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Some aspects of chemistry of the N→Si chelated aryloxydihydrosilanes $R(ArO)SiH_2(R{=}Ph, ArO)$ and of the 2,2-diaryloxytrisilane $(Me_3Si)_2Si(OAr)_2\{ArO{=}2,4,6\text{-}[(CH_3)_2NCH_2]_3C_6H_2O\}$

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Abstract

Reactions of the pentacoordinate aryloxydihydrosilane $Ph(ArO)SiH_2$ (**1**) with hydroxyl groups, carbonyl derivatives and PCl_5 resulted in formation of new alcoxylated, phenoxylated and halogenated hydrosilanes $Ph(ArO)(H)X$ (X = Cl, OR, OAr, OC(O)R) respectively. Treatment of the hexacoordinated (**4+2**) diaryloxydihydrosilane $(ArO)_2SiH_2$ (**2**) with *N*-chloro- or *N*-bromosuccinimide, trimethylsilyltriflate or iodine yielded the novel stable silicenium ion $[(ArO)_2(H)Si]^+X^-$. Reactions of **2** with sulfur S_8 and the transition metal complex $Fe(CO)_5$ have resulted in the isolation of the new complexes $(ArO)_2Si{=}E$ [E = S, $Fe(CO)_4$]. Decomposition modes of the tetracoordinate 2,2-diaryloxytrisilane $(Me_3Si)_2Si(OAr)_2$ (**3**) on thermolysis and photolysis have also been studied; two pathways involving formation of the two silylenes $(ArO)(Me_3Si)$: and $(ArO)_2Si$: have been identified by trapping experiments. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; Hypercoordination; Silicenium; Silanethione; Silanediyl–transition metal complexes; Silylene

1. Introduction

Current interest in the chemistry of hypercoordinated silicon compounds lies in use of their extreme reactivity. Various publications report that pentacoordinated hydrosilanes present a particularly reactive hydrogen function and behave as better hydride donors and reducting agents than simple silicon hydrides; particular catalytic properties were also highlighted for such derivatives [1,2]. Moreover various studies showed that trisilanes could be convenient sources of silylenes [R_2Si:] the fugacity and the great reactivity of which were also underlined [3–13].

We have recently reported a series of new silicon compounds with as supporting ligand a phenoxy group bearing in 2,4,6 positions (dimethylamino)methyl groups suitable for intramolecular coordination $\Sigma_{4-n}Si(OAr)_n$ and $RSiH_n(OAr)_{3-n}$ (ArO = 2,4,6-$[(CH_3)_2NCH_2]_3C_6H_2O$; Σ = Cl, Me, Me_3Si; R = Ph, ArO; n = 1, 2); some of these compounds present an hypervalent silicon center [14]. Herein we report on peculiar chemical properties of the aryloxydihydrosilanes $Ph(ArO)SiH_2$ (**1**) and $(ArO)_2SiH_2$ (**2**) in which the silicon center is penta- and hexacoordinated (bicapped tetrahedral) respectively [14]. In search for N→Si intramolecularly stabilized silylenes we also report on the thermolysis and photolysis of the tetracoordinate 2,2-diaryloxytrisilane $(Me_3Si)_2Si(OAr)_2$ (**3**).

2. Results and discussion

2.1. Hydrolysis of 1–3

The aryloxysilanes **1**, **2** are extremely sensitive to hydrolysis. A nucleophilic assistance due to an intramolecular Si···N coordination explains the important activation of the Si–O bonds of these hypercoordinate

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silicon complexes. The silane **3** is also particularly sensitive to hydrolysis; since this compound adopts a silicon tetracoordinated structure, an activation of the Si–O bonds by a chelate system can not be invoked in this case. However, such a 'nucleophile assisted' hydrolysis involving a pentacoordinated intermediate may be effective after the first hydrolysis of one Si–O bond, and thus explain the very fast formation of the siloxane $[(Me_3Si)_2SiO]_3$. This trisiloxane, already described [15], was crystallized in chloroform at 20 °C. The structure was determined by X-ray diffraction studies. Fig. 1 shows the molecular structure and Table 1 summarizes selected bond lengths and bond angles. This structure is comparable to those of trisiloxanes previously reported [16]. The molecule has D_3 symmetry. The heterocycle Si_3O_3 is perfectly plan (the sum of angles of cycle Si_3O_3 is of 719.9°). The Si–O bond length (1.63 Å) is in good agreement with literature values, and the average values of the O–Si–O and Si–O–Si angles are 133.7 and 106.28° respectively, (near by ~1° close to those observed in $(t\text{-}Bu_2SiO)_3$ [16a]). All three Si–Si–Si angles are different (109.82, 110.47, 111.78°) and slightly smaller than those observed in various other trisiloxanes [17].

2.2. The dihydrosilane $Ph(ArO)SiH_2$ (1) as reducing agent

The dihydrosilane **1**, which presents (according to its physicochemical characteristics) a pentacoordinated silicon (dynamic coordination) [14], possess a much more reactive hydrogen function than the simple organosilicon hydride $Ph(PhO)SiH_2$; it reacts very quickly with hydroxyl groups allowing the syntheses in near quantitative yields of many compounds, e.g. the alcoxyl and aryloxyl derivatives **4** and **5** or the silyl ester **6** (Scheme 1).

Table 1
Selected bond lengths (Å) and angles (°) for $[(Me_3Si)_2SiO]_3$

Bond lengths	
Si(1)–Si(2)	2.361(2)
Si(2)–Si(3)	2.361(2)
Si(2)–O(1)	1.650(2)
Si(2)–O(3)	1.659(2)
Si(4)–Si(5)	2.353(2)
Si(5)–Si(6)	2.365(2)
Si(5)–O(1)	1.654(2)
Si(5)–O(2)	1.657(2)
Si(7)–Si(8)	2.366(2)
Si(8)–Si(9)	2.361(2)
Si(8)–O(2)	1.649(2)
Si(8)–O(3)	1.648(3)
Bond angles	
O(1)–Si(2)–O(3)	106.45(12)
O(3)–Si(8)–O(2)	106.19(11)
O(1)–Si(5)–O(2)	106.20(12)
Si(2)–O(1)–Si(5)	133.49(13)
Si(8)–O(2)–Si(5)	133.93(17)
Si(1)–Si(2)–Si(3)	110.47(6)
Si(4)–Si(5)–Si(6)	109.82(5)
Si(7)–Si(8)–Si(9)	111.78(5)
Si(8)–O(3)–Si(2)	133.68(15)

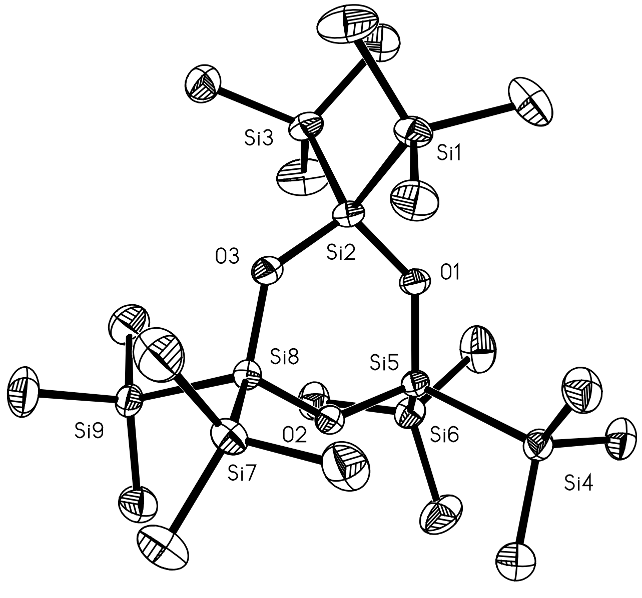


Fig. 1. Solid-state structure and atom numbering scheme of $[(Me_3Si)_2SiO]_3$.

