Synthesis, structures and oxidative addition reactions of new thermally stable silylenes; crystal structures of [$\overline{Si\{N(}$ $CH_2{}^tBu)\}_2C_6H_4$-1,2] and [($\overline{Si\{N(CH_2{}^tBu)\}_2C_6H_4}$-1,2)($\mu$-E)]$_2$ (E = Se or Te) [1]

Barbara Gehrhus [a], Peter B. Hitchcock [a], Michael F. Lappert [a,*], Joachim Heinicke [b],
Roland Boese [c], Dieter Bläser [c]

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK*
[b] *Institut für Anorganische Chemie der Universität Greifswald, Soldmannstr. 16, D-17487 Greifswald, Germany*
[c] *Institut für Anorganische Chemie der Universität-GH Essen, Universitätsstr. 5-7, D-45117 Essen, Germany*

Abstract

Treatment of the N,N'-dineopentyl-1,2-phenylenediamine 4-RC$_6$H$_3$[NH(CH$_2{}^t$Bu)]$_2$-1,2 (R = H or Me) with successively two equivalents of n-butyllithium and one of SiCl$_4$ yields the appropriate N,N'-dineopentyl-1,2-phenylenediaminodichlorosilane $\overline{Si[\{N(CH_2{}^t}$Bu)]$_2C_6H_3$-1,2-R-4]Cl$_2$ (R = H, **1**, or R = Me, **2**). The thermally stable, yellow, diamagnetic, volatile, crystalline silylene $\overline{Si[\{N(CH_2{}^t}$Bu)]$_2C_6H_3$-1,2-R-4] (R = H, **3**, or R = Me, **4**) is obtained from **1** or **2** by reaction with potassium in refluxing tetrahydrofuran. The silylene **3** undergoes oxidative addition with (i) MeI or EtOH to give [$\overline{Si\{N(CH_2{}^t}$Bu)]$_2C_6H_4$-1,2)(X)Y (X = Me and Y = I, **5**, or X = OEt and Y = H, **6**), or (ii) a chalcogen E to afford [($\overline{Si\{N(CH_2{}^t}$Bu)}$_2C_6H_4$-1,2)($\mu$-E)]$_2$ (E = S, **7**, Se, **8** or Te, **9**). Spectroscopic data are provided for compounds **1–9** and single crystal X-ray diffraction results for compounds **3**, **8** and **9**. The average Si–N distances are 1.750(4) Å for the silylene **3**, 1.719(4) Å for the cyclodisilaselenane **8** and 1.729(3) Å for the cyclodisilatellurane **9**, the N–Si–N' angles being 88.2(1)° for **3**, 93.5(2)° for **8** and 93.7(1)° for **9**.

Keywords: Silicon; Silylenes; Bis(amino)dichlorosilanes; Cyclodi(silachalcogenides); Cyclodisilaselenane; Cyclodisilatellurane; Crystal structure

