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Aminosilylation of heterocumulenes and the intramolecular decomposition of their silyl-functionalized adducts

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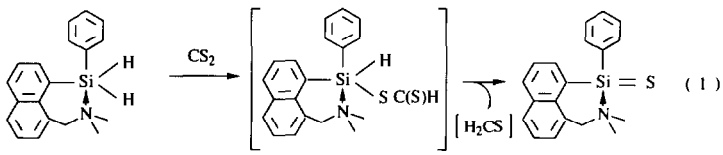
Abstract

Heteroorganic amidosilanes are readily obtained by interaction of CO_2, CS_2 and other heterocumulenes with pentacoordinated diaminosilanes. A comparison is made with the corresponding reactions of tetracoordinated species. Decomposition of these bifunctional organosilanes gives 2-substituted ureido derivatives and base-stabilized low coordinated silicon species, seemingly by a unimolecular thermal β-elimination.

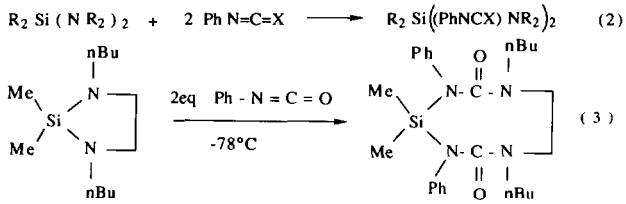
Introduction

Intramolecular base-stabilization has recently been used to enable isolation of silicon and germanium doubly-bonded systems [1–3]. In the case of silathione, the key step was the unexpectedly ready decomposition at room temperature of the bifunctional pentacoordinated hydrosilyl ester of dithioformic acid (eq. 1).



E S

We were interested in extending this approach to systems involving other functional groups on silicon [4]. A study of the Si–N bond seemed promising since Lappert many years ago observed the facile aminosilylation of heterocumulenes (eqs. 2 and 3) [5].



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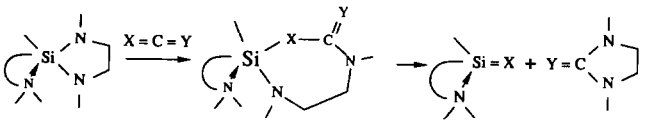
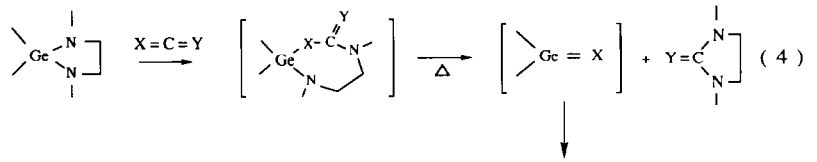


X = O, S, N-Ph

Scheme 1.

The insertion of PhNCO or PhNCS into acyclic compounds $R_2Si(NR'_2)_2$ was performed in refluxing benzene. In contrast the formation of 9-membered ring cyclic bis-ureidosilane from 1,3-dibutyl-2,2-dimethyl-1,3,2-diazasilacyclopentane and two equivalents of phenylisocyanate occurred even at $-78\,^{\circ}C$, showing that the cyclic compound has a high reactivity. The products of insertion of CO_2 and CS_2 into the diazasilacyclopentane ring were not described, and it suggested reasonably that such species would be too reactive to be isolated.

In the case of germanium compounds, Satgé reported that thermolysis of 1,3,2-diazagermacyclopentane derivatives in the presence of heterocumulenes gives transient germanones and germathiones along with 2-substituted imidazolidines [6–8].



(4)

The double-bonded germanium species have been characterized by trapping with appropriate reagents (eq. 4).

In the present paper we present the results of a study on the reactions of heterocyclic hypervalent organosilanes **1–3** (Scheme 2) with CO_2, CS_2, PhNCO, PhNCS and the ready decomposition of the insertion products (Scheme 1).

The reactions are compared with those of the acyclic derivative **4** and the related tetracoordinated-aminosilane **5**. Intramolecular stabilisation by the aminoaryl ligand has allowed isolation of the Si=S intermediates, confirming the postulated thermal decomposition scheme [9].

Results

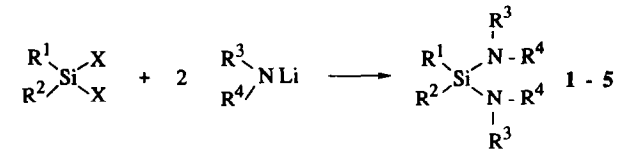
Pentacoordinated diaminosilanes

The diaminosilanes were obtained by reaction of aminolithium derivatives with the appropriate pentacoordinated difluoro- [10] or dimethoxy-silanes [11] (Scheme 2).

The yields are high (80–90%). The products are sensitive to moisture and must be handled in an inert atmosphere. The tetracoordinate species **5** has been previously described [12].

Aminosilylation of heterocumulenes or carbonyl species

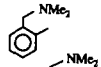
The insertions of heterocumulenes or other unsaturated species into the Si–N bonds were performed under the conditions summarized in Table 1. In some instances, the new compounds were sufficiently stable to be characterized by NMR

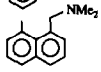


X = F, OMe

R^3 = Me

R^4 = Me, -(CH_2)$_2$-

$R^2 \equiv P_5 \equiv$ 

$R^2 \equiv N_6 \equiv$ 

	1	2	3	4	5
R^1	Ph	Me	Ph	Me	Me
R^2	N_6	P_5	P_5	P_5	Ph
R^3	Me	Me	Me	Me	Me
R^4	$(CH_2)_2$	$(CH_2)_2$	$(CH_2)_2$	Me	$(CH_2)_2$

Scheme 2.

Table 1a

Insertion of heterocumulenes: influence of the silane (reactions with CS_2)

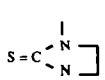
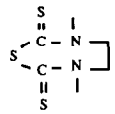
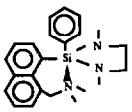
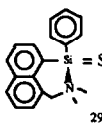
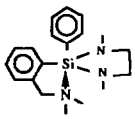
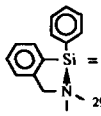
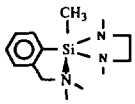
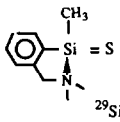
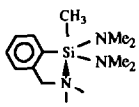
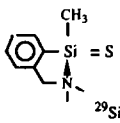
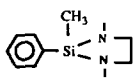
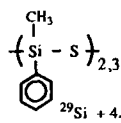
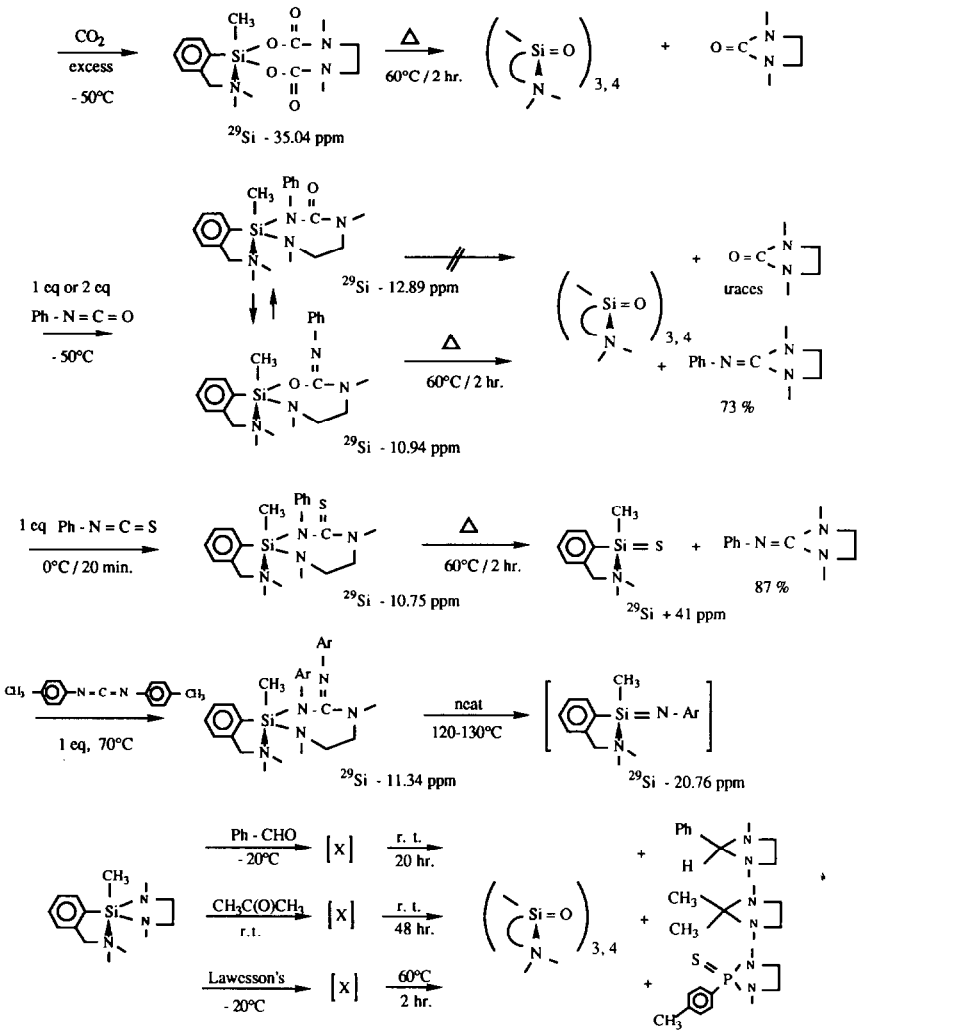
		Silicon	Organic (isolated)	
				