Partial chlorination of **1** can be easily carried out in homogeneous phase by PCl_5 in $CHCl_3$; the aryloxyhalogenohydride **7** is thus obtained in good yield (Scheme 1).

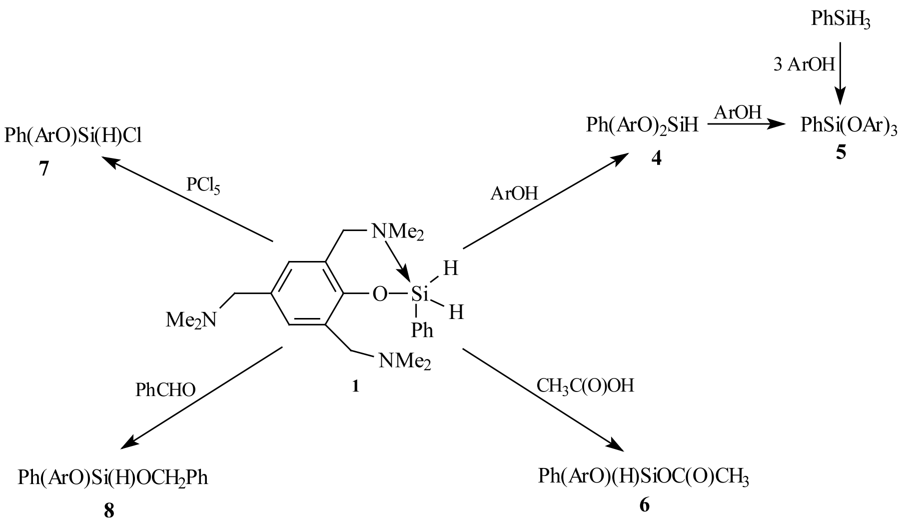
Compound **1** can also give reactions with carbonyl derivatives; in absence of any catalyst, $Ph(ArO)SiH_2$ condenses easily on benzaldehyde to give the alcoxyaryloxyhydride **8** (Scheme 1).

All these reactions are characteristic of silicon hydrides with a pentacoordinated silicon.

The new silanes **4**–**8**, with multiple functions, are relatively thermically stable and were fully physicochemically characterized. Note, as already observed for silicon esters with pentacoordinated silicon [18], that ester **6** decomposes thermically at relatively low temperatures (150 °C) leading to the trisiloxane **9** probably via the intermediate silanone $[Ph(ArO)Si{=}O]$ (**9′**) (Scheme 2).

2.3. Some aspects of the reactivity of the dihydrosilane $(ArO)_2SiH_2$ (2)

The various reactions which were studied are summarized by Scheme 3. They point out that the chemical properties of the hexacoordinated (4+2) silicon dihydride $(ArO)_2SiH_2$ **(2)** [14] differ greatly from those observed for various tetracoordinated and pentacoordinated silicon dihydrides.

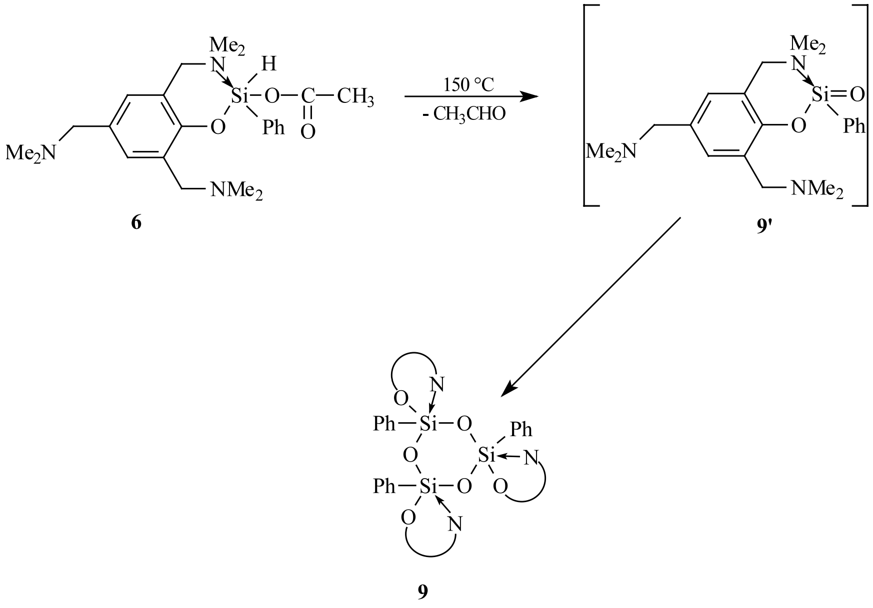


Scheme 1.

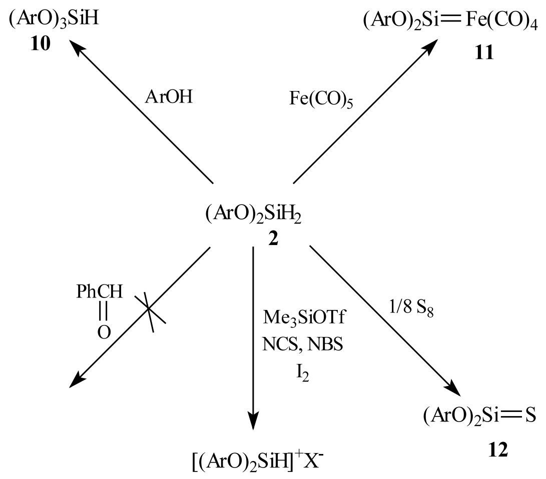
Though the reactivity of the dihydrosilane (ArO)$_2$SiH$_2$ towards compounds with an hydroxyl function is completely comparable with that of Ph(ArO)SiH$_2$, allowing thus easy passage from (ArO)$_2$SiH$_2$ to (ArO)$_3$SiH (**10**) in near quantitave yield, its reactivity towards carbonyl derivatives is on the contrary practically nil and reflects a quasi-inertia of **10** towards nucleophiles (Scheme 3).

(ArO)$_2$SiH$_2$ is very reactive towards various electrophiles such as *N*-chloro- or *N*-bromosuccinimide, trimethylsilyl trifluoromethanesulfonate and iodine (Scheme 3). In all the cases the reaction seems to proceed by extrusion of an hydride ion to induce the formation of a silyl cation. All these reactions lead to white powders, insoluble in hexane, benzene and diethylether, soluble in dichloromethane and chloroform. These properties evoke ionic structure of the type [(ArO)$_2$SiH]$^+$X$^-$] for the compounds **2a**–**d**, comparable with those already observed for hydrosilyl cations [RR′Si(H)]$^+$X$^-$ [19–23]. Confirmation of the ionic nature of derivatives **2a**–**d** was obtained by ^{1}H-, ^{29}Si-, ^{15}N-, ^{13}C-NMR spectroscopies, FAB mass spectrometry (positive and negative modes), IR and conductivity measurements. The observed data are almost identical for all derivatives **2a**–**d**, being hence characteristic of the same species.

The ^{29}Si-NMR (proton coupled) spectra of all these derivatives display a doublet $\delta = -106.3$ upfield compared with the characteristic signal of the SiH$_2$ group of the starting dihydrosilane. The ^{29}Si–H coupling constant ($^1J_{\text{Si–H}} = 345$ Hz) is definitely increased compared with that of the parent silane reflecting thus a strong s



Scheme 2.



