitrogen atoms and presents a tetrahedral environment. The Li–O bond lengths (average value: 1.87 Å; the smallest being Li(2)–O(2) = 1.854(4) Å) are among the shortest known [5,6], whereas the Li–N bond lengths (average value: 2.24 Å; the longest being Li(2)–N(6) = 2.410 Å) are relatively longer than that observed in typical tetracoordinated lithium compounds. The C_{ipso}–O are relatively short (average value: 1.32 Å); the short distances Li–O and C_{ipso}–O should be connected to a quasi-aromaticity of the cycle Li_3O_3 [6,7]. This structure is comparable to that reported for 4-Me-2,6-(Me$_2$N–CH$_2$)$_2$–C$_6$H$_2$OLi [6,8]. To our knowledge, (ArOLi)$_3$ is the second example of a trinuclear structure for a phenolate of lithium described to date in the literature; its specific originality is to be associated with the presence of a third potentially coordinating CH_2NMe_2 group in para position on every aryloxy group. In the solid state, the CH_2N hydrogen atoms, as well as the NMe_2 methyl groups of each of the six equivalent CH_2NMe_2 groups participating in the coordinations with the three atoms of lithium, are diastereotopic; however, in solution, they appear in the ^{1}H-NMR spectrum as singlets [$\delta(CH_2N) = 3.33$ ppm (12H); $\delta(CH_3) = 1.92$ ppm (36H)]. This equivalence could be due to the phe-

Table 1
Selected bond distances (Å) and angles (°) for (ArOLi)$_3$

Bond distances

Li(1)–O(2)	1.864(4)	Li(2)–O(2)	1.854(4)	Li(3)–O(1)	1.859(4)
Li(1)–O(1)	1.885(4)	Li(2)–O(3)	1.902(4)	Li(3)–O(3)	1.869(4)
Li(1)–N(3)	2.190(4)	Li(2)–N(9)	2.173(4)	Li(3)–N(7)	2.201(4)
Li(1)–N(4)	2.254(4)	Li(2)–N(6)	2.410(4)	Li(3)–N(1)	2.234(4)

Bond angles

O(2)–Li(1)–O(1)	113.0(2)	O(2)–Li(2)–O(3)	111.99(18)
O(2)–Li(1)–N(3)	124.35(19)	O(2)–Li(2)–N(9)	127.3(2)
O(1)–Li(1)–N(3)	95.32(16)	O(3)–Li(2)–N(9)	94.20(18)
O(2)–Li(1)–N(4)	93.96(16)	O(2)–Li(2)–N(6)	90.50(17)
O(1)–Li(1)–N(4)	124.11(18)	O(3)–Li(2)–N(6)	129.7(2)
N(3)–Li(1)–N(4)	108.74(17)	N(9)–Li(2)–N(6)	107.08(15)
O(1)–Li(3)–O(3)	109.27(19)	O(1)–Li(3)–N(1)	95.26(16)
O(1)–Li(3)–N(7)	123.59(19)	O(3)–Li(3)–N(1)	130.94(19)
O(3)–Li(3)–N(7)	94.83(16)	N(7)–Li(3)–N(1)	106.14(17)
Li(3)–O(1)–N(7)	129.26(16)	Li(2)–O(2)–Li(1)	126.50(18)
Li(3)–O(3)–Li(2)	129.75(17)		

$$SiCl_4 + n/3\ (ArOLi)_3 \xrightarrow[\text{Ether}]{25\,^\circ C} Cl_{4-n}Si(OAr)_n + (ArO)_2Li_{2+m}Cl_m$$

n = 1 ; 2   m = 1, 2, 3

Ether, 0 °C

ArOH + BuLi

Scheme 1.

$$(ArOLi)_3 + Me_3SiCl \xrightarrow[\text{Ether}]{25\,^\circ C} Me_3SiOAr + (ArO)_2Li_3Cl$$

1/n SiCl$_4$, 80 °C, - Me$_3$SiCl

1/n Cl$_{4-n}$Si(OAr)$_n$

n = 1 ; 2

Scheme 2.

nomenon of Li–N dissociation–association, with rapid rotation around the C_{ipso}–O bond.

One or two equivalents of $(ArOLi)_3$ were added, at ambient temperature, to a diethyl ether solution of tetrachlorosilane. The yields in chlorosilanes $Cl_{(4-n)}Si(OAr)_n$ of these reactions are limited ($< 40\%$); in fact, these reactions, along with chlorosilanes $Cl_{(4-n)}Si(OAr)_n$, afford a solid phase that mass spectrometric analysis showed to be a mixture of $Cl_{(4-n)}Si(OAr)_n$ and of the cluster $(ArO)_2Li_3Cl$. The cluster $(ArO)_2Li_3Cl$ was identified by comparison with an authentic sample obtained by mixing lithium phenolate and lithium chloride in diethyl ether (Scheme 1).

The low yields in $Cl_{(4-n)}Si(OAr)_n$ of the previous syntheses and the difficulties arising from the formation of by-products, which cannot be isolated, prompted us to explore alternate methods of preparing the di- and tri-chlorated derivatives. (i) With numerous exchange reactions between compounds with Si–Cl and Si–O bonds having been reported, we investigated the redistribution reactions between the silicon tetrachloride and the [2,4,6-tris((dimethylamino)methyl)phenoxy]trimethylsilane Me_3SiOAr to obtain the $Cl_{4-n}Si(OAr)_n$ structures. Me_3SiOAr, obtained by treatment of one equivalent of phenolate of lithium by one equivalent of methyltrichlorosilane in ether at ambient temperature, was submitted to the action of $SiCl_4$ in a sealed tube, in the absence of solvent, at 80 °C for 12 h (Scheme 2). By this method the expected derivatives $Cl_{4-n}Si(OAr)_n$ ($n = 1, 2$) can be obtained with good yields ($\sim 80\%$). (ii) The known extreme sensitivity of the silicon–nitrogen bond to reagents with some acidic character prompted us to carry out the reaction of the aminosilane $Cl_2Si(NEt_2)_2$ with the alcohol ArOH. The reaction is effected in refluxing toluene, the diethylamine by-product being eliminated by distillation. This reaction produces a few traces of $(ArO)_2Si(Cl)NEt_2$ and $(ArO)_3SiNEt_2$ in addition to the normal alcoholysis product $(ArO)_2SiCl_2$ [Eq. (1)].

$$(Et_2N)_2SiCl_2 + ArOH \xrightarrow{- (Et_2NH \cdot HCl)} (ArO)_2SiCl_2$$
$$+ (ArO)_2Si(Cl)NEt_2 + (ArO)_3SiNEt_2 + Et_2NH \quad (1)$$

The di- and tri-chlorosilanes, isolated as white solids (by precipitation in hexane), were fully characterized by the usual spectroscopic methods (^{1}H-, ^{13}C-, ^{29}Si-NMR) and mass spectrometry. It is noteworthy that $(ArO)_2SiCl_2$ suffers decomposition in a few hours, even in an inert atmosphere, to give a green–black unidentified solid that is insoluble in all solvents. All attempts at crystallization have failed.

2.1.2. Silanes R_3SiOAr (**3**, **5**) and $R_2Si(OAr)_2$ (**4**, **6**)

Following the same synthetic method, silanes Me_3SiOAr (**3**), $Me_2Si(OAr)_2$ (**4**), $(Me_3Si)_3SiOAr$ (**5**) and $(Me_3Si)_2Si(OAr)_2$ (**6**) were prepared by alcoholysis by the phenol of the corresponding aminosilanes [Eq. (2)].