	1 eq CS_2, -30°C / 5 min		87 %	8 %
	10eq CS_2, -30°C / 5 min	^{29}Si + 22.3 ppm	83 %	13 %
	1 eq CS_2, 25°C / 5 min		95 %	traces
	10 eq CS_2, 25°C / 5 min	^{29}Si + 34.2 ppm	92 %	3 %
	1 eq CS_2, 25°C / 15 min		91 %	
	1 eq CS_2, -20°C / 10 min	^{29}Si + 41.1 ppm	65 %	35 %
	1 eq CS_2, 25°C / 1 hr.		83 %	
	10 eq CS_2, 25°C / 10 min	^{29}Si + 41.1 ppm		87 %
	2 eq CS_2, 25°C / 45 min		77 %	
		^{29}Si + 4.09 ppm + 12.9 ppm		

Table 1b

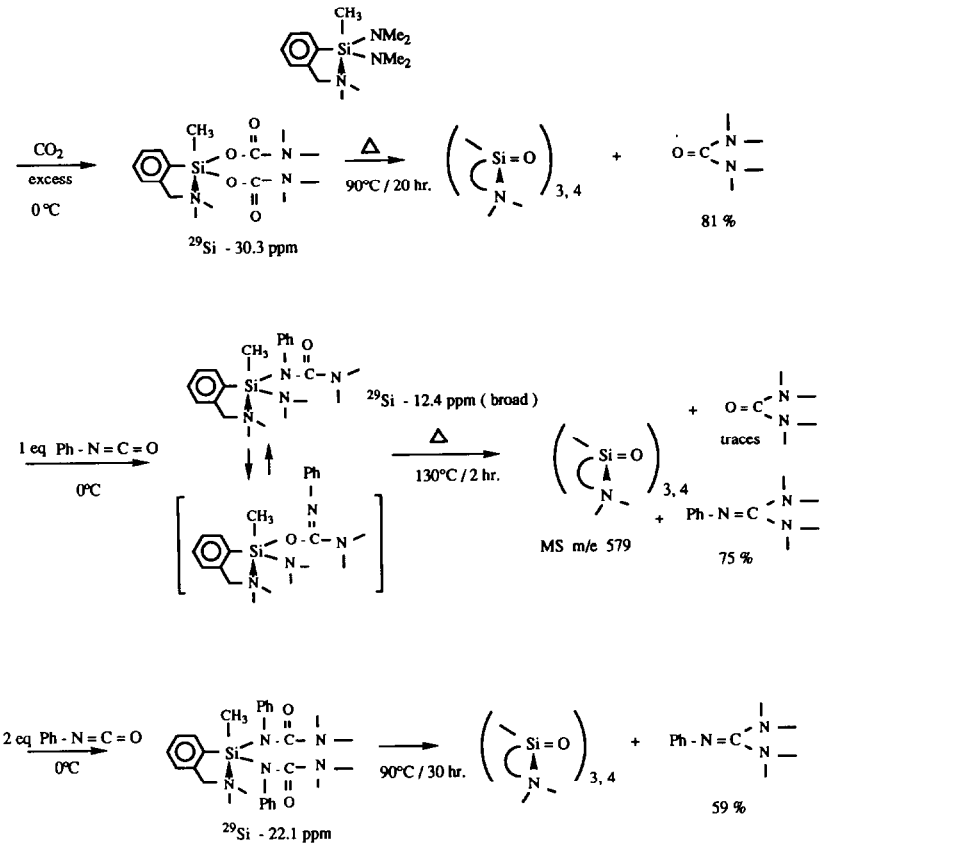
Insertion of heterocumulenes: insertion compounds, and reactions of **2** with various dipolar species



spectroscopy. The thermal decompositions were performed at various temperatures in the range -30 to $+130\,^{\circ}C$, and monitored by ^{1}H NMR spectroscopy. The product mixtures were fully analyzed by ^{1}H, ^{29}Si, and ^{13}C NMR spectroscopy. Subsequently the organic components were isolated by distillation or by flash chromatography on silica and identified by comparison with authentic samples [13]. The process is shown in Scheme 3 for the reaction starting from **1** and CS_2. The insertion compound cannot be detected even spectroscopically, but ^{29}Si NMR spectroscopy shows that the (previously described) silathione 8-dimethylaminomethylnaphthylphenylsilathione is formed as the only silicon derivative [1].

Table 1c

Insertion of heterocumulenes: Insertion compounds, and reactions of **4** with various dipolar species