[X = OTf (**2a**), Cl (**2b**), Br (**2c**), I (**2d**)]

Scheme 3.

character of the Si–H bond as expected for a sp^2-hybridized silicon atom. An intramolecular N···Si coordination, allows stabilization of this sp^2-hybridized silicon, and may also explain the upfield chemical shift (compared with the parent dihydrosilane) observed in the ^{29}Si-NMR spectrum. The same type of evolution was observed by Corriu and Belzner for $[L_2SiH]^+$ systems with silicon stabilized by L ligands of the type 8-(dimethylamino)naphthalene [21c] and 2-[(dimethylamino)methyl]phenyl [20] respectively, but the opposite shift was noted with the 2,6-bis[(dimethylamino)methyl]phenyl ligand [21a].

^{1}H-NMR spectra of **2a**–**d** at 20 °C all indicate coordination of two *o*-NMe_2 groups on the silicon atom since in all cases the ^{1}H-NMR spectra display four singlets for the 36 protons of the six NMe_2 groups [for example for $[(ArO)_2SiH]^+$ TfO^- $\delta = 2.15$ (12H), 2.35 (12H), 2.62 (6H), 2.85 (6H)] and two singlets [$\delta = 3.41$ (4H), $\delta = 3.55$ (4H)] for the 12 protons of the six CH_2N groups and an AB system [$\delta_A = 4.09$ (2H), $\delta_B = 4.50$ (2H), $^2J_{AB} = 14.66$ Hz].

The ^{13}C-NMR ($CDCl_3$) gives few informations on the existence of this coordination since one observes, for **2a** for example, only two signals at $\delta = 44.81$ and 45.27 ppm for the 12 methyl carbons and three signals at $\delta = 59.12$, 59.78 and 62.84 ppm for the six methylenic carbons of the dimethylaminomethyl groups.

The ^{15}N-NMR spectrum of **2a** (CCl_4, $CDCl_3$) exhibits three signals at $\delta = -336$ ppm (2 coordinating N_{ortho}), -348.5 ppm (2 N_{para}), -351 ppm (2 N_{ortho}), whereas only two signals at $\delta = -347.4$ ppm (2 N_{para}) and -348.4 ppm (4 N_{ortho}) were observed for the dihydrosilane $(ArO)_2SiH_2$ for which, as previously shown [14], a dynamic N···M···N coordination sequence in solution renders the four *o*-NMe_2 groups equivalent. In the spectrum of **2a** the splitting of the signal of the four *ortho* nitrogen atoms and the down field shift of one of these signals ($\delta = -336$ ppm) express also that two *o*-NMe_2 groups are chelated on the silicon atom in this compound.

All these spectroscopic characteristics for the compounds **2a**–**d** are consistent with an ionic silyl cation structure; silicon being most probably pentacoordinated with two *ortho* nitrogen atoms in apical positions (Scheme 4).

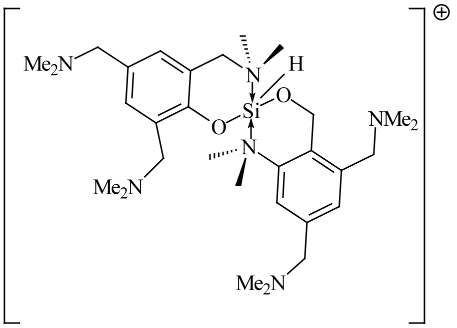
In such a geometry, almost a trigonal bipyramid in which nitrogens occupy axial positions, the two aryloxy groups are chemically equivalent. The two resonances observed in the ^{1}H-NMR spectrum for the two *o*-NMe_2 groups (one on each ArO group) coordinated to the silicon atom are due to the diastereotopic character of the *N*-methyl groups at each one of the two nitrogens.

It is worth noting that the counter-anion X^- has a weak influence on the chemical shifts in the ^{1}H-, ^{29}Si- and ^{15}N-NMR spectra of these $[(ArO)_2SiH]^+X^-$ compounds. Coordination of nucleophilic anions to a silyl cation having been already observed [20], we could also consider such a coordination in compounds **2a**–**d**; these derivatives would then adopt a structure in which silicon is not pentacoordinated, as proposed, but rather hexacoordinated. In this case only an octahedral structure with the hydrogen atom and the anion X^- *trans* to each other could be in agreement with the spectroscopic observations. Two geometries of C_2 and C_s types are possible (Scheme 5).

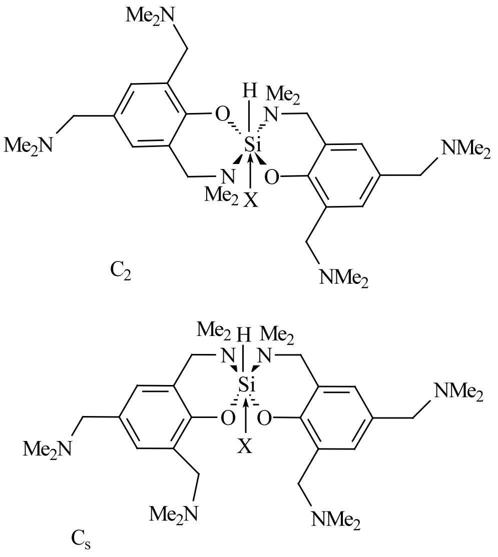
The IR spectra of **2a**–**d** are also consistent with a silylium structure since they present in all cases a strong υ_{Si-H} band at 2200 cm^{-1} characteristic of a silylium ion [21], remaining however close to that of the starting dihydrosilane $(ArO)_2SiH_2$.

The positive ion FAB mass spectra of these derivatives show the parent ion at *m/z* corresponding to the silylium $[(ArO)_2SiH]^+$ in all cases.

Furthermore the ionic nature of these compounds has also been confirmed by conductivity measurements. The specific conductivity of the compounds $[(ArO)_2SiH]^+Br^-$ and $[(ArO)_2SiH]^+TfO^-$, for example, are 24.9 and 30.2 ns cm^2 per equivalent, respectively (Fig. 2).



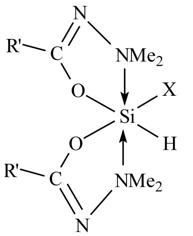
Scheme 4.



Scheme 5.

These results underline the strong bidendate nature of the 2,4,6-tris((dimethylamino)methyl)phenoxy ligand, which induces the ionic structure $[(ArO)_2SiH]^{+}X^{-}$ of compounds **2a**–**d**. It is worth noting that these derivatives are significantly different from the only three other known to date $(RO)_2SiH(X)$ compounds; these derivatives containing the $Me_2N{-}N{=}C(R')O$ bidentate ligand are neutral complexes with hexacoordinated silicon atoms [24–26] (Scheme 6).