These reactions gave high yields; the expected compounds **3** and **4** were isolated in the pasty form, and the derivatives **5** and **6** were obtained pure by crystallization (in pentane, at − 20 °C) as white solids. All these derivatives are soluble in common organic solvents and were characterized by multinuclear NMR analysis, mass spectrometry and elementary analysis.

$$R_{4-n}Si(NMe_2)_n + ArOH \xrightarrow{-nMe_2NH} R_{4-n}Si(OAr)_n \quad (2)$$
$$R = Me\ (n = 1,\ \mathbf{3};\ 2,\ \mathbf{4});\ Me_3Si\ (n = 1,\ \mathbf{5};\ 2,\ \mathbf{6}).$$

2.1.3. Phenylhydrosilanes of $Ph(ArO)SiH_2$ (**7**) and $Ph(ArO)_2SiH$ (**8**)

The usual method of alcoxy- and aryloxy-silanes synthesis by dehydrocondensation reactions between silicon hydrides and alcohols did not allow isolation of the hydrosilanes $Ph(ArO)SiH_2$ and $PhSiH(OAr)_2$ in a selective way. The reactions in various solvents of $PhSiH_3$ with ArOH in variable stoichiometric quantities resulted practically always in a mixture of di- and tri-aryloxysilanes; no traces of monoaryloxysilane were detected in these reactions. Their quantitative results are summarized in Table 2.

With access to dihydrosilane $Ph(ArO)SiH_2$ being impossible by this method, we considered its synthesis by means of the silyltriflate $Ph(TfO)SiH_2$, obtained by the protodearylation reaction of Ph_2SiH_2 by the trifluoromethanesulfonic acid (TfOH, triflic acid). One equivalent of ArOH reacts with $Ph(TfO)SiH_2$, in the presence of triethylamine in toluene at − 30 °C, to produce mainly the dihydrosilane **7**, as well as the hydrosilane **8** (relative percent estimated by ^{1}H-NMR analysis: **7**/**8** = 60/40) (Scheme 3). The two hydrosilanes could be isolated in pure form by distillation of **7** under vacuum. They are thermally stable.

2.1.4. Hydrosilanes $(ArO)_2SiH_2$ (**9**) and $(ArO)_3SiH$ (**10**)

It was also necessary to investigate different methods of synthesis to obtain $(ArO)_2SiH_2$ and $(ArO)_3SiH$ in

Table 2
Dehydrocondensation reactions between $PhSiH_3$ and ArOH

$PhSiH_3$ (g [mmol])	ArOH (g [mmol])	Conditions			Products (%)			
		Solvent	T (°C)	Time	$Ph(ArO)_2SiH$	$PhSi(OAr)_3$	$PhSiH_3$	ArOH
0.4 [3.77]	1 [3.77]	Ether	25	4 h	41	–	15	44
				48 h	62	–	23	15
0.4 [3.77]	1 [3.77]	Pentane	25	5 h	15	–	22	63
				24 h	18	–	27	55
			35	2.5 h	25	–	16	59
0.4 [3.77]	1 [3.77]	–	25	15 days	63	–	12	25
0.2 [1.88]	1 [3.77]	–	25	15 days	66	5	–	29
0.13 [1.25]	1 [3.77]	–	25	15 days	21	16	–	63

pure form. The reactions carried out are summarized in Scheme 4 and Table 3. Among the different methods used, the alcoholysis reactions of the silylamines $H_2Si(NR_2)_2$ by ArOH (R = Et, Me) worked clearly and rapidly, giving good yields in $(ArO)_2SiH_2$. In all the other reactions the yields were modest, and considerable quantities of by-products were always formed (formation of clusters in the reaction of the phenoxylithium with H_2SiI_2; formation of the ionic compound $[(ArO)_2SiH]^+I^-$ [9] in the direct treatment of H_2SiI_2 by ArOH; formation of $(ArO)_3SiH$ in several of the reactions). The hydrotriaryloxysilane $(ArO)_3SiH$ was easily made by reacting ArOH with $(ArO)_2SiH_2$ in CH_2Cl_2 at ambient temperature.

2.2. NMR, mass, UV–vis spectroscopies and structural characterization

All the silanes **1**–**6** are very sensitive to atmospheric oxygen and moisture; they are stable under a nitrogen atmosphere and were fully characterized by ^1H-, ^{13}C-, ^{29}Si-NMR, IR, UV–vis and mass spectrometry.

2.2.1. Silanes R_3SiOAr (3, 5) and $R_2Si(OAr)_2$ (4, 6)

The characteristic spectroscopy data of compounds **3**–**6** are reported in Table 4, together with the ^{29}Si-NMR chemical shifts of their respective phenoxylated analogs.

The ^1H-NMR spectra at 25 °C of silanes **3**–**6** reveal that the four o-NMe_2 groups are magnetically equivalent (broad singlet) [$\delta = 2.16$ ppm (**3**); $\delta = 2.16$ ppm (**4**); $\delta = 2.19$ ppm (**5**); $\delta = 2.16$ ppm (**6**)]; a singlet is also observed as signal for the protons of the corresponding CH_2N groups. Their ^{29}Si-NMR spectra all display a singlet, which is in the same range as those observed for the tetracoordinated corresponding phenoxylated analogs Me_3SiOPh, $Me_2Si(OPh)_2$, $(Me_3Si)_3SiOPh$ and $(Me_3Si)_2Si(OPh)_2$. Compounds **3**–**6** should, therefore, not present Si···N interaction in solution. ^{15}N-NMR also supports that the N_{ortho} nitrogen atoms of the ArO

ligands are not coordinated to the silicon, since the chemical shifts of the N_{ortho} nitrogen atoms of the aryloxy groups are quite comparable to those of N_{ortho} nitrogen atoms of the ArOH alcohol [**3**: ($\delta = -350.1$ ppm), ArOH: $\delta = -351.1$ ppm)]. Single crystals of **6** suitable for X-ray structure analysis were obtained from pentane. Fig. 2 shows the solid-state structure of **6**, together with the numbering scheme. Relevant bonds distances and angles are given in Table 5. This structure is comparable to those of trisilanes previously reported [10], the silicon being at the center of a tetrahedron. All the Si–Si, Si–O and Si–C distances correspond to the classic σ-bonds around a silicon atom. The Si–Si–Si angle (111.26°) is slightly smaller than those observed in various other trisilanes [11], whereas the Si–O–C angles (129.22 and 125.99°) are slightly more important than those observed in various silyl ethers; these results could be explained by steric hindrance of the ArO group.
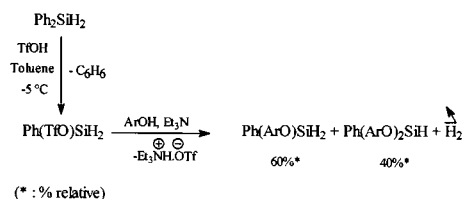
Scheme 3.
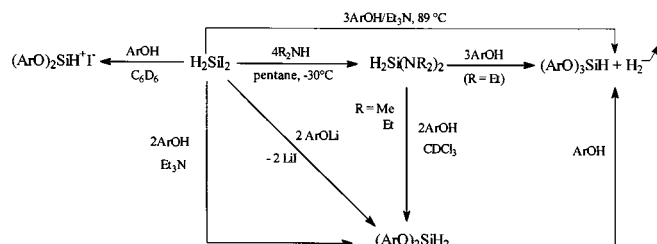
Scheme 4.