1. Introduction

Divalent, two-coordinate silicon compounds SiX$_2$ ($\overline{X}$ being a monodentate ligand) are known as silylenes. As transients, they were first reported about 30 years ago and have continued to be of considerable interest [1]. Initially they were identified by trapping reactions, later also by matrix isolation techniques. They are useful synthons in organosilicon chemistry, having a range of reactivity comparable with carbenes. Unlike CX$_2$, transient SiX$_2$ molecules invariably have a singlet electronic ground state, with a much larger singlet–triplet energy separation than CX$_2$.
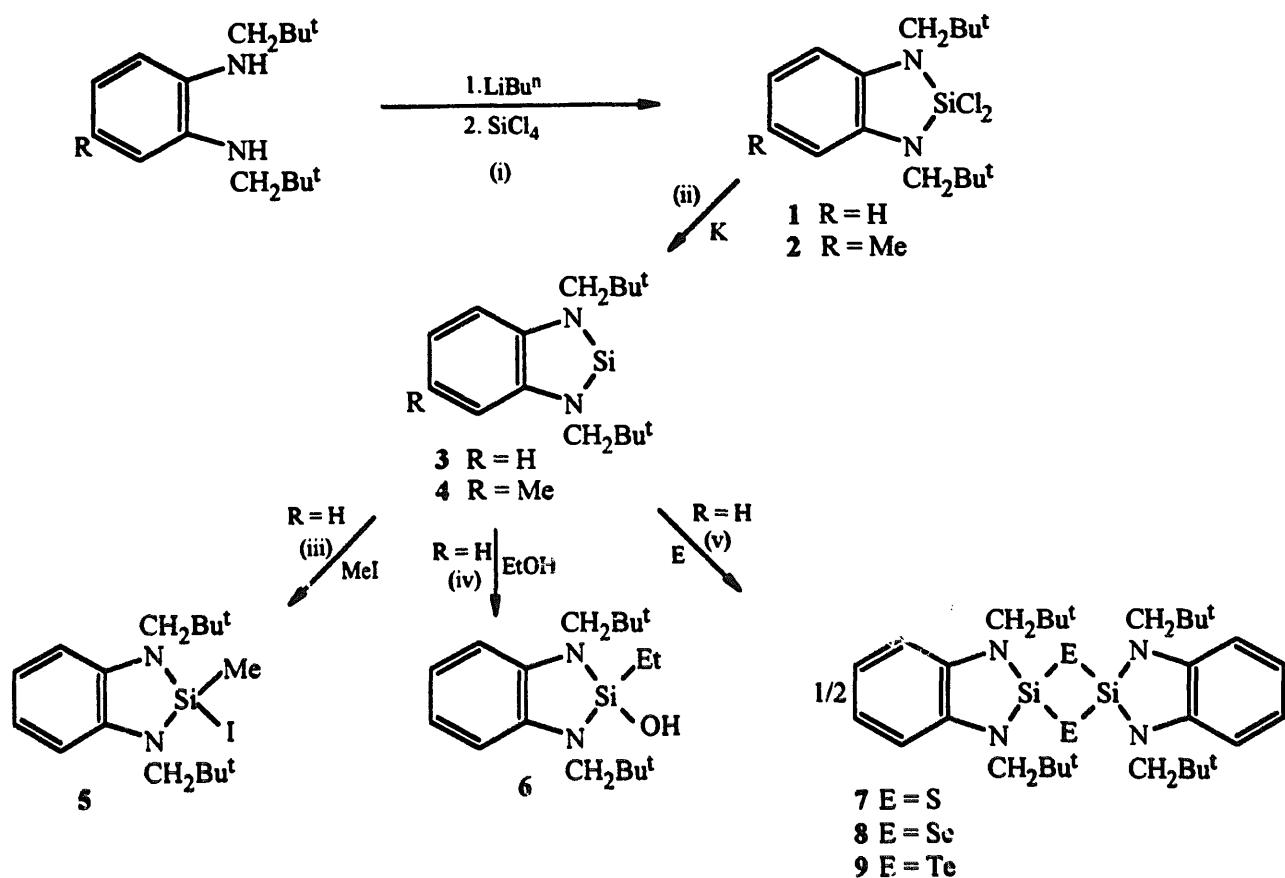
Two notable examples of crystalline mononuclear, silicon(II) compounds **A** and **B**, related to silylenes but having a higher silicon coordination number, have been reported. Decamethylsilicocene Si(η^5-C$_5$Me$_5$)$_2$ **A**, has two molecules in the crystalline unit cell, one with Si at the inversion centre and the other with an angle of 25.3° between the two C$_5$Me$_5$ planes [2]. The molecule $\overline{Si[(}$PMe$_2$)$_2$C(SiMe$_3$)] **B** has a distorted pseudo-trigonal bipyramidal structure with silicon as the spiro centre [3].