It has been noted that dehydrogenative/coupling reactions of pentacoordinated dihydrosilanes with metal carbonyls give efficient synthetic routes for preparation of silanediyl-transition metal complexes stabilized by intramolecular coordination [27–30]. According to this method the silylene-iron tetracarbonyl complex $(ArO)_2SiFe(CO)_4$ (**11**) was obtained in good yield by appropriate workup after simple mixing of $(ArO)_2SiH_2$ and $Fe(CO)_5$ at room temperature in pentane during 5 h. This complex obtained as brown solid is soluble in aromatic solvents, insoluble in pentane and presents a great sensitivity to oxygen and moisture. It has been characterized by spectroscopic ^{1}H-, ^{13}C-, ^{29}Si-NMR, mass and IR analyses. In the ^{1}H-NMR at room temperature the equivalence of the four o-NMe_2 groups denotes a dynamic flip-flop coordination, identical to that observed for the parent silane $(ArO)_2SiH_2$. In the ^{13}C-NMR the carbonyl groups appear at $\delta = 210.98$ revealing, in solution at room temperature, a fast exchange (on the NMR time scale) of equatorial and axial carbonyls. The IR data in the $\nu(CO)$ region (three absorption bands) are characteristic of an axial coordination of the divalent silicon to iron (C_{3v} symmetry); a complex of C_{2v} symmetry with $Si(OAr)_2$ group in equatorial position of the trigonal bipyramidal-coordinated iron atom, should present four IR bands ($2A_1 + B_1 + B_2$) (Scheme 7). It seems that the divalent silicon



R' = Me, Ph, CF_3; X = Cl

Scheme 6.

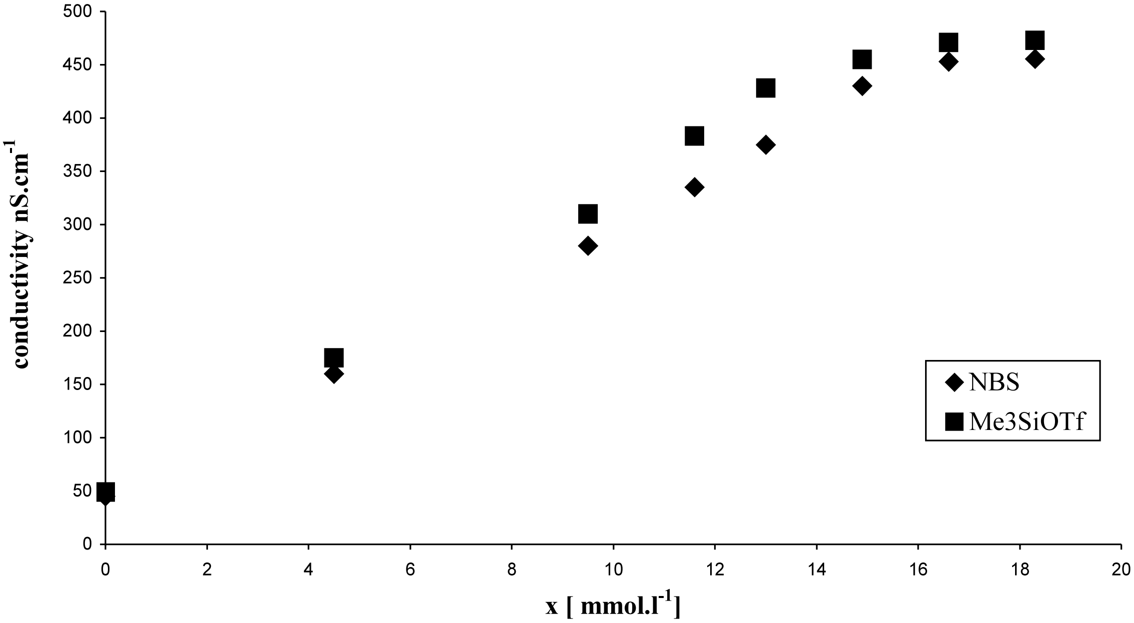
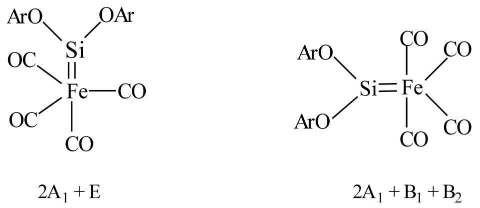


Fig. 2. The conductivity (χ) as a function of the amount of electrophilic reagent added (x) to a solution of 0.53 mmol l^{-1} of silane **1** in $CHCl_3$.



Scheme 7.

$Si(OAr)_2$ ligand acts as a strong σ-donor and a weak π-acceptor towards iron since theoretical studies have shown (i) that the axial or equatorial preference for a ligand L in the trigonal bipyramid carbonyl-d^8 metal (0) complexes is dependent on the σ-donor and π-acceptor characters of the ligand (ii) that low σ-donor and good π-acceptor ligands prefer equatorial sites [31–33].

The mass spectrum presents the molecular ion peak (weak intensity) and the fragmentation pattern characteristic of this structure (prominent peaks resulting from loss of the carbonyl groups and of the ArO groups on the silicon).

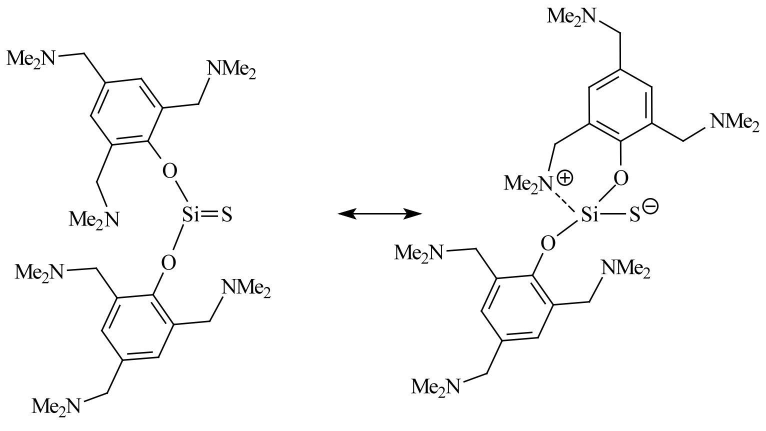
Early reports of Corriu and col. have shown that compounds with double bonded silicon ($R_2Si{=}Y$) are sufficiently stabilized by intramolecular complexation with a lewis base to permit their isolation as monomers [10,27,34]. Similarly the reaction of molecular sulfur with $(ArO)_2SiH_2$ in chloroform at room temperature gives the stable monomer $(ArO)_2Si{=}S$ (**12**) which can be formally considered as an adduct of the silylene $(ArO)_2Si$ and sulfur; **12** is thermically stable and has been characterized physicochemically. Mass spectroscopy analysis by electronic impact (70 eV) shows that the molecular ion peak is not detectable, the main peaks are attribuable to the fragment $[M-S]^+$ corresponding to the divalent silicon species. The particular stability at room temperature of **12** is probably due to on N···Si intramolecular coordination giving a structure between the two mesomeric forms represented in Scheme 8. Such structures have been previously evoked for Si, Ge, and Sn species [21a,21b,35–37] (Scheme 8). Quite recently the first isolable silanethione (Tbt)(Tip)Si=S {Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl)phenyl]-, Tip = 2,4,6-triisopropylphenyl-} which is stabilized sterically has been reported [38].