Table 3
Reactions carried out for synthesis of the hydrosilanes **9** and **10**

Reagents	Conditions			Products (%)
$H_2SiI_2 + 2ArOLi$	Ether	25 °C	12 h	Traces $(ArO)_2SiH_2$
	THF	65 °C	2 h	$(ArO)_2SiH_2$ (17%) + $(ArO)_2Li_3I$ + traces $[(ArO)_2SiI]^+$ (MS)
$H_2SiI_2 + 2ArOH$	C_6D_6	25 °C	5 min	$[(ArO)_2SiH]^+$ I^- (15%)
$H_2SiI_2 + 2ArOH/Et_3N$	Et_3N	25 °C	12 h	$(ArO)_2SiH_2$ (20%) + $(ArO)_3SiH$ (31.5%)
	Et_3N	89 °C	1 h	$(ArO)_3SiH$ (51%)
$H_2Si(NMe_2)_2 + 2ArOH$	Pentane	25 °C	45 min	$(ArO)_2SiH_2$ traces
	Pentane	reflux	2 h	$(ArO)_2SiH_2$ (42%) + $(ArO)_3SiH$ (18%) + ArOH (21%)
	Pentane	35 °C	3 h	$(ArO)_3SiH$ (40%)
$H_2Si(NEt_2)_2 + 2ArOH$	$CDCl_3$	25 °C	5 min	$(ArO)_2SiH_2$ (95%)
$H_2Si(NMe_2)_2 + 2ArOH$	$CDCl_3$	25 °C	10 min	$(ArO)_2SiH_2$ (78%)
$H_2Si(NEt_2)_2 + 3ArOH$	$CDCl_3$	25 °C	24 h	$(ArO)_3SiH$ (81%)

Table 4
Selected ^{29}Si- and ^1H-NMR data for silanes $R_2Si(OAr)_2$ and R_3SiOAr **3–6**

Compounds		δ ^{29}Si [CDCl$_3$] (ppm)	$\Delta\delta$ (ppm)	^1H-NMR (δ, ppm)			
				o-NMe$_2$	p-NMe$_2$	p-CH$_2$N	o-CH$_2$N
(**3**)	Me_3SiOAr	18.19	0.61	2.16	2.13	3.34	3.44
	Me_3SiOPh	18.8					
(**5**)	$(Me_3Si)_3SiOAr$	−15.9, −2.8	1.3	2.19	2.08	3.35	3.36
	$(Me_3Si)_3SiOPh$	[−15.7, −1.5]					
(**4**)	$Me_2Si(OAr)_2$	−3.02	1.4	2.16	2.15	3.32	3.50
	$Me_2Si(OPh)_2$	−1.62					
(**6**)	$(Me_3Si)_2\underline{Si}(OAr)_2$	−20.5, <u>8.0</u>	1.71	2.18	2.20	3.37	3.56
	$(Me_3Si)_2\underline{Si}(OPh)_2$	[−20.4, <u>9.71</u>]					

The analysis of mass spectroscopy of $(Me_3Si)_2$-$Si(OAr)_2$ obtained under 70 eV electronic impact reveals the peaks corresponding to the molecular ion $M^{+\bullet}$ (17%) and to the fragmentations $[M - Me_3Si]^+$, $[M - Me_3Si - 3Me]^+$, $[M - 2Me_3Si]^+$, $[M - OAr]^+$ and $[M - Me_3SiOAr]^+$ (relative intensities 42%, 31%, 2%, 100% and 6% respectively). The most intense peak corresponds to $[M - OAr]$, which suggests the formation of the silicon cation $[(Me_3Si)_2Si(OAr)]^+$, and which could be greatly stabilized by intramolecular coordination.

The UV spectrum of $(Me_3Si)_2Si(OAr)_2$, in cyclohexane, presents a strong absorption at $\lambda_{max} = 284$ nm ($\varepsilon = 31.623 \times 10^4$) (the characteristic absorption due to the trisilane fragment is hidden by this strong band).

2.2.2. Chlorosilanes 1 and 2

In these two cases the ^1H- and ^{29}Si-NMR studies allowed us to discuss the coordination around the central atom; the spectroscopic values are reported in Table 6.

At ambient temperature, the ^{29}Si-NMR spectra of compounds **1** and **2** exhibit resonances at -30.8 ppm and -42.4 ppm respectively (unfortunately the ^{29}Si chemical shifts of the corresponding trichlorophenoxy- and dichlorophenoxy-silanes are unknown). The ^1H-NMR spectra of **1** and **2** both reveal the equivalence of the o-NMe$_2$ groups [(**1**) $\delta = 2.16$ ppm and (**2**) $\delta = 2.13$ ppm]; a singlet is also observed for the protons of the corresponding CH$_2$N groups [(**1**) $\delta = 3.57$ ppm and
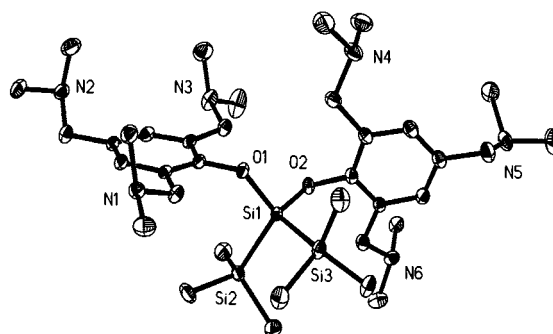
Fig. 2. Solid-state structure of $(Me_3Si)_2Si(OAr)_2$ (**6**).

Table 5
Selected bond lengths (Å) and angles (°) for **6**

Bond distances

Si(1)–O(1)	1.666(19)
Si(1)–O(2)	1.666(19)
Si(1)–Si(2)	2.363(10)
Si(1)–Si(2)	2.366(10)

Bond angles

O(2)–Si(1)–O(1)	106.94(9)
O(2)–Si(1)–Si(2)	108.84(8)
O(1)–Si(1)–Si(2)	110.61(7)
O(2)–Si(1)–Si(3)	111.08(7)
O(1)–Si(1)–Si(3)	108.03(7)
Si(2)–Si(1)–Si(3)	111.26(3)
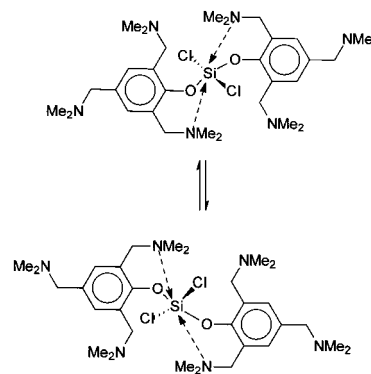
Scheme 5.