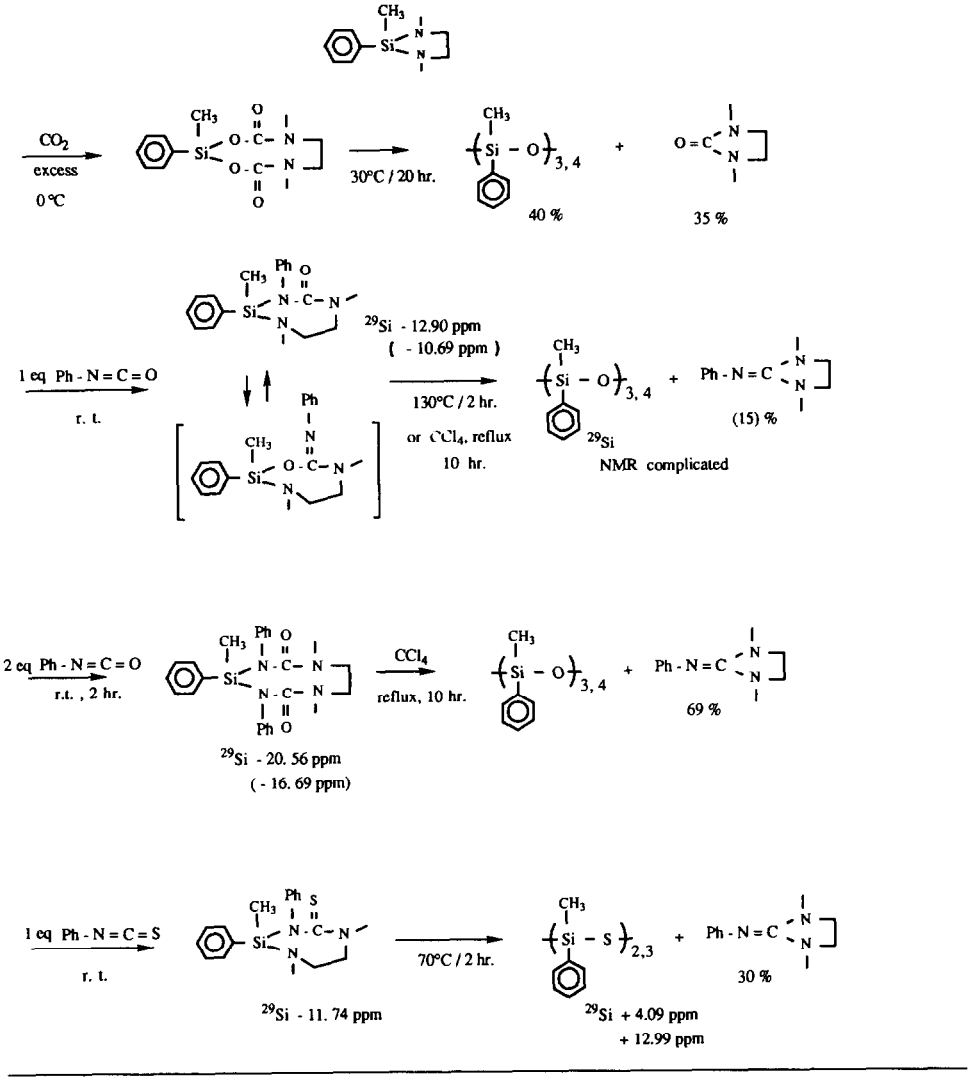


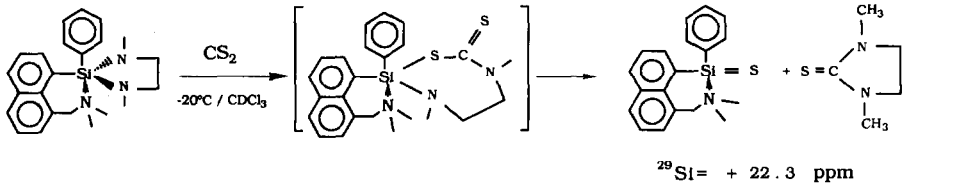
Some other systems were also studied; as an illustration we present in Scheme 4 the results obtained in the reaction of **2** with CS_2. When a stoichiometric amount of CS_2 is used, the organic product, $S{=}\dot{C}{-}N(Me)CH_2CH_2N(Me)$ can be isolated in 86% yield, along with traces of trithiocarbamate, $MeNC(S)SC(S)NMeCH_2CH_2$. Even when CS_2 is used in a large excess (10 equivalents) the yield of trithiocarbamate does not exceed 13%. In contrast, the reaction of CS_2 with the acyclic diaminosilane **4** is more specific; with 1 equivalent of CS_2, the organic product $S{=}C(NMe_2)_2$ is isolated in 87% yield, whereas with an excess of CS_2 (10 eq), $Me_2NC(S)SC(S)NMe_2$ is obtained (83%). There is only one silicon-containing product (^{29}Si δ +41.9), judged to be the silathione.

The tetracoordinated *N,N'*-dimethylmethylphenylsila-2-diazasilacyclopentane, **5**, reacts similarly under mild conditions with 2 equivalents of CS_2 at room temperature in the absence of any added catalyst. The ^{29}Si NMR spectrum of the product mixture shows the presence of dimeric and trimeric methylphenylsilathianes [14]; 1,3-dimethyl-2-thioimidazolidine is the only organic product.

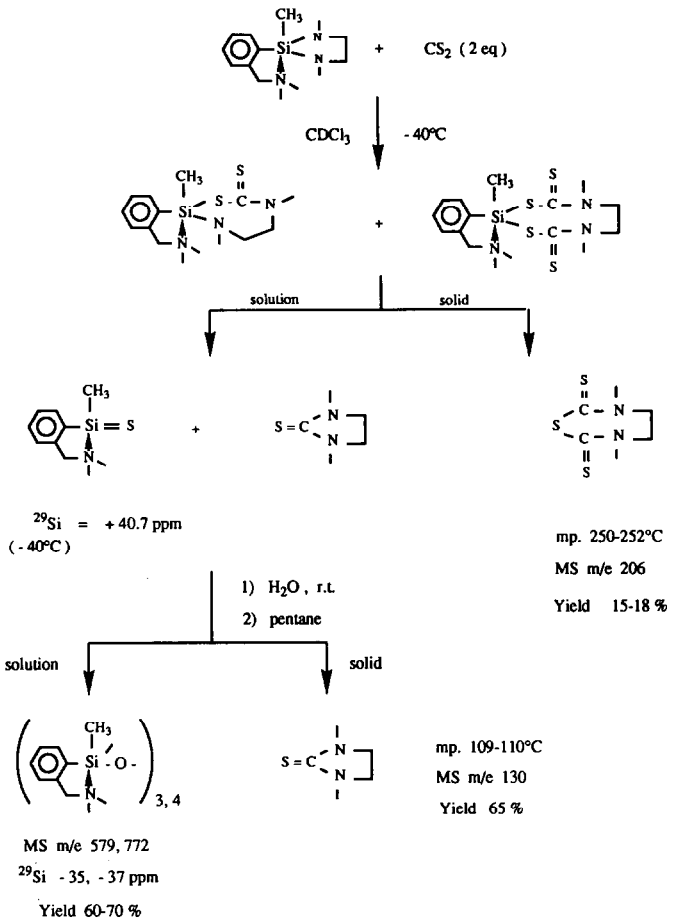
Table 1d

Insertion of heterocumulenes: insertion compounds, and reactions of **5** with various dipolar species





Scheme 3.



Scheme 4. Reaction of CS_2 with **2**.

Insertion of CO_2 into the Si–N bonds of **2–5** is observed under very mild conditions. With the pentacoordinated diaminosilanes, the diinsertion compounds decompose only when the mixtures are warmed up. In contrast, decomposition of the adducts from the tetracoordinated diazasilacyclopentane **5** occurs even at room temperature, with slow formation of a complicated mixture containing trimeric and tetrameric [16] cyclic siloxanes (^{29}Si NMR) and O=CN(Me)CH_2CH_2N(Me).

The reaction of CO_2 with **1** in $CDCl_3$ at room temperature gave only trimeric siloxane and 1,3-dimethyl-2-oxoimidazolidine. If the reaction is performed in the presence of hexamethyltrisiloxane (D3), the product of insertion of silanone into D3 was characterized by mass spectroscopy ($m/e = 527$) and by comparison with an authentic sample [4a].

The reactions of PhNCO, PhNCS and keto derivatives with the pentacoordinated organosilanes were carried out similarly at room temperature. With PhNCO, and also with benzaldehyde and acetone, the thermal decomposition products are always the cyclic siloxanes. With PhNCS and Lawesson's reagent the reactions give silathione. The decompositions of the inserted pentacoordinated cyclic diaminosi-

lanes occur readily under mild conditions (generally 30–40 °C for 2–3 h). With the pentacoordinated acyclic insertion products the decomposition process needs higher temperatures (80–90 °C for 20–24 h) for complete reaction.

The products of insertion of PhNCO and PhNCS into tetracoordinated **5** are stable in refluxing CCl_4 for 12 h. Heating at 120–130 °C for 2 h results in their thermal decomposition to give organic products and cyclic siloxanes or silathianes.

Discussion

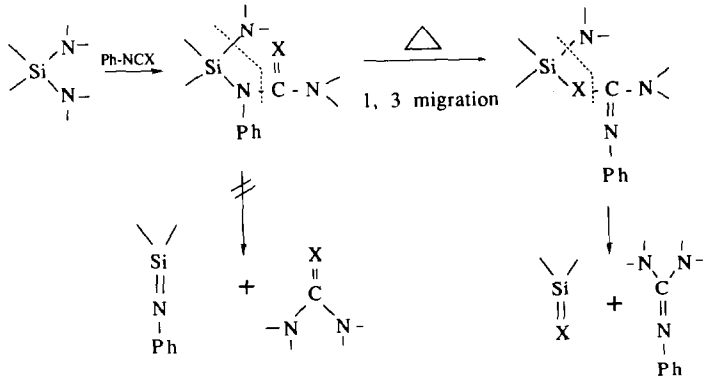
Aminometallation of heterocumulenes is a well-known process in organometallic chemistry. Insertions of carbon dioxide, carbon disulfide, phenyl iso- and isothiocyanate into Si–N, Ge–N, S–N, P–N, and B–N bonds have been described [5b,17]; cyclic systems were found to be especially reactive in the insertion. However, β-elimination from the insertion products has been reported only in the case of germanium compounds; the mechanism of this decomposition scheme was studied in detail by Satgé and al. (eq. 4) [9,13,18,19] who found that low coordinated germanium species are formed as transient intermediates, which were identified by trapping. We thought it of interest to use this approach to make low-coordinated silicon species under mild conditions and also, more importantly, to try to isolate a stable silathione, which would provide strong evidence for the β-elimination scheme.