2.4. Thermolysis and photolysis of the trisilane $(Me_3Si)_2Si(OAr)_2$ (3)

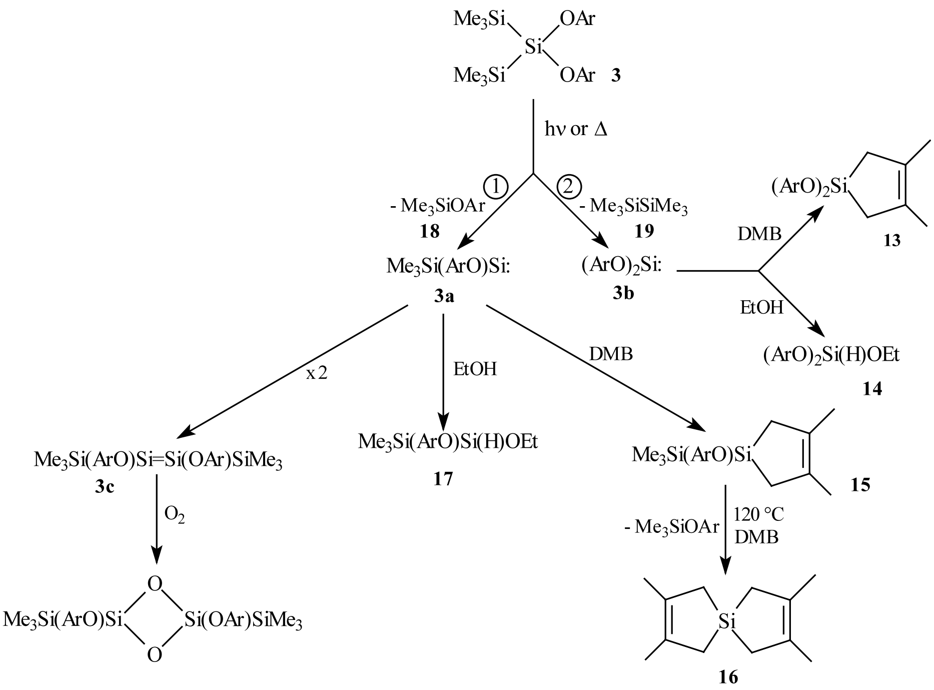
It is commonly accepted that polysilanes are effective sources of intermediate silylenes [3–14]. The UV characteristics (the maximum absorption band shifted towards the longwave lengths region) and the observed structure (relatively small Si–Si–Si angle) of compound **3** [14] have incited us to consider the thermolysis and photolysis of this trisilane as potential source of the silylene $(ArO)_2Si$, expecting a sufficient N···Si intramolecular coordination to allow its stabilization at room temperature as a monomer (or dimer). Few studies concerning the synthesis of N···Si stabilized silylene species have been performed [10–13]; to date no compound of this type has been isolated at room temperature.

On heating to 120 °C under anaerobic conditions for several hours or under UV irradiation (with a low pressure mercury lamp at 20 °C), $(Me_3Si)_2Si(OAr)_2$ decomposes in presence of excess of silylene trapping agents (ethanol or 2,3-dimethylbuta-1,3-diene) affording the silicon compounds **13**–**18**. These trapping experiments indicate that the decompositions are not specific forming both the heteroleptic silylene $(ArO)(Me_3Si)Si$: (**3a**) [way 1] and the homoleptic silylene $(ArO)_2Si$ (**3b**) [way 2], as shown in Scheme 9. Yields of these reactions are low (< 40%); the path 1 is always dominating on path 2 and more particularly in thermolysis [thermolysis ($\Delta = 120$ °C): **3a**/**3b** = 95/5; photolysis ($h\nu = 254$ nm): **3a**/**3b** = 75/25].

Photolysis of **3** is not so selective as its thermolysis since the formation of the four silanes $(Me_3Si)_2Si(OAr)H$, $Me_3SiSi(OAr)_2H$ and $[(Me_3Si)_2Si(OAr)_2$-1 or 2 $H_2C{=}NMe]$ are observed (mass spectrometry) in



Scheme 8.



Scheme 9.

small proportions in addition to those of Me_3SiOAr and $Me_3SiSiMe_3$. Note that $(Me_3Si)_2Si(OPh)_2$, the phenoxylated analogue of **3**, is thermically stable under the thermolysis conditions of **3** (it is necessary to maintain this derivative at 250 °C during 48 h to observe ~25% of decomposition).

Intramolecular stabilizations of the two divalent species **3a** and **3b** are not sufficient enough to allow their physicochemical characterization at room temperature; **3a** and **3b** have been only chemically characterized in situ by condensation on 2,3-dimethylbuta-1,3-diene or ethanol (Scheme 9). However, interestingly the addition of oxygen to a 10^{-1} M solution of **3** immediately after irradiation, led to the formation of the disiloxane $[(Me_3Si)(ArO)SiO]_2$ (characterized by mass spectroscopy). This siloxane can be regarded as the product of (i) the direct oxidation of the intermediate silylene **3a** followed by dimerisation of the silanone thus formed (ii) the direct oxidation of the intermediate disilene $[(Me_3Si)(ArO)Si{=}Si(OAr)(SiMe_3)]$ (**3c**) resulting from dimerization of **3a**. It is quite reasonable to assume the presence of **3c** since was observed an entity of molecular mass corresponding to disilene **3c** in the mass spectrum of a sample of **3** which was irradiated for 2 h at room temperature.

Although a more detailed study of these thermolysis and photolysis reactions is necessary, these first results (low yields of decomposition and path 1 dominating) highlight the particular stability of the intermediate silyl radicals $[(Me_3Si)(ArO)_2Si]$ and $[(Me_3Si)_2Si(OAr)]$ probably involved in the first step of these decomposition reactions. These observations are in agreement with the behavior of **3** under electronic impact since its mass spectrum (EI (electron impact) at 70 eV) shows the three ion peaks $[M-OAr]^+$ (100), $[M-Me_3Si]^+$ (42) and $[M]^+$ (17%).

3. Experimental

3.1. General procedures

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. ^1H-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_4Si as reference) and ^{13}C spectra on a AC 200 spectrometer operating at 50.32 MHz; the multiplicity of the ^{13}C-NMR signals was determined by the APT technique. ^{29}Si-NMR spectra were recorded on a Bruker ARX 400 operating at 79.47 MHz (Chemical shifts are reported in parts per million relative to external Me_4Si 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). ^{19}F-NMR spectra were recorded on a Bruker spectrometer AC 200 operating at 188.3 MHz (chemical shifts are reported in parts per million relative to external trifluoroacetic acid as reference). Mass spectra under EI or chemical ionisation (CH_4) conditions at 70 and 30 eV were obtained on Hewlett-Packard 5989 and Nermag R10-10H spectrometers. FAB spectra were performed at the service commun de spectrometrie de masse de l'Universite Paul–Sabatier de Toulouse. Irradiation were carried out at 25 °C by using a low-pressure mercury immersion lamp in a quartz tube ($\lambda = 254$ nm). 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 Supérieure de Chimie de Toulouse.

*3.2. Reaction of **1** with 2,4,6-tris((dimethylamino)methyl)phenol*

A solution of 2,4,6-tris((dimethylamino)methyl)phenol (0.14 g, 0.53 mmol) in 10 ml of pentane was added slowly to a stirred solution of [2,4,6-tris((dimethylamino)methyl)]-phenylsilane (0.2 g, 0.53 mmol) in 15 ml of pentane. The reaction mixture was stirred at room temperature (r.t.) until evolution of H_2 was ceased (3 h). The volatiles were removed in vacuo and the residue was distilled under vacuum to give **4** (0.32 g, 94%). Compound **4**: b.p. 180–182 °C/5×10^{-2} mmHg. ^{29}Si-NMR ($CDCl_3$): -46.7 (d, $^1J_{Si-H} = 288$ Hz). ^{15}N-NMR ($CDCl_3$): -347.7, -350.2. ^{1}H-NMR ($CDCl_3$): 1.95 (s, 12H), 2.20 (s, 24H), 3.30 (s, 4H), 3.38 (s, 8H), 5.25 (s, 1H), 7.05 (s, 4H), 7.10–7.40 (m, 5H). ^{13}C-NMR ($CDCl_3$): 45.00, 45.31, 59.21, 63.88, 127.38, 127.57, 128.54, 130.04, 131.20, 132.16, 136.60, 151.42. IR ($CDCl_3$, KBr, cm^{-1}): $\nu_{Si-H} = 2205$. MS: $m/z = 634$ [M]$^+$. Anal. Calc. for $C_{36}H_{58}N_6O_2Si$ ($M = 634.97$): C, 68.09; H, 9.21; N, 13.24. Found: C, 67.79; H, 9.41; N, 13.50%.