(**2**) $\delta = 3.54$ ppm]. These analytical data are consistent with either (i) a structure in which there is no intramolecular coordination of the o-NMe$_2$ units to silicon, thus allowing inversion of the nitrogen atom, or (ii) a dynamic N⋯M⋯N coordination–decoordination process involving the four o-NMe$_2$ groups. Such 'flip-flop' intramolecular coordination modes have already been reported for tetravalent tin and silicon derivatives [12–14]. In order to attempt to specify the nature and strength of possible coordination of nitrogen atoms to the silicon atom, a variable-temperature ^{29}Si- and ^{1}H-NMR study of compound **2** was carried out in CD$_2$Cl$_2$. At -60 °C the ^{29}Si signal drops to -52 ppm, suggesting more hypercoordination as expected. More information is given by the ^{1}H-NMR spectrum at -60 °C, which exhibits two large singlets of equal intensity for the o-N methyl protons ($\delta = 2.11$ and 2.12 ppm). Even though the magnetic non-equivalence of the two types of o-NMe$_2$ group observed at -60 °C could be attributed to the hindrance to O–Si–O rotation, these observations seem, rather, (i) to suggest that at this temperature the hypercoordination may be important and (ii) to confirm the hypothesis of the dynamic N⋯Si⋯N coordination. The non-equivalence of the protons of the o-NMe$_2$ groups might indicate that, at this low temperature, the flip-flop coordination process is slow enough that we can observe in ^{1}H-NMR, along with the p-dimethylamino group, two types of o-dimethylamino group. One type probably might correspond to two o-dimethylamino groups in dynamic

coordination and the other to two free o-dimethylamino groups far from the silicon atom; this is consistent with the two limiting forms represented in Scheme 5. It was impossible on lowering the temperature further (-75 °C) to observe rigid coordination of NMe$_2$ units to silicon, which should have implied diastereotopic methyl groups at nitrogen and an AB system for the corresponding benzylic phenyl CH$_2$N protons. We did mean to elucidate physically the degree of coordination of the NMe$_2$ groups to the silicon atom, but our repeated efforts to study these compounds in the solid state by X-ray crystallography have been unsuccessful.

2.2.3. Hydrosilanes Ph(ArO)SiH$_2$ (**7**), Ph(ArO)$_2$SiH (**8**) and (ArO)$_2$SiH$_2$ (**9**)

The silanes **7**–**9** have been characterized by ^{1}H-, ^{13}C-, ^{15}N-, ^{29}Si-NMR, IR and mass spectrometry; the main spectroscopic characteristics are reported in Table 7.

2.2.3.1. Phenylhydrosilanes **7** and **8**. ^{1}H-NMR spectra in CDCl$_3$, at room temperature, display in both cases a singlet [$\delta = 1.95$ ppm (**8**), $\delta = 2.08$ ppm (**7**)] for the protons of the two (**7**) or four (**8**) o-NMe$_2$ groups; a single broad signal is also observed for the protons of the corresponding CH$_2$N groups. These ^{1}H-NMR observations can be rationalized by a non-coordination or a rapid coordination–decoordination process N⋯Si⋯N of the o-N atoms to the silicon atom. With an increase in the number of coordination at silicon generally in-

Table 6
Selected ^{29}Si- and ^{1}H-NMR data [a] for chlorosilanes Cl$_3$Si(OAr) and Cl$_2$Si(OAr)$_2$

Compounds	δ ^{29}Si (CD$_2$Cl$_2$, ppm)	^{1}H-NMR (CD$_2$Cl$_2$, ppm)			
		o-NMe$_2$	p-NMe$_2$	p-CH$_2$N	o-CH$_2$N
Cl$_3$Si(OAr), 25 °C	-30.80	2.16 (s*)	2.18 (s*)	3.35 (s*)	3.57 (s*)
Cl$_2$Si(OAr)$_2$, 25 °C	-42.40	2.13 (s*)	2.16 (s*)	3.32 (s*)	3.54 (s*)
Cl$_2$Si(OAr)$_2$, -60 °C	-51.42	2.11 (s*), 2.12 (s*)	2.21 (s*)	3.30 (s*)	3.53 (s*), 3.48 (s*)

[a] s*: broad singlet.

ducing a displacement at upfield of the ^{29}Si-NMR chemical shifts [15,16], we compared the ^{29}Si-NMR chemical shifts of silanes **7** and **8** with those of their corresponding tetracoordinated silicon phenoxylate analogs PhSiH(OPh)$_2$ and PhSiH$_2$(OPh). The ^{29}Si-NMR chemical shifts of silanes **7** and **8** are upfield ($\Delta\delta \approx 10$ ppm) compared with those of their respective analogs Ph(PhO)$_2$SiH and Ph(PhO)SiH$_2$. The ^{29}Si–H coupling constants are increased compared with those observed for the corresponding species with non-functionalized ligands [$\Delta J = 14$ Hz for (**7**) and $\Delta J = 30$ Hz for the silane (**8**)]. These data are consistent with a hypercoordination of the silicon atom [15,17–22], presumably five or [4 + 1], in the silanes **7** and **8**. The equivalence of the *o*-dimethylamino groups in ^{1}H-NMR is, therefore, characteristic of an N···Si···N 'flip-flop' dynamic coordination process. Furthermore, it is worth noting that a weak downfield shift for the ^{15}N-NMR resonance of the *o*-NMe$_2$ groups of **7** and **8** is observed compared with that observed for ArOH ($\delta = -348.5$ (**7**); $\delta = -350.0$ (**8**); $\delta = -351.5$ ppm (ArOH)). The peculiar chemical reactivity of these compounds, and notably their strong hydride and reducing character, confirms the existence of this intramolecular coordination [23–28]. The dihydrosilane Ph(ArO)SiH$_2$, for example, reacted particularly rapidly with alcohols and acids to yield the corresponding silicon alkoxides (or aryloxides) and esters; it was also a powerful reducing agent for aldehyde and ketones [29].

2.2.3.2. Dihydrosilane 9.

In this case also, ^{29}Si-NMR, which allows the direct observation of the effect of the electronic environment of the silicon nucleus, is the most useful spectroscopic tool for study of coordination of the silicon atom. The ^{29}Si-NMR spectrum of the dihydrosilane **9** exhibits a triplet ($\delta = -69.87$ ppm) at higher field than that of its tetracoordinated analogs (PhO)$_2$SiH$_2$ ($\delta = -30.47$ ppm); furthermore, the $^1J_{\text{Si–H}}$ coupling constant ($^1J_{\text{Si–H}} = 302$ Hz) is significantly increased compared with that observed for (PhO)$_2$SiH$_2$ ($^1J_{\text{Si–H}} = 238$ Hz). The important displacement of the ^{29}Si chemical shift at higher field for **9**, compared with its respective tetracoordinated compound ($\Delta\delta = 39.4$ ppm), express a larger electronic density around silicon in **9** than in (PhO)$_2$SiH$_2$, and, therefore, is presumably characteristic of a formal hexacoordination of the silicon atom. In ^{1}H-NMR the equivalence of the four *o*-NMe$_2$ groups at room temperature, as well as the corresponding *N*-methylene protons, should result from a dynamic coordination–decoordination process, the *o*-NMe$_2$ groups displacing each other rapidly on the ^{1}H-NMR time scale. Furthermore, comparison of the ^{29}Si–^{1}H coupling constant of **9** with that of the analogous tetracoordinate compound (PhO)$_2$SiH$_2$ reveals a $\Delta^1J_{\text{Si–H}} = 64$ Hz characteristic of a bicapped tetrahedral complex. Effectively, it has been shown previously that increasing the coordination number of silicon with rehybridization at silicon is associated with a decrease of the coupling constant; in contrast, an increase of the coordination not associated with rehybridization in bicapped tetrahedral complexes resulted in an increase in the coupling constant ($^1J_{\text{Si–H}}$ is dependent on the s-character of the Si–H bond) [3a,15,30]. Additional evidence for the hypercoordination [4 + 2] at silicon in **9** was obtained from the ^{15}N-NMR spectrum: the ^{15}N-NMR chemical shift for the N$_{ortho}$ nitrogen atoms of the aryloxy group ($\delta = -348.4$ ppm) is downfield of the corresponding signal for the ArOH alcohol ($\delta = -351.5$ ppm). The idea of the 'flip-flop' coordination in solution (two *o*-NMe$_2$ groups displacing two others rapidly on the ^{1}H-NMR time scale) via a hexacoordinate intermediate is lent support by the