The synthesis and gas phase structure of the first thermally stable (b.p. 85°C/0.1 Torr) silylene $\overline{Si[N(^t}$Bu)CHCHN^{t}Bu] **C** was reported in 1994 [4]. By contrast, another bis(amino)silylene $\overline{Si[N(^t}$Bu)]$_2$SiMe$_2$ was stable only below 77 K [5].

The silicocene **A** underwent a number of oxidative addition reactions, yielding: (i) [Si(η-C$_5$Me$_5$)$_2$(μ-E)]$_2$ (E = S or Se) by treatment with S$_8$ or Bu$_3$P=Se [6]; (ii)

* Corresponding author.
[1] Dedicated to Professor R. Corriu, as a mark of esteem and friendship.
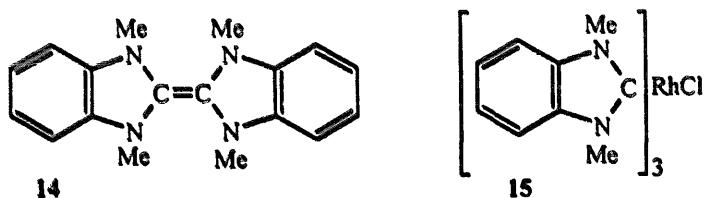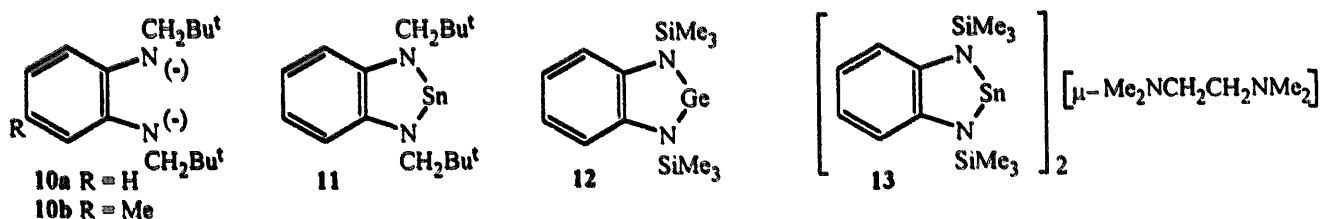
Scheme 1. Synthesis and reactions of the bis(amino)silylenes **3** and **4**, yielding the Si(IV) compounds **5–9**.

[Si(η-C$_5$Me$_5$)$_2$]$_2$(μ-Te)(μ-Te$_2$) D with Bu$_3$P=Te [6];
(iii) Si(η-C$_5$Me$_5$)$_2$(H)X with X = F, Cl, Br, OCOCF$_3$,
OCOEt, OPh, OC$_6$H$_4$Me-4, SC$_6$H$_4$Me-4, or ON=CRR'

(CRR' = HMe or C(CH$_2$)$_4$CH$_2$) [7]; (iv) Si(η^5-C$_5$Me$_5$)$_2$(OC$_6$H$_3$O-2-R-4) with (HO)$_2$C$_6$H$_3$R-4 (R = H or Me) [7]. With elemental selenium or tellurium it

reacted only at elevated temperatures to give a complicated mixture of products [6].

The silylene C afforded oxidative elimination products with Ph_3CN_3 to give $\overline{Si[N('Bu)CHCHN'Bu]}$ $(=NR)L$ (R = CPh_3 and L = THF) or $\overline{Si[N('Bu)CH}$ $\overline{CHN'Bu]}(N_3)[N(SiMe_3)_2]$ with Me_3SiN_3; but C did not react with $Et_3Si–H$ [8].