Before discussing the mechanism, however, we would like to consider some earlier results, as follows. Breederveld has shown that the insertion of CO_2 and CS_2 into the Si–N bond is thermally reversible [20]. Lappert has observed that CO_2 and CS_2 are more reactive than the aryl iso(thio)cyanates towards diaminosilanes, but only CS_2 gives the monoinsertion compound (even when the dipolar species is in excess). In all other cases, bis-ureido species are obtained [5a]. Another significant feature is the higher reactivity of the cyclic diaminosilane towards PhNCO, the diinsertion product being formed (eq. 3).

We found the pentacoordinated diaminosilanes **1**, **4** similarly give insertion of heterocumulenes, but the difference in reactivity between the cyclic and acyclic diaminosilanes is not so pronounced in this case. With CO_2, the diinsertion compound is readily formed in all cases (exothermic reaction). However, the decomposition occurs only for the monoinsertion species, since the organic product is always the 2-oxo-imidazolidine. The decomposition is unexpectedly easy with the cyclic tetracoordinated species (room temperature instead of the 60–90 °C necessary for the pentacoordinated organosilanes derivatives).

As observed by Lappert, CS_2 in excess was found to react immediately with the diaminosilanes, giving the monoinserted compounds. Only in the case of **2** is diinsertion possible, but then, and in contrast to the reaction with CO_2, the decomposition occurs directly with that species, giving silathione and $MeNC(S)SC(S)N(Me)CH_2CH_2$.

In the reaction of the cyclic tetracoordinated silane **5** with CS_2 only the products corresponding to decomposition of the monoinserted species were observed. PhNCO and PhNCS are selective, giving mono or diinsertion depending on the ratio of the reactants. We obtained clear spectroscopic evidences for the initial regioselective formation of ureido (thio)silanes (*N*-silylation). The fact that the thermal decomposition requires high temperatures, and gives only siloxanes and silathio com-



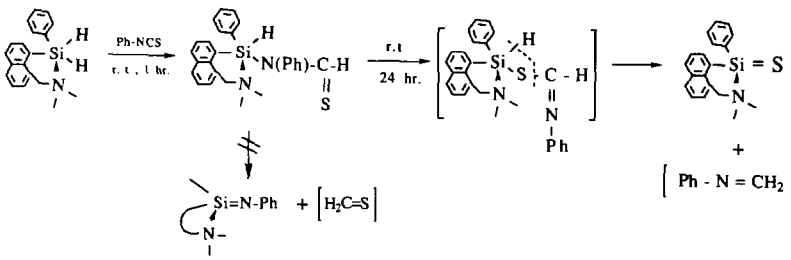
Scheme 5.

pounds (no Si–H species), along with 2-imido-imidazoline, implies that there is a rearrangement before the decomposition step (Scheme 5).

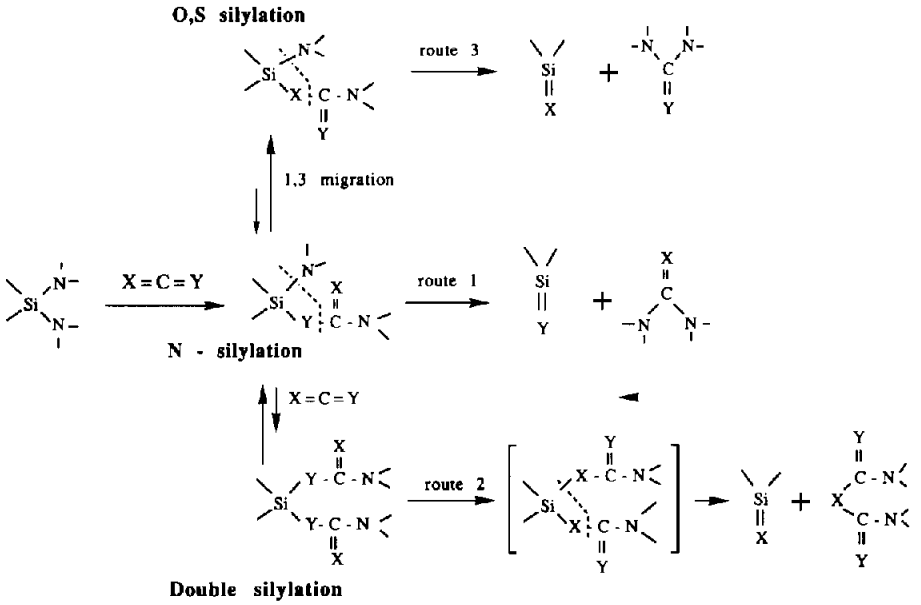
1,3-Migration in amidosilanes is a well-known process [21]. Such a rearrangement was previously suggested to take place during the decomposition of a thioamido pentacoordinated silane [22]. The β-elimination reaction gives the low-coordinated silicon Si=S species and imine (Scheme 6).

All the results could be rationalized in terms of an overall scheme in which there is an equilibrium between mono and diinsertion species, with 1,3 silyl migration occurring when necessary before decomposition (Scheme 7).

In contrast to the isolable N-silylamido species, the monoinsertion compounds with ≡Si–O–C(X)< or ≡Si–S–C(X)< bonds are not thermally stable, and decompose intramolecularly by β-elimination to give the low-coordinated silicon species and ureido derivatives. The process involves nucleophilic attack of X on the electrophilic carbon atom, surrounded by two hetero atoms, and elimination in a 2 + 2 reverse fashion. Silanones have never been isolated [23], and are expected to immediately rearrange to trimers/tetramers. In the case of compound **1**, the transient silanone was trapped with $(Me_2SiO)_3$. On the other hand, since we have shown [1] that zwitterionic base-stabilized silathiones are sufficiently stable in solution to be identified, the compounds we observed giving ^{29}Si NMR signals in the range +30, + 40 ppm can reasonably be assumed to be such species. In the case of tetracoordinated diaminosilane **5** there was no such stabilisation, and the silathione is converted into a dimer/trimer mixture [24]. Only in one case did we observe the decomposition of the diinsertion compound (route 2) to give the silathione and



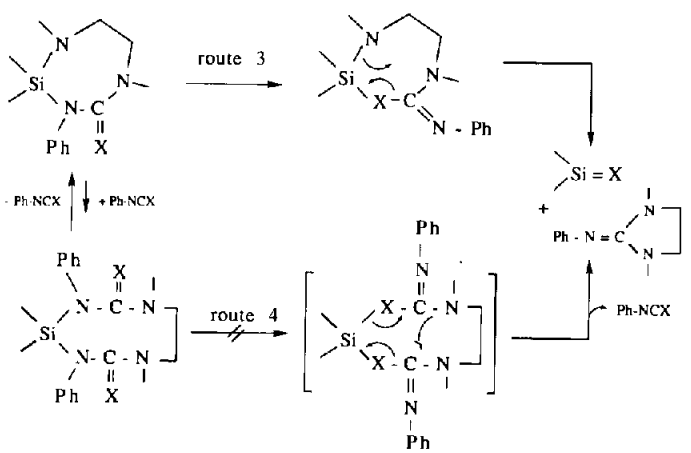
Scheme 6.



Scheme 7.

dithioanhydride and, significantly, the reaction took place at $-20\,^{\circ}C$ (Scheme 8). With the bis-adducts from PhNCS the reverse reaction to regenerate the monoinsertion compound, followed by 1,3-migration and β-elimination, is probably preferred over the direct six-membered ring decomposition process (route 4).

The intramolecular thermal decomposition of cyclic ureidosilanes or analogues to give low coordinated silicon species and 2-substituted imidazolidines, appears to be a general process. In the case of pentacoordinated aminoarylsilicon derivatives it was possible to isolate the intermediate base-stabilized silathiones, confirming the β-elimination mechanism. Work is now in progress to extend the thermal decomposition to other heterocyclic organosilanes.



Scheme 8.

Experimental

All reactions were carried out under argon or nitrogen, with dry and degassed solvents. ^{1}H NMR spectra were recorded on a BRUKER AW60 spectrometer with TMS as an internal reference. ^{29}Si and ^{13}C NMR spectra were recorded on a Bruker SP 250 AC or a Bruker WP 200 SY instrument. Mass spectra were recorded on a Jeol-DX 300 spectrometer (electron-impact mode, 70 eV). Elemental analysis were performed by the Laboratoire de Microanalyse du CNRS, Villeurbanne, France. The organosilicon starting materials were prepared by standard procedures.