Table 7
Selected (^{29}Si-, ^{1}H- and ^{15}N-) NMR data for hydrosilanes **7–10**

| Compounds		δ ^{29}Si (CDCl$_3$, ppm)	$\Delta\delta$ (ppm)	^{1}H-NMR (CDCl$_3$) (δ, ppm)				^{15}N-NMR (CDCl$_3$) (δ, ppm)	
				o-NMe$_2$	*p*-NMe$_2$	*p*-CH$_2$N	*o*-CH$_2$N	*o*-NMe$_2$	*p*-NMe$_2$
ArOH				2.16	2.12	3.25	3.48	−351.5	−347.0
(**8**)	PhSiH(OAr)$_2$	−46.71, $^1J_{\text{SiH}} = 288$ Hz	10.65	1.95	2.20	3.30	3.38	−350.2	−347.7
	PhSiH(OPh)$_2$	−36.46, $^1J_{\text{SiH}} = 258$ Hz							
(**7**)	PhSiH$_2$(OAr)	−29.69, $^1J_{\text{SiH}} = 236$ Hz	9.21	2.08	2.19	3.32	3.37	−348.5	−347.53
	PhSiH$_2$(OPh)	−20.48, $^1J_{\text{SiH}} = 222$ Hz							
(**9**)	(ArO)$_2$SiH$_2$	−69.87, $^1J_{\text{SiH}} = 302$ Hz	39.4	2.17	2.10	3.31	3.48	−348.4	−347.4
	(PhO)$_2$SiH$_2$	−30.47, $^1J_{\text{SiH}} = 238$ Hz							
	(2,6-R$_2$C$_6$H$_3$-O)$_2$SiH$_2$	−37.3 (R = ^{i}Pr); −37.0 (R = ^{t}Bu)							
(**10**)	(ArO)$_3$SiH	−102.04, $^1J_{\text{SiH}} = 358$ Hz	30.58	2.15	2.02	3.26	3.28		
	(PhO)$_3$SiH	−71.46, $^1J_{\text{SiH}} = 321$ Hz							
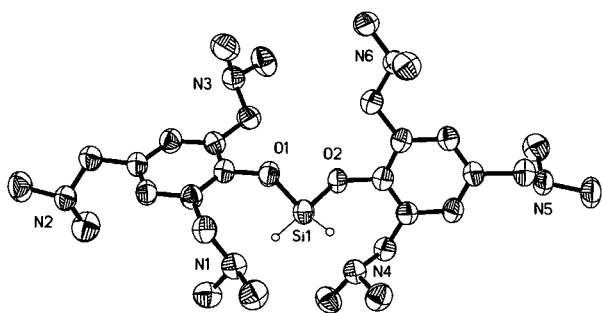
Fig. 3. Solid-state structure of (ArO)$_2$SiH$_2$ (**9**).

Table 8
Selected bond lengths (Å) and angles (°) for **9**

Bond distances	
Si(1)–H(1)	1.569
Si(1)–H(2)	1.560
Si(1)–O(1)	1.668(3)
Si(1)–O(2)	1.654(3)
Si(1)–N(1)	2.986
Si(1)–N(4)	2.630
Bond angles	
H(1)–Si(1)–H(2)	126.7
O(2)–Si(1)–O(1)	101.21(17)
O(1)–Si(1)–H(1)	105.5
O(2)–Si(1)–H(2)	108.2
O(1)–Si(1)–H(2)	126.7
O(2)–Si(1)–H(2)	108.4

single crystal X-ray diffraction study performed on **9**. Translucent crystals were grown from a pentane solution cooled at −20 °C. Fig. 3 shows the solid-state structure of **9**; the relevant bond lengths and angles are given in Table 8. The solid-state structure reveals a hexacoordinate silicon center in an approximately C_2 symmetrical molecule. The dimethylamino groups directed towards the silicon center are located trans to the oxygen centers forming N···Si···O angles of 81.79 and 75.34°. The Si···N distances of 2.98 and 2.68 Å are significantly shorter than the sum of the van der Waals radii (3.5 Å) [31] and thus are in the range of Si···N distances of hexacoordinate silicon compounds [15,30]. Actually, the geometry around the silicon atom, with angles of 126.7° (H$_1$–Si–H$_2$), 105.5° (O$_1$–Si–H$_1$), 126.7° (O$_1$–Si–H$_2$) and 101.21° (O$_2$–Si–O$_1$), is best described as that of a distorted tetrahedron than that of an octahedron. Two faces of the tetrahedron are 'capped' by two ortho dimethylamino groups; both coordinating nitrogen atoms belong to different ligands and are in a cis configuration. It is worth underlining the fact that only three hexacoordinate bis(N–Si) chelates with two Si–O bonds have previously been described; they have a near-octahedral arrangement around silicon, with relatively short Si···N distances (ca. 2 Å) [3].

The chemistry of these 2,4,6-tris((dimethylamino)-methyl)phenoxysilicon compounds has been explored.

The hydrosilanes behave as good reduction agents and are also potential precursors of silyliums, silanethiones and transition-metal-silylene complexes; trisilane could be a source of silylene. The peculiar chemical properties of the dihydrosilanes Ph(ArO)SiH$_2$ and (ArO)$_2$SiH$_2$ and of the silane (Me$_3$Si)$_2$Si(OAr)$_2$ will be reported in future publications.

3. Experimental section

3.1. General procedures

Cl$_2$Si(NEt$_2$)$_2$ [32] and H$_2$Si(NEt$_2$)$_2$ [33] were prepared as described in the appropriate references; (Me$_3$Si)$_3$-SiNR$_2$ and (Me$_3$Si)$_2$Si(NR$_2$)$_2$ [34] were obtained by reactions of the corresponding halosilanes (Me$_3$Si)$_2$-SiCl$_2$ and (Me$_3$Si)$_3$SiCl [35] with the lithium derivatives of the amines R$_2$NH.

All the compounds described are sensitive to oxygen and moisture. All manipulations were performed under an inert atmosphere of nitrogen or argon using standard Schlenk and high-vacuum-line techniques. Dry, oxygen-free solvents were employed throughout. All solvents were distilled from sodium benzophenone before use. ^{1}H-NMR spectra were recorded on a Bruker AC 80 spectrometer operating at 80 MHz (chemical shifts are reported in parts per million relative to internal Me$_4$Si as reference) and ^{13}C spectra on an AC 200 spectrometer; the multiplicity of the ^{13}C-NMR signals was determined by the APT technique. ^{1}H-decoupled ^{29}Si-NMR spectra were recorded on a Bruker ARX 400 (chemical shifts are reported in parts per million relative to external Me$_4$Si as reference). [15]N spectra were recorded on a Bruker ARX 400 spectrometer (chemical shifts are reported in parts per million relative to external nitromethane as reference). [7]Li spectra were recorded on a Bruker AC 200 spectrometer (chemical shifts are reported in parts per million relative to external LiCl/D$_2$O as reference). Mass spectra under electron impact (EI) or chemical ionization (CH$_4$) conditions at 70 and 30 eV were obtained on Hewlett-Packard 5989 and Nermag R10-10H spectrometers. IR and UV spectra were recorded on Perkin–Elmer 1600 FT-IR and Lambda-17 spectrophotometers. Melting points were taken uncorrected on a Leitz Biomed hot-plate microscope apparatus. Elemental analyses (C, H, N) were performed at the microanalysis Laboratory of the Ecole Nationale Superieure de Chimie de Toulouse.