*3.3. Reaction of **4** with 2,4,6-tris((dimethylamino)methyl)phenol*

Using the same experimental procedure as for the synthesis of **4**, the reaction of **4** (1.2 g, 1.89 mmol) with 2,4,6-tris((dimethylamino)methyl)phenol (0.5 g, 1.89 mmol) afforded **5**. Yield: 1.6 g, 94%. Compound **5**: ^{29}Si-NMR ($CDCl_3$): -9.7. ^{1}H-NMR ($CDCl_3$): 1.98 (s, 18H), 2.14 (s, 36H), 3.24 (s, 6H), 3.46 (s, 12H), 7.12 (s, 6H), 7.35–7.55 (m, 5H). ^{13}C-NMR ($CDCl_3$): 45.26, 45.52, 58.28, 59.17, 128.41, 128.93, 129.17, 129.63, 132.16, 132.87, 135.36, 149.76. MS: $m/z = 897$ [M]$^+$. Anal. Calc. for $C_{51}H_{83}N_9O_3Si$ ($M = 898.35$): C, 68.18; H, 9.31; N, 14.03. Found: C, 67.78; H, 9.01; N, 13.72%.

3.4. Reaction of phenylsilane with 2,4,6-tris((dimethylamino)methyl)phenol

A mixture of $PhSiH_3$ (0.07 g, 0.65 mmol) and 2,4,6-tris((dimethylamino)methyl)phenol (0.52 g, 1.96 mmol) leads to **5** (0.18 g, 31%).

*3.5. Reaction of **1** with acetic acid*

A solution of acetic acid (0.02 g, 0.32 mmol) in chloroform (10 ml) was added to **1** (0.12 g, 0.32 mmol) in chloroform (10 ml). The reaction mixture was stirred at r.t. for 12 h. The volatiles were removed in vacuo to afford **6** (0.13 g, 95%). Compound **6**: ^{29}Si-NMR ($CDCl_3$): -63 (d, $J_{Si-H} = 304$ Hz). ^{1}H-NMR ($CDCl_3$): 2.07 (s, 3H), 2.16 (s, 6H), 2.22 (s, 12H), 3.23 (s, 2H), 3.37(s, 4H), 5.22 (s, 1H), 7.07 (s, 2H), 7.3–7.5 (m, 5H). ^{13}C-NMR ($CDCl_3$): 21.20, 45.10, 45.19, 60.22, 63.88, 127.03, 127.65, 128.62, 130.27, 131.74, 132.42, 136.52, 152.01, 161.82. IR (KBr, $CDCl_3$, cm^{-1}): $\nu_{Si-H} = 2201$; $\nu_{CO} = 1693$. MS: $m/z = 428$ [M$-$1]$^+$. Anal. Calc. for $C_{23}H_{35}N_3O_3Si$ ($M = 429.63$): C, 64.30; H, 8.21; N, 9.78. Found: C, 64.09; H, 8.43; N, 9.63%.

*3.6. Reaction of **1** with phosphorus pentachloride*

To a solution of phosphorus pentachloride (0.08 g, 0.4 mmol) in 10 ml of chloroform was added dropwise a solution of **1** (0.15 g, 0.4 mmol) in 10 ml of chloroform. The mixture was stirred at r.t. for 2 days, the solvent was removed under vacuum and ether (15 ml) was added. By filtration **7** was obtained as a white solid (0.08 g, 50%). Compound **7**: ^{29}Si-NMR ($CDCl_3$): -71.8 (d, $^1J_{Si-H} = 328.4$ Hz). ^{1}H-NMR ($CDCl_3$): 2.02 (s, 6H), 2.25 (s, 12H), 3.52 (s, 2H), 3.80 (s, 4H), 5.71 (s, 1H), 7.05 (s, 2H), 7.15–7.39 (m, 5H). ^{13}C-NMR ($CDCl_3$): 45.12, 45.25, 59.20, 64.01, 126.91, 127.46, 128.64, 130.10, 131.41, 132.18, 136.48, 151.49. IR (KBr, $CDCl_3$, cm^{-1}): $\nu_{Si-H} = 2195$. MS: $m/z = 404$ [M$-$1]$^+$. Anal. Calc. for $C_{21}H_{32}N_3OClSi$ ($M = 406.04$): C, 62.12; H, 7.94; N, 10.35. Found: C, 62.31, H, 8.12; N, 10.14%.

*3.7. Reaction of **1** with benzaldehyde*

A solution of benzaldehyde (0.034 g, 0.32 mmol) in chloroform (10 ml) was added dropwise to **1** (0.12 g, 0.32 mmol) in chloroform (10 ml). The mixture was stirred at r.t. for 24 h. After removal of the solvent, **8** was obtained (0.15 g, 99%). Compound **8**: ^{29}Si-NMR ($CDCl_3$): -66.7 (d, $J_{Si-H} = 304$ Hz). ^{1}H-NMR ($CDCl_3$): 2.16 (s, 6H), 2.23 (s, 12H), 3.24 (s, 2H), 3.36 (s, 4H), 4.51 (s, 2H), 5.22(s, 1H), 7.07 (s, 2H), 7.30–7.52 (m, 10H). ^{13}C-NMR ($CDCl_3$): 45.21; 45.12, 60.22, 63.86, 76.51, 127.01, 127.64, 128.03, 128.12, 128.62, 129.10, 130.27, 131.72, 132.39, 136.48, 139.50, 151.52. IR (KBr, $CDCl_3$, cm^{-1}): $\nu_{Si-H} = 2204$. MS: $m/z = 476$ [M$-$1]$^+$. Anal.

Calc. for $C_{28}H_{39}N_3O_2Si$ ($M = 477.71$): C, 70.40; H, 8.23; N, 8.80. Found: C, 70.18; H, 8.42; N, 8.56%.

3.8. *Thermolysis of* **6**

Compound **6** (0.2 g, 0.5 mmol) was sealed in an evacuated tube and heated at 150 °C for 12 h. After cooling to r.t., the tube was opened and the product was analyzed by NMR and mass spectroscopy. Decomposition of **6** was complete, and compound **9** was identified as $[Ph(ArO)SiO]_3$. Compound **9**: ^{29}Si-NMR ($CDCl_3$): −81.3. ^{1}H-NMR ($CDCl_3$): 2.12 (s, 18H), 2.26 (s, 36H), 3.28 (s, 6H), 3.30 (s, 12H), 7.01–7.82 (m, 21H). ^{13}C-NMR ($CDCl_3$): 45.31, 45.52, 58.21, 59.12, 127.15, 127.53, 128.23, 130.37, 131.65, 132.72, 136.56, 151.42. MS: $m/z = 1155$ $[M]^+$.

3.9. *Reaction of* **2** *with 2,4,6-tris((dimethylamino)methyl)phenol*

A solution of 2,4,6-tris((dimethylamino)methyl)phenol (0.20 g, 0.75 mmol) in chloroform (5 ml) was added slowly to **2** (0.42 g, 0.75 mmol) in chloroform (10 ml). An evolution of H_2 was observed. The reaction mixture was stirred at r.t. for 24 h. Compound **10** was obtained after evaporation of the solvent in vacuo. Yield: 0.55 g, 90%. **10**: ^{29}Si-NMR ($CDCl_3$): −102 (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}): $\nu_{Si-H} = 2243$. MS: $m/z = 821$ $[M]^+$. Anal. Calc. for $C_{45}H_{79}N_9O_3Si$ ($M = 822.25$): C, 65.73; H, 9.68; N, 15.33. Found: C, 65.89; H,9.85; N, 15.36%.