Preparation of diaminosilanes

A solution of nBuLi (22 mmol, 2.5 *M* in hexane) was added to a solution of dimethylethylenediamine (1.05 g, 12 mmol) in Et_2O (20 mL) at 0 °C. The mixture was stirred at room temperature for 24 h then slowly added at −20 °C to a solution of (8-dimethylaminomethyl)naphthylphenyldifluorosilane [10] (3.3 g, 10 mmol) in THF (20 mL). After 24 h stirring at room temperature, the mixture was concentrated *in vacuo*. Pentane (50 mL) was added, and the solution filtered through celite to remove LiF. *N,N'*-Dimethyl[(8-dimethylaminomethyl)naphthyl]phenylsila-2-imidazoline, **1**, was isolated after removal of the solvent (3.3 g, 86%). ^{1}H NMR ($CDCl_3$): δ 1.85 (s, 6H, $N(CH_3)_2$); 2.34 (s, 6H, 2 × NCH_3); 3.01 (s, 4H, 2 × NCH_2); 3.42 (s, 2H, $ArCH_2N$); 7.00–8.50 (m, 10H, ArH). ^{13}C NMR ($CDCl_3$): δ −36.33 (q, 2 × NCH_3); 45.30 (q, $N(CH_3)_2$); 52.58 (t, 2 NCH_2); 63.86 (t, CH_2N); 124.4–139.9 (m, C-Ar). ^{29}Si NMR ($CDCl_3$): δ −13.48. Mass spectrum (70 eV): *m/e* 375 ($[M]^+$, 23%). Found: C, 73.07; H, 7.54; N, 10.65; Si. 7.03. $C_{23}H_{29}N_3Si$ calc.: C, 73.54; H, 7.78; N, 11.19; Si, 7.48%.

The similar coupling reaction of lithiated dimethylethylenediamine with 8-(dimethylaminomethyl)-1-naphthylphenyldimethoxysilane [11], in refluxing THF for 24 h, gave **1** in 55% yield.

A suspension of lithiated dimethylethylenediamine (0.01 mol) in Et_2O (20 mL) was added slowly to a solution of [2-(dimethylaminomethyl)phenyl]methyldiethoxysilane [10] (2.6 g, 0.01 mol) in THF (20 mL) at −18 °C. After 36 h stirring at room temperature, pentane (20 mL) was added, and lithium ethanolate filtered off. The solution was concentrated *in vacuo* and the pure diaminosilane, **2**, isolated by distillation: b.p. 95 °C (0.02 mmHg), 1.9 g, 72% with essential characteristics: ^{1}H NMR ($CDCl_3$): δ 0.30 (s, 3H, CH_3); 2.10 (s, 6H, $N(CH_3)_2$); 2.30 (s, 6H, 2 × NCH_3); 2.95 (s, 4H, 2 × CH_2); 3.40 (s, 2H, CH_2N); 6.90–7.50 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$): δ −2.14 (q, $SiCH_3$); 34.66 (q, 2 × NCH_3); 45.96 (q, $N(CH_3)_2$); 52.44 (t, 2 × NCH_2); 64.24 (t, CH_2N); 126.5–146.5 (m, C-Ar). ^{29}Si NMR ($CDCl_3$): δ −3.50. Mass spectrum (70 eV): *m/e* 263 ($[M]^+$, 26%). Found: C, 63.57; H, 9.45; N, 15.58; Si, 10.45. $C_{14}H_{25}N_3Si$ calcd.: C, 63.81, H, 9.56; N, 15.95; Si, 10.66%.

Dilithiated dimethylethylenediamine (prepared as above) (0.01 mol) was added slowly at −18 °C to a solution of [2-(dimethylaminomethyl)phenyl]phenyldimethoxysilane [10] (3 g, 0.01 mol) in THF (20 mL). The mixture was stirred for 36 h at room temperature then pentane (20 mL) was added and the lithium methanolate filtered off. Evaporation of the solvent left a solid, which was recrystallized from pentane at −80 °C to give **3**, a white solid of low m.p. (< 0 °C) (2.7 g, 83%). ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 6H, $N(CH_3)_2$); 2.51 (s, 6H, 2 × NCH_3); 3.07 (s, 4H, 2 × NCH_2); 3.19 (s, 2H, CH_2N); 6.80–7.92 (m, 9H, ArH). ^{13}C NMR ($CDCl_3$): δ

34.80 (q, $2NCH_3$); 45.07 (q, $N(CH_3)_2$); 52.03 (t, $2NCH_2$); 64.04 (t, CH_2N); 126.1–146.8 (m, C-Ar). ^{29}Si NMR ($CDCl_3$): δ −16.01. Mass spectrum (70 eV): *m/e* 326 ($[M]^+$, 9%). Found: C, 69.67; H, 8.56; N, 12.97; Si, 8.74. $C_{19}H_{27}N_3Si$ calc.: C, 69.89; H, 8.64; N, 12.87; Si, 8.60%.

Dimethylamine (0.9 g, 0.02 mol) was lithiated in Et_2O and the solution was added dropwise to [2-dimethylaminomethyl)phenyl]methyldifluorosilane [10] (2.15 g, 0.01 mol) in THF (20 mL) at −20 °C during 1 h. The mixture was allowed to warm to room temperature and stirred overnight. The solution was filtered through Celite, the solvent evaporated off *in vacuo* and compound **4** then isolated by distillation, b.p. 84–87 °C (0.02 mmHg). ^1H NMR ($CDCl_3$): δ 0.18 (s, 3H, $SiCH_3$); 2.07 (s, 6H, $N(CH_3)_2$); 2.34 (s, 12H, $2 \times N(CH_3)_2$); 3.52 (s, 2H, CH_2N); 6.95–7.56 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$): δ 1.58 (q, $SiCH_3$); 38.25 (q, $2 \times N(CH_3)_2$); 45.91 (q, $N(CH_3)_2$); 63.62 (t, CH_2); 126.25–146.1 (m, C-Ar). ^{29}Si NMR ($CDCl_3$): δ −9.10. Mass spectrum (70 eV): *m/e* 265 ($[M]^+$, 11%). Found: C, 64.03; H, 9.85; N, 15.51; Si, 10.64. $C_{14}H_{27}N_3Si$ calc.: C, 63.39; H, 10.18; N, 15.84; Si, 10.56%.

Dilithiated dimethylethylenediamine (0.02 mol), prepared as above, was slowly added to methylphenyldichlorosilane (3.8 g, 0.02 mol) in THF (20 mL) at −20 °C. The mixture was stirred at room temperature for 24 h, pentane was added to precipitate the LiCl. After filtration of the solution and concentration *in vacuo*, the residue was distilled at 65 °C (0.02 mmHg) giving a colourless liquid, identified as pure **5**. NMR characteristics: ^1H NMR ($CDCl_3$): δ 0.29 (s, 3H, SiMe); 2.38 (s, 6H, $2 \times NCH_3$); 2.99 (s, 4H, $2 \times NCH_2$); 7.10–7.70 (m, 5H, ArH). ^{13}C NMR: δ −4.49 (q, $SiCH_3$); 34.72(q, $2 \times NCH_3$); 52.66 (t, $2 \times NCH_2$); 128.0–137.7 (m, C-Ar), ^{29}Si NMR: δ −2.06. Mass spectrum (70 eV): *m/e* 206 ($[M]^+$, 7%).