3.2. [2,4,6-Tris((dimethylamino)methyl)phenoxy]lithium trimer (ArOLi)$_3$

[n]BuLi (0.04 mmol, 25 ml of a solution in hexane) was added to [2,4,6-tris((dimethylamino)methyl)phenol (10.6 g, 0.04 mmol) in dry diethyl ether (100 ml). The

solution was cooled to 0 °C for 30 min. The mixture was stirred for a further 2 h at room temperature and the solvent was removed in vacuo. The residue was extracted with a 1/1 ether/pentane solution (80 ml); after cooling to −20 °C for 12 h, (ArOLi)$_3$ was filtered off as white crystals and dried in vacuo (9.8 g, 90%). (ArOLi)$_3$: m.p. 168–170 °C. ^{7}Li-NMR (C$_6$D$_6$): 0.78. ^{1}H-NMR (C$_6$D$_6$): 1.92 (s, 36H), 2.23 (s, 18H), 3.33 (s, 12H), 3.42 (s, 6H), 7.14 (s, 6H). ^{13}C-NMR (C$_6$D$_6$): 45.38, 45.92, 63.90, 65.03, 121.38, 126.42, 131.53, 167.12. MS: $m/z = 813$ [M]$^{+\bullet}$. Anal. Calc. for C$_{45}$H$_{78}$Li$_3$N$_9$O$_3$: C, 66.42; H, 9.59; N, 15.49. Found: C, 66.22; H, 9.54; N, 15.44%.

3.3. Trichloro[2,4,6-((dimethylamino)methyl)phenoxy]-silane Cl$_3$SiOAr (1)

(1) A solution of [2,4,6-tris((dimethylamino)methyl)-phenoxy]lithium (1.12 g, 4.13 mmol) in 20 ml of ether was added dropwise to a stirred solution (cooled at 0 °C) of tetrachlorosilane (0.7 g, 4.13 mmol) in 50 ml of ether. The mixture was stirred at room temperature for 2 days. Filtration, followed by drying in vacuo, afforded crude **1** (0.6 g, 25%). **1**: m.p. 180–182 °C. ^{29}Si-NMR (CD$_2$Cl$_2$): −30.80. ^{1}H-NMR (CD$_2$Cl$_2$): 2.16 (s, 6H), 2.18 (s, 12H), 3.35 (s, 2H), 3.57 (s, 4H), 7.22 (s, 2H). ^{13}C-NMR (CD$_2$Cl$_2$): 43.10, 45.83, 58.32, 61.76, 119.91, 123.80, 126.96, 152.33. MS: $m/z = 398$ [M − H]$^+$. Anal. Calc. for C$_{15}$H$_{26}$Cl$_3$N$_3$OSi: C, 45.20; H, 6.52; N, 10.53. Found: C, 45.38; H, 6.34; N, 10.42%.

(2) A mixture of Me$_3$SiOAr (0.5 g, 1.48 mmol) and tetrachlorosilane (0.25 g, 1.48 mmol) was heated at 80 °C, in a sealed tube, overnight. Addition of 20 ml of pentane, filtration and drying in vacuo gave **1** as a white solid (0.48 g, 82%).

3.4. Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]-dichlorosilane Cl$_2$Si(OAr)$_2$ (2)

(1) A solution of [2,4,6-tris((dimethylamino)methyl)-phenoxy]lithium (1.52 g, 5.68 mmol) in 30 ml of ether was added dropwise to a stirred solution at 0 °C of tetrachlorosilane (0.47 g, 2.8 mmol) in 25 ml of ether. The mixture was stirred at room temperature for 2 days. After elimination of LiCl and (ArO)$_2$Li$_3$Cl by filtration, the filtrate was concentrated in vacuo to give crude **2** as a white solid (0.4 g, 23%). **2**: m.p. 150–190 °C (dec.). ^{29}Si-NMR (CD$_2$Cl$_2$): −42.40; at −60 °C (CD$_2$Cl$_2$): −51.42. ^{1}H-NMR at 25 °C (CD$_2$Cl$_2$): 2.13 (broad singlet (s*), 12H), 2.16 (s*, 24H), 3.32 (s*, 4H), 3.54 (s*, 8H), 7.69 (s, 4H); at −60 °C (CD$_2$Cl$_2$): 2.11 (s*, 12H), 2.12 (s*, 12 H), 2.21 (s*, 12H), 3.30 (s*, 4H), 3.48 (s*, 4H), 3.53 (s*, 4H), 7.71 (s, 4H). ^{13}C-NMR (CD$_2$Cl$_2$): 43.70, 44.08, 58.81, 62.05, 120.09, 124.86, 132.96, 158.18. MS: $m/z = 590$ [M − HCl]$^+$. Anal. Calc.

for C$_{30}$H$_{52}$Cl$_2$N$_6$O$_2$Si: C, 57.44; H, 8.29; N, 13.39. Found: C, 57.58; H, 7.97; N, 13.27%.

(2) A mixture of tetrachlorosilane (0.2 g, 1.2 mmol) and [2,4,6-tris((dimethylamino)methylphenoxy]tri-methylsilane (0.81 g, 2.4 mmol) was heated, at 80 °C, in a sealed tube overnight. The wet solid obtained was washed with pentane (20 ml) and dried in vacuo to give **2** (0.6 g, 80%).

A solution of 2,4,6-tris((dimethylamino)methyl)-phenol (2.84 g, 10.7 mmol) in 100 ml of dry toluene was slowly added to a solution of bis(diethylamino)-dichlorosilane [32] (1.3 g, 5.37 mmol) in 50 ml of dry toluene heated at 110 °C. Slow distillation (6 h) of the solvent and of the diethylamine formed led to a white solid, which was washed with 30 ml of dry pentane and dried in vacuo to afford crude **2** (1.07 g, 23%). The analysis by mass spectroscopy (EI, 70 eV) showed trace amounts of two other species, $m/z = 663$ [(ArO)$_2$Si-(Cl)NEt$_2$]$^{+\bullet}$ and $m/z = 892$ [(ArO)$_3$SiNEt$_2$]$^{+\bullet}$, besides **2**.