In a preliminary communication we reported: (i) that reduction of the dichlorosilane $\overline{Si[\{N(CH_2'Bu)\}_2C_6H_3-}$ 1,2-R-4]Cl$_2$ (R = H, 1, or Me, 2) with potassium yielded the crystalline silylene $\overline{Si[\{N(CH_2'Bu)\}_2C_6H_3-1,2-R-4]}$ (R = H, 3, or Me, 4); (ii) the first X-ray structure of a silylene, namely 3; (iii) that oxidative addition of MeI or EtOH to 3 gave $[\overline{Si\{N(CH_2'Bu)\}_2C_6H_4-1,2](X)Y}$ (X = Me and Y = I, 5, or X = OEt and Y = H, 6) [9]. We now provide full details of (i)–(iii); (iv) show that 3 undergoes facile oxidative addition reactions with a chalcogen yielding $[(\overline{Si\{N(CH_2'Bu)\}_2C_6H_4-1,2})(\mu-E)]_2$ (E = S, 7, Se, 8 or Te, 9); (v) provide single crystal X-ray diffraction data for the cyclodisilaselenane 8 and the cyclodisilatellurane 9.

2. Results and discussion

The N,N'-disubstituted arenediamides $[\overline{N(R')}]_2C_6H_3-$ 1,2-R-4 10 (R' = $CH_2'Bu$ and R = H, 10a, or Me, 10b) were chosen as the chelating ligands in our quest for a thermally stable, crystalline silylene. Earlier we had used 10a to stabilise a stannylene 11 [10], while a stable

germylene 12 [11] or the stannylene analogue as the TMEDA adduct 13 [10] had been obtained with another ligand 10 (R' = $SiMe_3$ and R = H); and carbon(II) had been characterised as the electron-rich olefin 14 or a derived carbenerhodium(I) complex 15 [12].

Treatment of the dilithium N,N'-dineopentyl-1, 2-phenylenediamidodilithium compound $4-R-C_6H_3-$ $[N(Li)(CH_2'Bu)]_2-1,2$ (R = H, I, or Me, II) (their synthesis and structures will be reported elsewhere), prepared in situ from the diamine and $2Li^nBu$, with a slightly greater than an equimolar portion of silicon tetrachloride yielded the pale yellow, viscous bis(amino)dichlorosilane $\overline{Si[\{N(CH_2'Bu)\}_2C_6H_3-1,2-R-}$ 4]Cl$_2$ (R = H, 1, 77% or R = Me, 2, 80%) ((i) in Scheme 1). Prolonged heating under reflux of 1 or 2 in THF with two equivalents of potassium ((ii) in Scheme 1), followed by removal of solvent, and for 3 extraction into hexane, evaporation and distillation of the residue gave an orange oil of the silylene 3; sublimation yielded yellow crystals of 3 (65%) or for 4 sublimation of the residue gave yellow crystals of the silylene 4 (50%).

The bis(amino)silylenes 3 (m.p. 61°C, b.p. 112–113°C/10^{-4} Torr) and 4 (m.p. 88°C, subl. at 10^{-5} Torr from a bath at 150°C) are evidently thermally stable. They were soluble in hydrocarbons. They gave satisfactory microanalytical data, multinuclear NMR spectra and showed, in high intensity, the parent molecular monocation in their EI mass spectra.

The bis(amino)silylene 3 readily underwent an oxidative addition with iodomethane, ethanol, or a chalcogen