Coupling reaction with heterocumulenes: typical procedure

Reaction of CS_2 with **2**. A solution of 2-silaimidazolidine, **2**, (3.2 g, 12 mmol) in freshly distilled and degassed $CDCl_3$ (10 mL) was made up in a Schlenk tube kept at −40 °C and CS_2 (1.44 mL, 24 mmol) was added dropwise from a syringe. The colouration changed immediately to orange with separation of a white solid (400 mg), which was identified as dimethylethylenetrithiocarbamate, m.p. 250–252 °C (yield 16–17%). The solution was analyzed by NMR spectroscopy. The ^{29}Si NMR spectrum showed predominantly a broad signal at δ +41. The ^1H and ^{13}C NMR spectra were also recorded, revealing the presence of two compounds: [2-(dimethylaminomethyl)phenyl]methylsilathione and *N,N'*-dimethyl-2-thioimidazolidine [12]. NMR data for 2-$(CH_3)_2NCH_2C_6H_4(CH_3)Si{=}S$ at 25 °C ($CDCl_3$). ^1H NMR: δ 0.60 (s, 3H, $SiCH_3$); 2.58 (br. s, 6H, $N(CH_3)_2$); 3.95 (br. s, 2H, CH_2N). ^{13}C NMR: δ 4.52 (br. s, $SiCH_3$); 45.45–46.45 (br. s, $N(CH_3)_2$), 65.56 (s, CH_2N); 124–137 (m, C-Ar). ^{29}Si NMR: δ 39.5–41.9 (br.). At −50 °C (mixture $CDCl_3$, CD_2Cl_2 50/50). ^1H NMR: δ 0.55 (s, 3H, $SiCH_3$); 2.75–2.85 (2s, 6H, $N(CH_3)_2$); 4.20 (2d, 2H, CH_2N); 6.90–8.10 (m, 4H, ArH). $^{13}C\{^1H\}$ NMR: δ 3.50 (s, $SiCH_3$); 44.9, 46.65 (2 s, $N(CH_3)_2$); 64.42 (s, CH_2N); 124.3–138.6 (m, C-Ar). ^{29}Si NMR: δ +40.75. NMR characteristics of the thiourea: ^1H NMR ($CDCl_3$): δ 2.89 (s, 6H, $2NCH_3$); 3.29 (s, 4H, 2 NCH_2). ^{13}C NMR ($CDCl_3$): δ 35.46 (q, NCH_3); 48.65 (t, NCH_2); 183.75 (s, C=S). The thiourea, identified in the mixture was separated by flash chromatography on silica (eluent $CHCl_3$), and crystallized from pentane (30 mL), as a white solid, 0.97 g (65%), m.p. 109–110 °C. Mass spectrum (70 eV): *m/e* 130 ($[M]^+$, 100%). The filtrate was concentrated *in vacuo* and shown to contain a mixture of

cyclic siloxanes (from hydrolysis during chromatography). ^{29}Si NMR: δ −35, −37 ppm. Mass spectrum (70 eV): *m/e* 772 ($[M]^+$ for tetramer), 579 ($[M]^+$ for trimer).

Reaction of CS_2 (excess) with 2

The above reaction was repeated with an excess of CS_2 (5 mL, 0.1 mol) with **2** (1.6 g, 6 mmol) in $CDCl_3$ (20 mL) at −20 °C. A solid separated and was identified as S=C(-NCH2C(CH3)2CH2NCH2-C(S)S, 440 mg (35% yield). Characteristics of dimethylethylene trithiocarbamate. *Mass spectrum (70 eV): m/e 206 ($[M]^+$, 20%),* 130(100), 115(5), 105(12), 100(5), 98(10), 87(7), 73(25) 60(20), 58(20), 44(40). Found: C, 34.07; H, 4.65; N, 14.16; S, 44.6. $C_6H_{10}N_2S_3$ Calc.: C, 34.95; H, 4.89; N, 13.59; S, 46.57%.

Reaction of 1 with CS_2

A solution of **1** (1.87 g, 5 mmol) in $CDCl_3$ (20 mL) was treated, at −30 °C, with CS_2 (0.3 mL, 5 mmol). After filtration to remove solid dimethylethylene trithiocarbamate (0.4 mmol, 8%) the ^{29}Si NMR spectrum of the filtrate showed the presence of only [8-(dimethylaminomethyl)-1-naphthyl]phenylsilathione [1], δ +22.3. Flash chromatography on silica gave 2-thioimidazolidine, 0.56 g (87%).

When the same procedure was repeated but with an excess of CS_2 (0.05 mol), the trithiocarbamate was first isolated (13% yield). Further treatment as above gave *N,N'*-dimethyl-2-thio-imidazolidine, 0.54 g (83%).

Reaction of 3 with CS_2

By the procedure described above, 3 (3.26 g, 10 mmol) in $CDCl_3$ (20 mL) was treated with CS_2 (0.6 mL, 10 mmol) at 25 °C for 2 h. The ^{29}Si NMR spectrum of the product solution showed a broad peak at +34.2, which became a sharp singlet at −50 °C (δ +34.18 ppm). Chromatography on silica (eluent $CHCl_3$) gave the *N,N'*-dimethyl-2-thioimidazolidine, 1.22 g (94%). Characteristics of the [(2-dimethylaminomethyl)phenyl]phenylsilathione. ^1H NMR ($CDCl_3$): δ 2.40 (br. s, 6H, $NCH_3)_2$); 3.90 (br. s, 2H, CH_2N); 6.60–8.36 (m, 9H, ArH). ^{13}C NMR (25 °C): δ 46.1–46.3 (br. q, $N(CH_3)_2$); 64.64 (br. t, CH_2N); 124.5–146.5 (m, C-Ar). ^{13}C NMR (−50 °C): δ 46.01; 47.67 (2q, $N(CH_3)_2$); 64.94 (t, CH_2N); 124.5–140.5 (m, C-Ar). When the reaction was performed with an excess of CS_2 (10 equivalents) the same organic product, 2-thioimidazolidine was formed (yield 92%). Traces of *N,N'*-dimethylethylenetrithiocarbamate (3%) were separated from the product mixture.

Reaction of 4 with CS_2

(a) A solution of **4** (2.12 g, 8 mmol) in $CDCl_3$ (10 mL) was treated at −25 °C with a stoichiometric amount of CS_2 (0.5 mL), and stirred for 2 h at room temperature. NMR spectrometry showed that 2-methylaminomethylphenylmethylsilathione (^{29}Si δ +41) and tetramethylthiourea were the only products. Chromatography on silica led to isolation of the organic product in 83% yield.

(b) An excess of CS_2 (2 mL) was added dropwise to **4** (1.35 g, 5 mmol) in $CDCl_3$ (10 mL) at −20 °C, and the mixture allowed to warm to room temperature during 15 min. The solution rapidly turned yellow. The ^{29}Si NMR spectrum of the reaction mixture showed the presence of silathione (δ +42) as the only silicon-containing product. Chromatography on silica (eluent $CHCl_3$) and concentration of the solution *in vacuo*, followed by recrystallization from pentane gave the tetramethyltri-

thiocarbamate (0.9 g, 87%), identified from its mass spectrum and by comparison of its spectroscopic properties with those of authentic samples; ^{1}H NMR ($CDCl_3$): δ 3.46. Mass spectrum (70 eV): *m/e* 208 ([*M*]$^+$, 23%), 132 (100).

Reaction of 5 with CS_2

A solution of **5** (2.0 g, 10 mmol) in $CDCl_3$ (10 ml) was treated with CS_2 (0.6 mL, 20 mmol) at $-20\,^\circ$C and the mixture then stirred at room temperature for 45 min. When reaction was complete, NMR spectroscopy showed the presence of two silathianes (dimer and trimer) and the expected organic product *N,N'*-dimethylethylene-2-thio-imidazolidine, which was isolated after chromatography on silica and recrystallization from pentane (77%). NMR data for the phenylmethyl (di- or tri-)silathianes: ^{1}H NMR δ 0.52, 0.74 (2 br. s, 3H, $SiCH_3$); 6.9–7.4 (m, 5H, ArH). ^{13}C NMR: δ −0.58 (q, $SiCH_3$); +3.41 (q, $SiCH_3$). ^{29}Si NMR: δ +4.1, +13.0.

Reaction of 1 with CO_2

A solution of **1** (1.12 g, 3 mmol) and $(Me_2SiO)_3$ (6.66 g, 30 mmol) in $CDCl_3$ (20 mL) was treated with an excess of dry CO_2 (solid) at $-20\,^\circ$C. The mixture was stirred for 24 h at room temperature and its NMR (^{29}Si, ^{1}H) and mass spectra then showed the presence of trimeric (8-dimethylaminomethyl)-1-naphthylphenylcyclotrisiloxane (65% *m/e* = 915) the insertion product 8-dimethylaminomethyl)-1-naphthylphenylhexamethylcyclotetrasiloxane (35% *m/e* = 527), and *N,N*-dimethyl-2-oxo-imidazolidine (83%). Authentic samples [4a] of the organosilanes were available for comparison.