3.5. [2,4,6-Tris((dimethylamino)methyl)phenoxy]-trimethylsilane Me$_3$SiOAr (3)

(1) To a solution of chlorotrimethylsilane (0.77 g, 7.08 mmol) in 15 ml of ether was slowly added a solution of [2,4,6-tris((dimethylamino)methyl)phenoxy]-lithium (1.92 g, 7.08 mmol) in 25 ml of ether. The reaction mixture was stirred at room temperature for 2 days. Filtration of LiCl and (ArO)$_2$Li$_3$Cl, followed by concentration under vacuum, afforded **3** (0.71 g, 30%). **3**: b.p. 113–114 °C/6 × 10^{-2} mmHg. ^{29}Si-NMR (CDCl$_3$): 18.19. ^{15}N-NMR (CDCl$_3$): −347.5, −350.1. ^{1}H-NMR (C$_6$D$_6$): 0.24 (s, 9H), 2.11 (s, 12H), 2.13 (s, 6H), 3.30 (s, 2H), 3.38 (s, 4H), 7.4 (s, 2H). ^{13}C-NMR (C$_6$D$_6$): 1.08, 45.37, 45.63, 59.61, 64.26, 129.78, 130.69, 132.45, 152.18. MS: $m/z = 337$ [M]$^{+\bullet}$. Anal. Calc. for C$_{18}$H$_{35}$N$_3$OSi: C, 64.09; H, 10.38; N, 12.46. Found: C, 64.41; H, 10.42; N, 12.65%.

(2) A solution of 2,4,6-tris((dimethylamino)methyl)-phenol (2.5 g, 9.43 mmol) in 30 ml of pentane was slowly added to a stirred solution of (dimethylamino)-trimethylsilane (1.1 g, 9.43 mmol) in 20 ml of pentane. Concentration and distillation gave **3** (3 g, 94%).

3.6. Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]-dimethylsilane Me$_2$Si(OAr)$_2$ (4)

(1) To a suspension of [2,4,6-tris((dimethylamino)-methyl)phenoxy]lithium (2.12 g, 7.82 mmol) in 25 ml of ether was slowly added a solution of dichloro-dimethylsilane (0.5 g, 3.91 mmol) in 15 ml of ether. The reaction mixture was stirred at room temperature for 2 days. Filtration, concentration and distillation in vacuo yielded **4** (0.64 g, 28%). **4**: b.p. 180–182 °C/ 0.1 mmHg. ^{29}Si-NMR (CDCl$_3$): −3.02. ^{1}H-NMR

(CDCl$_3$): 0.19 (s, 6H), 2.15 (s, 12H), 2.16 (s, 24 H), 3.32 (s, 4H), 3.50 (s, 8H), 7.02 (s, 4H). ^{13}C-NMR (CDCl$_3$): 14.16, 45.40, 45.64, 59.05, 63.98, 129.43, 130.50, 131.86, 151.35. MS: $m/z = 586$ [M]$^{+\bullet}$. Anal. Calc. for C$_{32}$H$_{58}$N$_6$O$_2$Si: C, 65.55; H, 9.89; N, 14.32. Found: C, 65.83; H, 10.29; N, 14.11%.

(2) A solution of 2,4,6-tris((dimethylamino)-methyl)phenol (2 g, 7.54 mmol) in 30 ml of pentane was added dropwise to a solution of bis(diethyl-lamino)dimethylsilane (0.55 g, 3.77 mmol) in 30 ml of pentane. The reaction mixture was stirred and heated to reflux for 2 hours. After returning to room temperature, the solution was concentrated in vacuo and the residue was distilled in vacuo to give **4** (2 g, 91%).

3.7. [2,4,6-Tris((dimethylamino)methyl)phenoxy]-tris(trimethylsilyl)silane (Me$_3$Si)$_3$SiOAr (**5**)

(1) To a solution of tris(trimethylsilyl)chlorosilane [36] (0.48 g, 1.69 mmol) in 15 ml of ether was added a suspension of [2,4,6-tris((dimethylamino)methyl)phe-noxy]lithium (0.46 g, 1.69 mmol) in 20 ml of ether. The mixture was stirred at room temperature for 2 days. Filtration and concentration in vacuo afforded pure **5** (0.2 g, 23%). **5**: ^{29}Si-NMR (CDCl$_3$): -15.9, -2.8. ^{1}H-NMR (CDCl$_3$): 0.23 (s, 27H), 2.08 (s, 6H), 2.19 (s, 12H), 3.35 (s, 2H), 3.36 (s, 4H), 7.12 (s, 2H). ^{13}C-NMR (CDCl$_3$): -0.25, 45.01, 45.42, 58.1, 63.70, 128.82, 129.58, 129.89, 152.22. MS: $m/z = 511$ [M]$^{+\bullet}$; 438 [M $-$ Me$_3$Si]$^+$. Anal. Calc. for C$_{24}$H$_{53}$N$_3$OSi$_4$: C, 56.38; H, 10.36; N, 8.21. Found: C, 56.04; H, 10.52; N, 8.46%.

(2) To a solution of (dimethylamino)tris(trimethyl-silyl)silane (1.0 g, 3.77 mmol) in 15 ml of pentane was slowly added a solution of 2,4,6-tris((dimethylamino)-methyl)phenol (1.09 g, 3.77 mmol) in 15 ml of pentane. The reaction mixture was refluxed for 2 h. After return-ing to room temperature, the volatiles were removed in vacuo to give **5** (1.6 g, 83%).

3.8. Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]-bis(trimethylsilyl)silane (ArO)$_2$Si(SiMe$_3$)$_2$ (**6**)

To a stirred solution of bis(dimethylamino)bis-(trimethylsilyl)silane (1.3 g, 4.96 mmol) in 20 ml of tolu-ene was slowly added a solution of 2,4,6-tris((dimethyl-lamino)methyl)phenol (2.63 g, 9.93 mmol) in 30 ml of toluene. The reaction mixture was refluxed for 2 h. The volatiles were removed in vacuo. Addition of 30 ml of pentane and crystallization at -20 °C gave **6** (3.3 g, 95%) as white crystals. **6**: m.p. 70–72 °C. ^{29}Si-NMR (CDCl$_3$): -20.5, 8.00. ^{1}H-NMR (CDCl$_3$): -0.01 (s, 18H), 2.18 (s, 12H), 2.20 (s, 24H), 3.37 (s, 4H), 3.56 (s, 8H), 7.22 (s, 4H). ^{13}C-NMR (CDCl$_3$): -0.27, 45.20, 45.55, 58.44, 63.92, 128.94, 129.61, 129.66, 152.32. MS: $m/z = 702$ [M]$^{+\bullet}$. Anal. Calc. for C$_{36}$H$_{70}$N$_6$O$_2$Si$_3$: C,

61.53; H, 9.96; N, 11.95. Found: C, 61.75; H, 10.04; N, 11.81%.

3.9. [2,4,6-Tris((dimethylamino)methyl)phenoxy]phenyl- and bis[2,4,6-tris((dimethylamino)methyl)phenoxy]-phenyl-silane Ph(ArO)SiH$_2$ (**7**) and Ph(ArO)$_2$SiH (**8**)