3.10. *Reaction of* **2** *with pentacarbonyliron*

A solution of pentacarbonyliron (0.11 g, 0.53 mmol) in 10 ml of pentane was added slowly to a solution of 2 (0.30 g, 0.53 mmol) in 15 ml of pentane. The mixture was stirred at r.t. for 5 h. The precipitate formed was filtered and dried in vacuo to afford pure **11** (0.15 g, 40%) as a maroon powder. Compound **11**: ^{29}Si-NMR (C_6D_6): −98.9. ^{1}H-NMR (C_6D_6): 2.05 (s, 12H), 2.16 (s, 24H), 3.36 (s, 4H), 3.53 (s, 8H), 7.26 (s, 4H). ^{13}C-NMR (C_6D_6): 45.57, 45.71, 59.87, 64.81, 129.26, 130.26, 132.64, 152.38, 210.98 (CO). IR (KBr, C_6D_6, cm^{-1}): ν_{CO}: 1958, 2010. MS (IC/NH_3): $m/z = 725$ $[M+1]^+$. Anal. Calc. for $C_{34}H_{52}N_6O_6FeSi$ ($M = 724.75$): C, 56.35; H, 7.23; N, 11.60. Found: C, 56.31; H, 7.28; N, 11.82%.

3.11. *Reaction of* **2** *with sulfur*

To a stirred suspension of sulfur (0.012 g, 0.38 mmol) in 10 ml of chloroform was added a solution of **2** (0.212 g, 0.38 mmol) in 10 ml of chloroform. The mixture was stirred at r.t. for 3 h. The solvent was removed under vacuum and the residue yellow solid product **12** was purified by crystallization from toluene–pentane (1/1, 40 ml) at −30 °C. Yield: 0.21 g, 96%. Compound **12**: m.p. 145–146 °C. ^{29}Si-NMR ($CDCl_3$): −82.3. ^{1}H-NMR ($CDCl_3$): 2.23 (s, 12H), 2.45 (s, 24H), 3.26 (s, 4H), 3.48 (s, 8H), 6.93 (s, 4H). ^{13}C-NMR ($CDCl_3$): 45.39, 45.47, 63,37, 64.08, 123.20, 130.86, 131.04, 151.20. MS (I.E.): $m/z = 556$ $[M-S]^+$. MS (IC/CH_4): $m/z = 589$ $[M+1]^+$. Anal. Calc. for $C_{30}H_{52}N_6O_2SSi$ ($M = 588.92$): C, 61.18, H, 8.90; H, 14.27. Found: 61.24; H, 8.69; N, 14.49%.

3.12. *Reaction of* **2** *with trimethylsilyl trifluoromethanesulfonate*

A solution of trimethylsilyl trifluoromethanesulfonate (0.11 g, 0.5 mmol) in 10 ml of ether was added dropwise at −65 °C to a solution of **2** (0.28 g, 0.5 mmol) in 10 ml of ether. The reaction mixture was warmed to r.t. and stirred for 1 h. After filtration, the residue solid obtained was washed twice with pentane (10 ml) and dried in vacuo. Compound **2a** (0.27 g, 77%) was isolated as a white powder. Compound **2a**: m.p. 125–127 °C (dec.). ^{29}Si-NMR (CCl_4–$CDCl_3$): −106 (d, $J_{Si-H} = 344$ Hz). ^{15}N-NMR (CCl_4–$CDCl_3$): −336.0, −348.5, −351.0. ^{19}F-NMR (CCl_4–$CDCl_3$): −2.69. ^{1}H-NMR (CCl_4–$CDCl_3$): 2.15 (s, 12H), 2.35 (s, 12H), 2.62 (s, 6H), 2.85 (s, 6H), 3.41 (s, 4H), 3.55 (s, 4H), 4.09 (d, 2H, $J = 14.66$ Hz), 4.50 (d, 2H, $J = 14.66$ Hz), 4.42 (s, 1H), 7.25 (s, 4H). ^{13}C-NMR (CCl_4–$CDCl_3$): 44.81, 45.27, 59.12, 59.78, 62.84, 119.98, 120.61 (q, $^1J_{CF} = 315$ Hz), 129.49, 131.57, 149.64. IR (KBr, CCl_4–$CDCl_3$, cm^{-1}): ν_{Si-H}: 2189. MS (MNBA) FAB > 0: $m/z = 557$ $[(ArO)_2SiH]^+$, FAB < 0: $m/z = 149$ $[CF_3SO_3]^-$. Anal. Calc. for $C_{31}H_{53}N_6O_5F_3SSi$ ($M = 706.94$): C, 52.67; H, 7.56; N, 11.89. Found: 52.63; H, 7.25; N, 11.56%.

3.13. *Reaction of* **2** *with N-chlorosuccinimide*

A suspension of *N*-chlorosuccinimide (0.08 g, 0.6 mmol) in dichloromethane (15 ml) was slowly added to a solution of **2** (0.35 g, 0.6 mmol) in dichloromethane (15 ml). The mixture was then stirred at r.t. for 12 h. After the succinimide was filtered off and the solvent was removed in vacuo, **2b** was obtained as a white powder. Yield: 0.25 g, 70%. Compound **2b**: m.p. 189–190 °C (dec.). ^{29}Si-NMR ($CDCl_3$): −105.9 (d, $J_{Si-H} = 344.2$ Hz). ^{15}N-NMR ($CDCl_3$): −336.2, −345.4, −350.4. ^{1}H-NMR ($CDCl_3$): 2.17 (s, 12H), 2.39 (s, 12H), 2.66 (s, 6H), 2.87 (s, 6H), 3.45 (s, 4H), 3.68 (s, 4H), 4.15 (d, 2H, $J = 17.1$ Hz), 4.51 (d, 2H, $J = 17.1$ Hz), 4.43 (s, 1H), 7.34 (s, 4H). ^{13}C-NMR ($CDCl_3$): 43.62, 44.40, 45.30, 58.76, 59.31, 61.94, 119.96, 131.04, 133.02, 149.82. IR (KBr, $CDCl_3$, cm^{-1}): ν_{Si-H}: 2207. MS (MNBA) FAB > 0: $m/z = 557$ $[(ArO)_2SiH]^+$, FAB < 0:

$m/z = 35$ $[Cl]^-$. Anal. Calc. for $C_{30}H_{53}N_6O_2ClSi$ (M = 593.32): C, 60.73; H, 9.00; N, 14.16. Found: C, 60.50; H, 8.84; N, 13.86%.