Table 1
Interatomic bond lengths (Å) and angles (deg) in compound 3

Si–N(1)	1.752(3)	Si–N(2)	1.747(3)
N(1)–C(6)	1.385(5)	N(1)–C(7)	1.459(4)
N(2)–C(5)	1.380(5)	N(2)–C(12)	1.461(4)
C(1)–C(2)	1.382(6)	C(1)–C(6)	1.392(5)
C(2)–C(3)	1.375(6)	C(3)–C(4)	1.372(6)
C(4)–C(5)	1.396(6)	C(5)–C(6)	1.417(5)
C(7)–C(8)	1.544(6)	C(8)–C(9)	1.510(7)
C(8)–C(10)	1.527(5)	C(8)–C(11)	1.519(6)
C(12)–C(13)	1.535(5)	C(13)–C(14)	1.514(6)
C(13)–C(15)	1.522(5)	C(13)–C(16)	1.519(6)
N(1)–Si–N(2)	88.2(1)	Si–N(1)–C(6)	114.1(2)
Si–N(1)–C(7)	122.6(3)	C(6)–N(1)–C(7)	123.0(3)
Si–N(2)–C(5)	114.1(2)	Si–N(2)–C(12)	123.7(3)
C(5)–N(2)–C(12)	121.9(3)	C(2)–C(1)–C(6)	120.2(3)
C(1)–C(2)–C(3)	120.3(4)	C(2)–C(3)–C(4)	120.7(4)
C(3)–C(4)–C(5)	120.5(3)	N(2)–C(5)–C(4)	129.2(3)
N(2)–C(5)–C(6)	111.9(3)	C(4)–C(5)–C(6)	118.9(3)
N(1)–C(6)–C(1)	129.3(3)	N(1)–C(6)–C(5)	111.3(3)
C(1)–C(6)–C(5)	119.4(4)	N(1)–C(7)–C(8)	117.0(3)
C(7)–C(8)–C(9)	110.9(4)	C(7)–C(8)–C(10)	107.1(3)
C(9)–C(8)–C(10)	109.9(4)	C(7)–C(8)–C(11)	110.0(3)
C(9)–C(8)–C(11)	109.8(4)	C(10)–C(8)–C(11)	109.1(4)
N(2)–C(12)–C(13)	116.2(3)	C(12)–C(13)–C(14)	111.1(3)
C(12)–C(13)–C(15)	107.5(3)	C(14)–C(13)–C(15)	110.0(3)
C(12)–C(13)–C(16)	110.5(3)	C(14)–C(13)–C(16)	109.2(3)
C(15)–C(13)–C(16)	108.4(3)		

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for compound 3

	x	y	z	U_{eq} [a]
Si	3158(1)	0	7456(1)	55(1)
N(1)	3704(1)	1888(5)	8212(2)	50(1)
N(2)	2527(1)	1797(6)	7565(2)	48(1)
C(1)	3687(2)	5307(8)	9288(3)	60(1)
C(2)	3298(2)	6880(8)	9602(3)	66(2)
C(3)	2635(2)	6841(8)	9221(3)	66(2)
C(4)	2347(2)	5231(8)	8532(3)	54(1)
C(5)	2724(2)	3593(6)	8212(3)	47(1)
C(6)	3408(2)	3647(6)	8594(3)	49(1)
C(7)	4405(2)	1508(7)	8494(3)	55(1)
C(8)	4804(2)	2542(7)	7799(3)	58(2)
C(9)	4769(2)	5083(9)	7808(4)	87(2)
C(10)	5507(2)	1772(10)	8204(3)	86(2)
C(11)	4552(2)	1677(9)	6724(3)	82(2)
C(12)	1841(2)	1347(7)	7103(3)	54(1)
C(13)	1572(2)	2272(7)	6029(3)	53(1)
C(14)	1644(2)	4809(8)	6006(3)	70(2)
C(15)	857(2)	1625(9)	5697(3)	84(2)
C(16)	1923(2)	1212(8)	5299(3)	72(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

((iii)–(v) respectively in Scheme 1) to give [Si{N(CH₂ᵗBu)}₂C₆H₄-1,2](X)Y (X = Me and Y = I, 5, 95%; or X = OEt and Y = H, 6, 95%) or [(Si{N(CH₂ᵗBu)}₂C₆H₄-1,2)(μ-E)]₂ (E = S, 7, 72%; Se, 8, 89%; or Te, 9, 82%).