Reaction of 2 with various dipoles

CO_2: An excess of solid CO_2 was added in small portions to **2** (2.1 g, 8 mmol) in $CDCl_3$ (10 mL), at $-50\,^\circ$C. The mixture was stirred at 25 °C for 2 h and its NMR spectra then recorded: ^{1}H NMR: δ 0.51 (s, 3H, $SiCH_3$); 1.96 (s, 6H, $N(CH_3)_2$); 2.74 (s, 6H, $2NCH_3$); 3.25 (s, 4H, $2NCH_2$); 3.35 (s, 2H, CH_2N); 6.74–7.88 (m, 4H, ArH). ^{13}C NMR: δ 0.31 (q, $SiCH_3$); 35.92 (q, $2NCH_3$); 45.42 (q, $N(CH_3)_2$); 47.59 (t, $2NCH_2$); 64.26 (t, CH_2N); 126.9–145.0 (m, C-Ar); 155.0 (s, C=O). ^{29}Si NMR: δ −35.04 (attributed to the diinsertion product).

The mixture was refluxed for 2 h. Examination by NMR and mass spectroscopy showed the presence of siloxane and *N,N'*-dimethyl-2-oxo-imidazolidine, ^{1}H NMR: δ 2.73 (6H); 3.22 (4H). Data for [(2-methylaminomethyl)phenyl]methylcyclosiloxane: ^{1}H NMR (CDCld3): δ 0.51 (br. s, 3H, $SiCH_3$); 2.02–2.09 (m, 6H, $N(CH_3)_2$); 3.50 (m, 2H, CH_2N); mass spectrum (70 eV): *m/e* 772 ([*M*]$^+$ for tetramer), 712, 638, 579 ([*M*]$^+$ for trimer), 519, 478, 386 ([*M*]$^+$ for dimer), 341, 267, 179, 134, 105, 91, 58.

PhNCO: (a) A solution of PhNCO (0.065 g, 3 mmol) in $CDCl_3$ (2 mL) was added rapidly to one of **2** (0.8 g, 3 mmol) in $CDCl_3$ (10 mL) at $-50\,^\circ$C. After 15 min at $-50\,^\circ$C the mixture was allowed warm to ambient temperature and then stirred for 2 h. The ^{29}Si NMR spectrum showed the complete disappearance of **2**; the two signals observed, δ −12.89 (major), −10.95 (minor), were ascribed to O-silyl and N-silyl monoamido species [22]. The ^{1}H NMR spectrum showed only broad signals. ^{13}C NMR: δ 0.61 (q, $SiCH_3$); 35.91, 38.56 (2 q, $2NCH_3$); 46.25 (q, $N(CH_3)_2$); 48.04, 49.49 (2 t, $2NCH_2$); 63.14 (t, CH_2N); 120.2–150.7 (m, C-Ar); 156.5 (s, O–C=N); 162.6 (s, N–C=O).

(b) A similar procedure but starting with two equivalents of PhNCO (6 mmol), gave the same NMR spectra for the insertion product. The mixture was refluxed for 2 h and stirred overnight. The ^{29}Si NMR spectrum then showed the presence of only siloxane (trimer + tetramer see above). Kugelrohr distillation (b.p. 105°C/0.02 mmHg) gave analytically pure *N,N'*-dimethyl-2-phenyliminoimidazolidine [13] (73%). ^{13}C NMR: δ 21.20 (q, C–CH_3); 35.86 (q, 2NCH_3); 49.06 (t, 2NCH_2); 115.62, 122.7, 129.5, 130.2 (4d, C-ArH); 144.2 (s); 147.7 (s); 156.1 (s, C=N). ^{1}H NMR ($CDCl_3$): δ 2.58 (br. s, 2 × NCH_3); 3.20 (br,s, 2 × NCH_2); 6.6–7.4 (m, 5H, ArH). Mass spectrum (70 eV): *m/e* 189 ([*M*]$^+$, 20), 167(20), 135(100), 93(30), 77(80), 69(10), 57(16).

PhNCS: Phenylisothiocyanate (0.7 g, 5 mmol), was slowly added at 0°C to a solution of **2** (1.35 g, 5 mmol) in $CDCl_3$ (10 mL), the solution immediately turning yellow. After 20 min ^{29}Si NMR spectroscopy showed the absence of **2** and the presence of the monoinsertion product. ^{29}Si NMR: δ −10.75. ^{13}C NMR: δ −0.11 (q, $SiCH_3$); 37.83, 41.87 (2q, 2NCH_3); 46.37 (q, N$(CH_3)_2$); 49.82, 54.26 (t, 2NCH_2); 63.79 (t, CH_2N); 120.4–137.1 (m, C–Ar); 193.1 (s, N–C=S).

The mixture was refluxed at 60°C for 2 h. NMR spectroscopy then showed the presence of 2-(methylaminomethyl)phenylmethylsilathione and *N,N'*-dimethyl-2-phenyliminoimidazolidine, identified by comparison with samples prepared as described above.

$CH_3C_6H_4N{=}C{=}NC_6H_4CH_3$: A solution of di-*p*-tolylcarbodiimide (0.364 g, 3.45 mmol) in $CDCl_3$ (5 mL) was added at room temperature to a solution of **2** (0.92 g, 3.45 mmol) in $CDCl_3$ (5 mL). The mixture was stirred overnight without any change. It was then refluxed for 48 h and the *N*-silylimido insertion product then shown to be present by NMR spectroscopy. [^{1}H NMR (broad signals): δ 0.26 (3H, $SiCH_3$); 2.0 (12 H, 2CH_3–Ar + N$(CH_3)_2$); 2.37–2.47 (6H, 2NCH_3); 2.80–3.40 (2m, 6H, CH_2N + 2 × NCH_2). ^{13}C NMR: δ 1.4 (q, $SiCH_3$); 21.10 (q, C–CH_3); 37.5 (br q, NCH_3); 46.0 (q, N$(CH_3)_2$; 51.3–52.4 (2 br t, NCH_2); 63.4 (t, CH_2N); 120.1–148.2 (m, C-Ar); 151.7 (s C=N). ^{29}Si NMR: δ −11.34.] The solvent was removed *in vacuo*, and the residue heated at 120–130°C for 5 h. Addition of $CDCl_3$ (20 mL) afforded a clear solution, the NMR spectrum of by which showed the presence of only one silicon product, assumed to be [2-(methylaminomethyl)phenyl]methyl, *N*-ptolylsilaimine (^{29}Si NMR: δ −20.76), and *N,N'*-dimethyl-2-*p*-tolylimino-imidazolidine: the latter was isolated by distillation, b.p. 110°C/0.05 mmHg, 550 mg (85% yield) and identified by comparison with a sample prepared as described above. NMR data for the silaimine: ^{13}C NMR: δ 1.50 (q, $SiCH_3$); 21.20 (q, CH_3–Ar); 45.4 (q, N$(CH_3)_2$); 65.42 (t, CH_2N); 117.16–147.9 (m, C-Ar). Hydrolysis followed by extraction with chloroform gave the expected siloxane.

PhCHO: Benzaldehyde (0.3 mL, 3 mmol) was added dropwise to a solution of **2** (0.8 g, 3 mmol) in $CDCl_3$ (10 mL) at room temperature. The reaction was exothermic. The mixture was stirred for 12 h, and then examined by NMR spectroscopy which showed the presence of the expected siloxane (see above) and *N,N'*-dimethyl-2-phenylimidazolidine [13]. The latter was separated by distillation, b.p. 127°C/0.02 mmHg, 450 mg (85%).

$CH_3C(O)CH_3$: Dry acetone (0.16 g, 2.8 mmol) was added slowly to **2** (0.726 g, 2.75 mmol) in $CDCl_3$ (10 ml) at room temperature and the mixture was stirred for 24 h then examined by ^{1}H NMR spectroscopy, which show the presence of siloxane (δ 0.15 (3H); 1.95 (6H); 3.45 (2H); 7–8 (4H)) and *N,N'*-dimethyl-2-dimethylim-

idazolidine (δ 0.76 (6H, $2 \times NCH_3$); 2.09 (6H, $2 \times NCH_3$); 2.57 (4H, $2 \times NCH_2$)) which was identified by comparison with an authentic sample [13].