To a solution of trifluoromethanesulfonate of phenyl-silane [35] (8 g, 31.25 mmol) in 80 ml of toluene at -30 °C was added dropwise a mixture of 2,4,6-tris-((dimethylamino)methyl)phenol (8.28 g, 31.25 mmol) and triethylamine (3.15 g, 31.25 mmol). The reaction mixture was stirred at room temperature for 3 h. After decanting and elimination by siphoning of the Et$_3$N·TfOH formed, the residual solution was concen-trated and distilled under vacuum to give **7** (6.9 g, 60%) and **8** (3.96 g). **7**: b.p. 108–110 °C/5 × 10^{-2} mmHg. ^{29}Si-NMR (CDCl$_3$): -29.69 (t, $^1J_{Si-H} = 236$ Hz). ^{15}N-NMR (CDCl$_3$): -347.53, -348.5. ^{1}H-NMR (CDCl$_3$): 2.08 (s, 6H), 2.19 (s, 12H), 3.32 (s, 2H), 3.37 (s, 4H), 5.12 (s, 2H), 7.05 (s, 2H), 7.10–7.40 (m, 5H). ^{13}C-NMR (C$_6$D$_6$): 45.38, 59.85, 64.25, 122.06, 129.39, 130.54, 132.65, 132.99, 134.42, 137.15, 151.82. IR (CDCl$_3$, KBr, cm^{-1}): $\nu_{Si-H} = 2157$. MS: $m/z = 370$ [M $-$ 1]$^+$. **8**: b.p. 180–182 °C/5 × 10^{-2} mmHg. ^{29}Si-NMR (CDCl$_3$): -46.71 (d, $^1J_{Si-H} = 288$ Hz). ^{15}N-NMR (CDCl$_3$): -347.7, -350.2. ^{1}H-NMR (CDCl$_3$): 1.95 (s, 12H), 2.2 (s, 24H), 3.3 (s, 4H), 3.38 (s, 8H), 5.25 (s, 1H), 7.05 (s, 4H), 7.1–7.4 (m, 5H). ^{13}C-NMR (CDCl$_3$): 45, 45.31, 59.21, 63.88, 127.38, 127.57, 128.54, 130.04, 131.2, 132.16, 136.6, 151.42. IR (CDCl$_3$, KBr, cm^{-1}): $\nu_{Si-H} = 2205$. MS: $m/z = 634$ [M]$^{+\bullet}$.

3.10. Bis[2,4,6-tris((dimethylamino)methyl)phenoxy]-dihydrosilane (ArO)$_2$SiH$_2$ (**9**)

A solution of 2,4,6-tris((dimethylamino)methyl)-phenol (6.12 g, 23.1 mmol) in 20 ml of chloroform was slowly added to a stirred solution of bis(diethyl-lamino)dihydrosilane in 10 ml of chloroform. The reac-tion mixture was stirred at room temperature for 15 min. The volatiles were removed under reduced pres-sure. Crystallization from pentane (30 ml) at -20 °C afforded **9** (6.2 g, 96%) as white crystals. **9**: ^{29}Si-NMR (CDCl$_3$): -69.87 (t, $^1J_{Si-H} = 302$ Hz). ^{1}H-NMR (CDCl$_3$): 2.10 (s, 12H), 2.17 (s, 24H), 3.31 (s, 4H), 3.48 (s, 8H), 4.36 (s, 2H), 7 (s, 4H). ^{15}N-NMR (CDCl$_3$): -348.4, -347.4. ^{13}C-NMR (CDCl$_3$): 45.26, 45.43, 59.16, 60.02, 127.73, 129.95, 130.61, 152.49. IR (CDCl$_3$, KBr, cm^{-1}): $\nu_{Si-H} = 2195$. MS: $m/z = 557$ [M $-$ 1]$^+$.

3.11. Tris[2,4,6-tris((dimethylamino)methyl)phenoxy]-hydrosilane (ArO)$_3$SiH (**10**)

A mixture of tris(dimethylamino)hydrosilane (1.7 g, 6.94 mmol) and 2,4,6-tris((dimethylamino)methyl)-

phenol (5.52 g, 20.83 mmol) was heated in a sealed tube at 110 °C for 2 days in the presence of ammonium sulfate (catalytic amount). The crude reaction product was washed with 20 ml of pentane. Filtration and concentration in vacuo gave **10** (5.24 g, 92%). **10**: ^{29}Si-NMR (CDCl$_3$): −102.04 (d, $^1J_{Si-H}$ = 358 Hz). ^{1}H-NMR (CDCl$_3$): 2.02 (s, 18H), 2.15 (s, 36H), 3.26 (s, 6H), 3.28 (s, 12H), 5.11 (s, 1H), 7.03 (s, 6H). ^{13}C-NMR (CDCl$_3$): 45.32, 45.50, 58.10, 59.02, 128.21, 130.35, 132.70, 151.29. IR (CDCl$_3$, KBr, cm^{-1}): ν_{Si-H} = 2243. MS: m/z = 821 [M]$^{+\bullet}$.

3.12. X-ray crystallographic studies of compounds 3, 6 and 9

Crystal data for all structures are presented in Table 9. Data were collected at low temperatures on a Stoe-IPDS diffractometer with Mo−K$_\alpha$ (λ = 0.71 073 Å). The structures were solved by direct methods by means of SHELXS-97 [37] and refined with all data on F^2 by means of SHELXL-97 [38]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. The disorder of a dimethylamino group in **6** was refined on two positions with the help of 50 ADP and distance restraints.

Table 9
Summary of crystal data and structure refinement for (ArOLi)$_3$, (Me$_3$Si)$_2$(OAr)$_2$ (**6**) and (ArO)$_2$SiH$_2$ (**9**)

	(ArOLi)$_3$	6	9
Formula	C$_{45}$H$_{78}$Li$_3$N$_9$O$_3$	(C$_{18}$H$_{35}$N$_3$OSi)$_{1.5}$	C$_{30}$H$_{54}$N$_6$O$_2$Si
M_T	813.98	351.63	558.88
T (K)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	Ia	$P\bar{1}$
a (Å)	20.836(4)	19.087(2)	9.426(2)
b (Å)	20.613	11.465(2)	11.740(3)
c (Å)	8.798(2)	19.734(2)	16.245(3)
α (°)	90	90	70.54(2)
β (°)	97.26(2)	94.930(10)	76.66(2)
γ (°)	90	90	84.83(3)
V (Å^3)	5021(2)	4302.5(10)	1649.1(16)
Z	4	8	2
ρ_{calcd} (Mg m^{-3})	1.077	1.086	1.126
Crystal size (mm^3)	0.6 × 0.5 × 0.1	0.6 × 0.5 × 0.1	0.6 × 0.4 × 0.1
μ (mm^{-1})	0.067	0.146	0.106
R ($I > 2\sigma(I)$)	0.397	0.0364	0.0606
wR_2 [a] (all data)	0.0784	0.0961	0.1521

[a] $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)^2 / \Sigma\, w(F_o^2)^2]^{1/2}$.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center, CCDC 158701–158703. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambrige CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[9] [(ArO)$_2$SiH]$^+$I$^-$ was identified by comparison of the spectral data with those of an authentic sample. Improved detailed procedures for its synthesis will be reported in a publication currently in preparation. M.p. 204–205 °C (dec.). ^{29}Si-NMR (CDCl$_3$): -106.28 (d, $^1J_{SiH} = 347$ Hz). ^{15}N-NMR (CDCl$_3$): -335.1, -343.9, -350. ^{1}H-NMR (CDCl$_3$): 2.12 (s, 12H), 2.39 (s, 12H), 2.67 (s, 6H), 2.86 (s, 6H), 3.37 (s, 4H), 3.68 (s, 4H), $\delta_A = 4.19$ (2H) and $\delta_B = 4.48$ (2H) $^2J_{AB} = 13.2$ Hz, 7.31 (s, 4H). ^{13}C-NMR (CDCl$_3$): 43.93, 44.73, 45.37, 59.22, 59.84, 62.29, 120.02, 127.99, 130.86, 149.99. IR (KBr, CDCl$_3$, cm^{-1}): $\nu_{Si-H} = 2212$. MS: FAB (MNBA) > 0, $m/z = 557$ [(ArO)$_2$SiH]$^+$, FAB < 0, $m/z = 127$ [I]$^-$.

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