Some of the above oxidative addition reactions of the bis(amino)silylene 3 have parallels with earlier data on the behaviour of bis(amino)germylenes and -stannylenes M[N(SiMe₃)₂]₂(M = Ge or Sn) with (i) MeI to yield M[N(SiMe₃)₂]₂(Me)I [13] and (ii) a chalcogen to give [M{N(SiMe₃)₂}₂(μ-E)]₂ (E = S, Se or Te) [14]. The cyclic bis(amido)germanium(II) or -tin(II) compounds M[N(Buᵗ)]₂SiMe₂, likewise afforded similar cyclic chalcogenides [(M{N(ᵗBu)}₂SiMe₂)(μ-E)]₂ [15], but a six-membered Ge(II) cyclic amide Ge[N(ᵗBu)Si(Me)N-(ᵗBu)]₂ with S₈ gave a four-coordinate Ge(IV) compound, having three Ge–N endocyclic and a Ge–S exocyclic bonds [16]. The amides M[N(SiMe₃)₂]₂ readily underwent M–N cleavage with protic compounds,
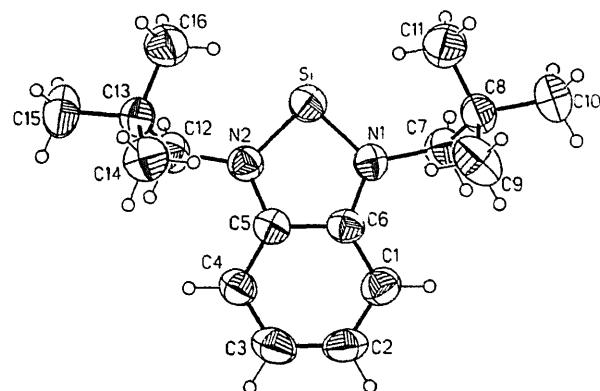

Fig. 1. Molecular structure of [Si{N(CH₂ᵗBu)}₂C₆H₄-1,2] (3) with the atom numbering scheme.

by contrast to the reaction of 3 with EtOH, to yield the oxidative adduct 6 (although using an excess of EtOH caused cleavage of the endocyclic Si–N bonds to occur); the latter reaction ((iv) in Scheme 1) is similar to that between Ge[CH(SiMe₃)₂]₂ and EtOH giving Ge[CH(SiMe₃)₂]₂(OEt)H [17] and those between the silicocene A with a phenol (see Introduction) [7]. It is interesting that A did not readily react with Se or Te, and under forcing conditions gave unidentified mixtures, although with S₈ [Si(η⁵-C₅Me₅)₂(μ-S)]₂ was obtained [6].

The molecular structure of the crystalline silylene 3, with atom labelling, is shown in Fig. 1; there are no close contacts between monomeric units [9]. The ᵗBu fragments of the neopentyl groups are arranged cis- to one another and out of the SiN₂(C₂)C₆H₄ near-plane, the nitrogen atoms are in an essentially trigonal planar environment, the sum of the bond angles at each N being 359.7(3)°. The two-coordinate (N–Si–N′, 88.2(1)°) silicon atom is sited in a lipophilic pocket, the distance between the closest H-atoms at C(11) and C(16) being 3.61 Å. Bond lengths and angles are shown in Table 1 and non-hydrogen atomic coordinates in Table 2. From the electron diffraction data for the gaseous silylene Si[N(ᵗBu)CHCHN′ᵗBu] C, five geometric parameters were determined and these, together with corresponding X-ray data for 3, are listed in Table 3

Table 3
Some comparative structural and NMR spectra data for the silylenes Si[N(ᵗBu)CHCHN′ᵗBu] C and Si[{N(CH₂ᵗBu)}₂C₆H₄-1,2] 3 and the cyclodisilachalcogenides 8 and 9