3.14. Reaction of **2** with *N*-bromosuccinimide

Using the same experimental procedure as for the synthesis of **2a**, the reaction of **2** (0.35 g, 0.6 mmol) with *N*-bromosuccinimide (0.11 g, 0.6 mmol) afforded **2c**. Yield: 0.28 g, 74%. Compound **2c**: m.p. 194–195 °C (dec.). ^{29}Si-NMR ($CDCl_3$): −106.1 (d, $J_{Si-H} = 348.34$ Hz). ^{15}N-NMR ($CDCl_3$): −335.5, −345.5, −350.2. ^{1}H-NMR ($CDCl_3$): 2.15 (s, 12H), 2.33 (s, 12H), 2.70 (s, 6H), 2.88 (s, 6H), 3.39 (s, 4H), 3.56 (s, 4H), 4.14 (d, 2H, J = 15.07 Hz), 4.57 (d, 2H, J = 15.07 Hz), 4.47 (s, 1H), 7.27 (s, 4H). ^{13}C-NMR ($CDCl_3$): 43.81, 44.49, 45.31, 59.19, 59.66, 62.28, 119.91, 129.83, 132.68, 149.68. IR (KBr, $CDCl_3$, cm^{-1}): ν_{Si-H}: 2206. MS (MNBA) FAB > 0: $m/z = 557$ $[(ArO)_2SiH]^+$, FAB < 0: $m/z = 80$ $[Br]^-$. Anal. Calc. for $C_{30}H_{53}N_6O_2BrSi$ (M = 637.77): C, 56.50; H, 8.38; N, 13.18. Found: C, 56.26; H, 8.14; N, 12.84%.

3.15. Reaction of **2** with iodine

A solution of iodine (0.08 g, 0.32 mmol) in 5 ml of ether was added dropwise, at 0 °C, to a solution of **2** (0.36 g, 0.64 mmol) in 10 ml of ether. The resulting mixture was stirred until evolution of H_2 was ceased. The precipitate formed was filtered and washed twice with ether (10 ml) to give **2d** (0.21 g, 48%) as a white powder. Compound **2d**: m.p. 204–205 °C (dec.). ^{29}Si-NMR ($CDCl_3$): −106.2 (d, $J_{Si-H} = 347$ Hz). ^{15}N-NMR ($CDCl_3$): −335.1, −343.9, −350.0. ^{1}H ($CDCl_3$): 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) et $\delta_B = 4.48$ (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}): ν_{Si-H}: 2212. MS: (MNBA) FAB > 0: $m/z = 557$ $[(ArO)_2SiH]^+$, FAB < 0: $m/z = 127$ $[I]^-$. Anal. Calc. for $C_{30}H_{53}N_6O_2ISi$ (M = 684.77): C, 52.62; H, 7.80; N, 12.27. Found: C, 52.31; H, 7.58; N, 12.39%.

3.16. Thermolysis of **3** in the presence of ethanol

A mixture of **3** (0.50 g, 0.71 mmol) and an excess of ethanol (1 ml) was sealed in an evacuated tube and heated at 120 °C for 3 days. After addition of pentane (20 ml) to the mixture, a yellow precipitate was obtained, and then filtered to give $(ArO)_2Si(H)OEt$ (~2%). Analyses of the filtrate by ^{1}H-NMR and GC–MS show the formation of $Me_3SiSiMe_3$ (~2%), Me_3SiOAr (33%), $ArO(Me_3Si)Si(H)OEt$ (32%) and $(ArO)_2Si(SiMe_3)_2$ (62%). After precipitation at −20 °C of $(ArO)_2Si(SiMe_3)_2$ all the volatiles were eliminated in vacuo (80–82 °C/10^{-3} mmHg, 3 h) and $ArO(Me_3Si)Si(H)OEt$ was obtained. Yield: 0.09 g, 31%. $(ArO)_2Si(H)OEt$: m.p. 189–190 °C (dec.). ^{1}H-NMR (C_6D_6): 1.12 (t, 3H, $^3J_{H-H} = 7$ Hz), 2.05 (s, 24H), 2.14 (s, 12H), 3.3 (s, 4H), 3.47 (s, 8H), 3.65 (q, 2H, $^3J_{H-H} = 7$ Hz), 4.79 (s, 1H), 7.45 (s, 4H). MS: $m/z = 602$ $[M]^+$. $ArO(Me_3Si)Si(H)OEt$: ^{1}H-NMR (C_6D_6): 0.25 (s, 9H), 1.15 (t, 3H, $^3J_{H-H} = 7$ Hz), 2.04 (s, 12H), 2.12 (s, 6H), 3.25 (s, 2H), 3.43 (s, 4H), 3.67 (q, 2H, $^3J_{H-H} = 7$Hz), 4.65 (s, 1H), 7.43 (s, 2H). MS: $m/z = 411$ $[M]^+$.

3.17. Photolysis of **3** in the presence of ethanol

A mixture of **3** (0.6 g, 0.85 mmol) and an excess of ethanol (1 ml) in cyclohexane (5 ml) was irradiated for 4 h. By a procedure analogous to that described above formations, $(ArO)_2Si(H)OEt$ (6%), $ArO(Me_3Si)Si(H)OEt$ (20%), $Me_3SiSiMe_3$ (7%) and Me_3SiOAr (23%) were characterized beside $(ArO)_2Si(SiMe_3)_2$ (68%) and another unidentified product.

3.18. Thermolysis of **3** in the presence of 2,3-dimethylbuta-1,3-diene

A mixture of **3** (0.36 g, 0.51 mmol) and an excess of 2,3-dimethylbuta-1,3-diene was sealed in an evacuated tube and heated at 120 °C for a week. After addition of pentane (20 ml) to the mixture and elimination of $(ArO)_2Si(SiMe_3)_2$ (63%) by precipitation at −20 °C, the analysis of the filtrate by ^{1}H-NMR and GC–MS reveals the formations of 1,1-diaryloxy-3,4-dimethyl-1-silacyclopent-3-ene (~2%), 1-aryloxy-1-trimethylsilyl-3,4-dimethyl-1-silacyclopent-3-ene (29%), Me_3Si- OAr (32%) and $Me_3SiSiMe_3$ (3%) beside another product unidentified.

- $(ArO)_2SiCH_2C(CH_3)=C(CH_3)CH_2$: ^{1}H-NMR ($CDCl_3$): 1.67 (s, 4H), 2.02 (s, 4H), 2.20 (s, 12H), 2.22 (s, 24H), 3.37 (s, 4H), 3.51 (s,8H), 7.33 (s, 4H). MS: $m/z = 638$ $[M]^+$.
- $(ArO)(Me_3Si)SiCH_2C(CH_3)=C(CH_3)CH_2$: ^{1}H-NMR ($CDCl_3$): 0.23 (s, 9H), 1.63 (s, 6H), 2.03 (s, 4H), 2.21 (s, 6H), 2.23 (s, 12H), 3.40 (s, 2H), 3.57 (s, 4H), 7.3 (s, 2H). MS: $m/z = 447$ $[M]^+$.

Crystal data for $[(Me_3Si)_2SiO]_3$: $C_{18}H_{54}O_3Si_9$, M = 571.42, monoclinic, $P2_1/c$, $a = 18.677(2)$ Å, $b = 10.545(1)$ Å, $c = 20.167(3)$ Å, $\beta = 115.58(2)°$, $V = 3582.6(7)$ Å^3, Z = 4, ρ_c 1.059 Mg m^{-3}, $F(000) = 1248$, $\lambda = 0.71073$ Å, $T = 173(2)$ K, μ (Mo–K$_\alpha$) = 0.349 mm^{-1}, crystal size 0.4 × 0.3 × 0.2 mm, $2.28 < \Theta < 24.10°$, 4527 reflections (3530 independent) were collected at low temperatures using an oil-coated shock-cooled crystal on a STOE IPDS diffractometer. The structure was solved by direct methods (SHELXS-97) [39] and 289 parameters were refined using the least-squares method on F^2 [40]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Largest electron density residue: 0.247 e Å^{-3}, R_1 (for $I > 2\sigma(I)) = 0.0408$ and $wR_2 = 0.1051$ (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma\, w(F_o^2 - F_c^2)^2/\Sigma\, w(F_o^2)^2)^{0.5}$.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179386. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge 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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