Lawesson's reagent

A solution of **2** (2.6 g, 10 mmol) in $CDCl_3$ (5 mL) was added at room temperature to a stoichiometric amount of 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4- disulfide (4 g, 10 mmol) in $CDCl_3$ (5 mL). The mixture was refluxed for 2 h and the solvent then evaporated *in vacuo*. Pentane was added (50 mL) and a solid separated. The solution was filtered, the pentane removed, and the residue extracted into $CDCl_3$. The ^{2}Si NMR and ^{13}C spectra showed the presence of 2-dimethylaminomethylphenylmethylsilathione, ^{29}Si δ +41. The solid product was dissolved in CH_2Cl_2, and flash chromatographed over silica to give pure *N,N'*-dimethyl-2-*p*-methoxyphenylphosphonoimidazolidine, 1.7 g (66%). ^{1}H NMR ($CDCl_3$): δ 2.45 (d, 6H, P–N–CH_3, ^3J(P–H) 12.6 Hz); 3.22 (d, 4H, P–N–CH_2, ^2J(P–H) 9.6 Hz); 2.81 (s, 3H, OCH_3); 6.8–7.1 and 7.6–8.0 (2m, 4H, ArH). ^{13}C{^{1}H} NMR: 31.83 (d, NCH_3, ^2J(P–C), 6Hz); 49.06 (d, NCH_2, ^2J(P–C) 6 Hz); 55.11 (s, OCH_3); 113.31 (d, 2C (Ar), ^2J(P–C) 15 Hz); 125.7 (d, C–P, ^1J(P–C) 123 Hz); 133.64 (d, 2C-Ar, ^2J(P–C) 12 Hz); 162.17 (s, C–O). Mass spectrum (70 eV): *m/e* 256 ([*M*]$^+$, 100), 223(40), 213(10), 200(40), 180(15), 170(42), 163(55), 155(18), 139(20), 121(38), 108(7), 92(10), 85(70), 74(15), 61(35), 58(21).

Reactions of 4 with heterocumulenes

CO_2: An excess of CO_2 (dry ice) was added in small portions to **4** (1.82 g, 6.9 mmol) in $CDCl_3$ (30 mL), and the mixture was stirred for 2 h. The ^{1}H NMR spectrum showed that diinsertion had occurred: δ 0.56 (s, 3H, $SiCH_3$); 2.01 (s, 6H, $(CH_3)_2$); 2.78 (s, 12H, $4 \times NCH_3$); 3.40 (s, 2H, CH_2N); 6.85–8.10 (m, 4H, ArH). ^{29}Si NMR: δ −30.3. The solution was concentrated and kept at 90 °C for 20 h. The NMR and mass spectra showed the presence of 2-(dimethylaminomethyl)phenylmethylsiloxane (trimer and tetramer), and tetramethylurea. The organic product (650 mg, 81%) was isolated by distillation (b.p. 43 °C/0.1 mmHg) and compared with an authentic sample.

PhNCO (monoinsertion): A solution of phenylisocyanate (1.6 g, 13.4 mmol) in $CDCl_3$ (10 mL) was added dropwise to **4** (3.55 g, 13.4 mmol) in $CDCl_3$ (10 mL) at 0 °C. NMR spectroscopy showed that no starting **4** remained, and that the monoinsertion silicon compound was present. ^{13}C NMR: 1.26 (q, $SiCH_3$); 38.41–38.43 (2 br. q, $2 \times N(CH_3)_2$); 63.96 (t, CH_2N); 119.9–146.3 (m, C–Ar); 156.5 (s, O–C=N); 162.5 (s, N–C=O). ^{29}Si NMR: δ −12.4 (broad). The mixture was concentrated *in vacuo* and kept at 130 °C for 2 h. Kugelrohr distillation then gave *N*-phenyltetramethylamidine, b.p. 67 °C/0.02 mmHg, 1.9 g (75%). ^{1}H NMR: 2.78 (br. s, 12H, $2 \times N(CH_3)_2$), 68–73 (m, 5H, ArH). Mass spectrum (70 eV): *m/e* 191 ([*M*]$^+$, 100).

PhNCO (diinsertion): A solution of phenylisocyanate (1.6 g, 13.4 mmol) in $CDCl_3$ (10 mL) was added dropwise to **4** (1.8 g, 6.7 mmol) in $CDCl_3$ (10 mL) at 0 °C. After 2 h stirring at room temperature, NMR spectroscopy showed that **4** had been completely converted into the diinserted compound: ^{13}C NMR: δ 1.75 (q, $SiCH_3$); 38.09 (q, $2 \times N(CH_3)_2$); 45.63 (q, $N(CH_3)_2$); 63.97 (t, CH_2N); 120.3–146.2 (m, C-Ar), 155.6 (s, O–C=N). ^{29}Si NMR: δ −22.1. The mixture was evaporated *in vacuo* and the residue heated at 90 °C for 30 h. Kugelrohr distillation gave $PhN{=}C(NMe_2)_2$, 0.75 g (59%), identified as above.

Reaction of **5** *with heterocumulenes*

CO_2: A large excess of CO_2 was slowly added in portions to **5** (2 g, 10 mmol) in $CDCl_3$ (20 mL). After 20 h stirring at room temperature the mixture was concentrated *in vacuo* and the residue extracted into pentane. The NMR spectra of the solution show the presence of $(PhMeSiO)_{3,4}$ (40%), and *N,N*-dimethyl-2-oxoimidazolidine (35%), which was identified by comparison with authentic samples. NMR ($CDCl_3$) data for the siloxanes: ^{29}Si NMR: δ −21.8, −23.4 (2m, trimer); −32.4, −33.0 (2m, tetramer).

PhNCO (monoinsertion): A solution of phenylisocyanate (1.2 g, 10 mmol) in $CDCl_3$ (5 mL) was added at room temperature to **5** (2 g, 10 mmol) in $CDCl_3$ (5 mL). The mixture was stirred for 2 h then examined by NMR spectroscopy: ^{13}C NMR: δ 2.05 (q, $SiCH_3$); 36.03, 38.37 (2q, NCH_3); 51.21–51.32 (2t, NCH_2); 120–142 (m, C–Ar); 162.6 (s, N–C=O). ^{29}Si NMR: δ −12.90 (major); −10.69 (minor). No change was evident after the solution had been refluxed for 2 h and so the solvent was removed *in vacuo*, and the residue heated at 130 °C for 2 h. Thermal decomposition gave an untractable mixture, in which siloxane (trimer) and *N,N*-dimethyl-2-oxo-imidazolidine were identified by mass spectrometry, but were present in low yields.

PhNCO (diinsertion): Phenylisocyanate (2.4 g, 20 mmol) was added to **5** (10 mmol) as above, and NMR spectra of the $CDCl_3$ solution recorded after 2 h at room temperature. ^{29}Si NMR: 4 signals δ −10.69, −12.94, −16.69, −20.56 in a relative ratio 5/45/20/30. ^{13}C NMR ($CDCl_3$): δ −3.64, −2.03 ($SiCH_3$); 36.01, 38.38, 38.51 (NCH_3); 49.71, 50.58, 51.17, 51.28 (NCH_2); 120–148 (C–Ar); 162.5, 164.6 (N–C=O). The mixture was evaporated *in vacuo* and the residue refluxed with CCl_4 for 10 h. Kugelrohr distillation gave analytically pure *N,N*-dimethyl-2-phenyliminoimidazolidine, 1.3 g (69%), identified by comparison with an authentic sample (see above).

PhNCS: A solution of phenylisothiocyanate (0.4 g, 3 mmol) in $CDCl_3$ (5 mL) was added at room temperature to **5** (0.63 g, 3 mmol) in $CDCl_3$ (5 mL) and the mixture was stirred for 2 h. Analysis by NMR spectroscopy showed that monoinsertion had occurred: ^{13}C NMR: δ 2.15 (q, $SiCH_3$); 38.36, 42.27 (2q, $2NCH_3$); 50.01, 54.34 (2t, $2NCH_2$); 192.9 (s, N–C=S). ^{29}Si NMR: δ −11.74. The solvent was removed, and the residue maintained at 70 °C for 2 h. Extraction with pentane (50 mL) followed by evaporation of the extract *in vacuo* left a gum, which was examined by NMR spectroscopy ($CDCl_3$), which showed the presence of phenylmethylcyclosilathiane (dimer and trimer), characterized as above (^{29}Si NMR: +4.09, +12.99), and *N,N*-dimethyl-2-phenyliminoimidazolidine (30%).

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