Compound	Si–N (Å)	N–C$_{sp³}$ [a] (Å)	C$_{sp²}$–C′$_{sp²}$ [b] (Å)	N–Si–N′ (deg)	N–C$_{sp³}$–C′$_{sp³}$ [b] (deg)	$\delta[^{29}Si(^1H)]$ [c]	$\delta[^{15}N]$ [d]
C	1.753(5)	1.400(9)	1.347(21)	90.5(10)	114.1(5)	78.3	−170.3
3	1.752(3)	1.385(5)	1.417(5)	88.2(1)	111.9(3)	96.92 [e]	−225.0
	1.747(3)	1.380(5)			111.3(3)		
8	1.718(4)	1.413(5)	1.408(6)	93.5(2)	113.4(4)		
	1.720(4)	1.401(5)			112.4(4)		
9	1.727(3)	1.408(3)	1.409(4)	93.67(12)	113.3(2)		
	1.732(2)	1.412(4)			113.2(2)		

[a] N(1)–C(6) and N(2)–C(5) for 3. [b] C and C′ refer to C(5) and C(6) for 3. [c] Relative to SiMe₄. [d] Relative to MeNO₂.
[e] This may be compared with δ −40.7 for [C]Cl₂ [4], δ −24.08 for 1, δ −24.02 for 2 and δ 97.72 for 4. Thus the ²⁹Si NMR spectral chemical shift difference between 1 and [1]Cl₂ (= 4) = 121 ppm, which compares well with the 119 ppm between C and [C]Cl₂.
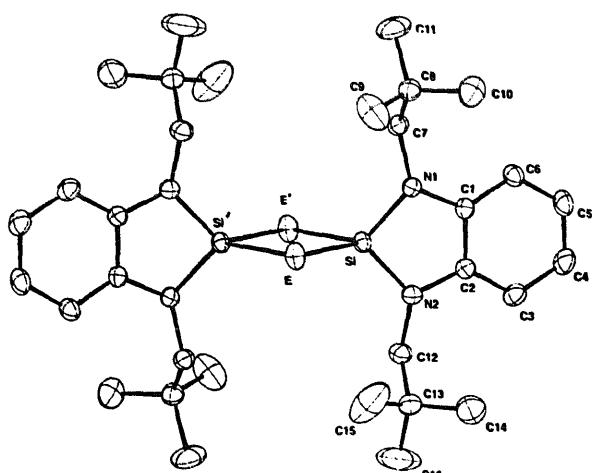
Fig. 2. Molecular structures of [(Si{N(CH$_2$Bu)}$_2$C$_6$H$_4$-1,2)(μ-E)]$_2$ (E = Se (8) or Te (9)).

(which, additionally, shows some comparative X-ray data for the cyclodisilachalcogenides 8 and 9 and ^{29}Si and ^{15}N NMR spectroscopic chemical shifts); in our preliminary publication [9] these experimentally determined molecular dimensions for 3 and C were compared with those derived from MO calculations on model compounds [4,18,19]. Such calculated data, as well as UV photoelectron spectra, are also available for models more closely relevant to 3 [19]. We have previ-

ously concluded that C=C–N delocalisation is less important than N–Si in stabilising the silylenes C, 3 and 4 [9].

The molecular structures of the crystalline isomorphous cyclodisilaselenane 8 and cyclodisilatellurane 9, with atom labelling, are shown in Fig. 2 (E = Se or Te). Bond lengths and angles are shown in Tables 4 (8) and 5 (9) and non-hydrogen atom coordinates in Tables 6 (8) and 7 (9). In 8 or 9, the four-membered SiESiE ring core is planar, the centre of the ring being an inversion centre and the endocyclic angle at silicon being wider (8, 93.6(2)°, 9, 93.67(12°) than at the chalcogen (8, 83.02(5)°; 9, 82.13(3)°). The benzene ring and attached N atoms in both structures 8 and 9 are co-planar and make an angle of 12° with the SiN$_2$ plane. Each of the atoms C(7), C(12) and Si is bent out of the C$_6$N$_2$ plane in the same direction (deviation (Å): C(7) 0.27, C(12) 0.33, Si 0.25 for E = Se; C(7) 0.30, C(12) 0.37, Si 0.26 for E = Te). The SiN$_2$ planes make angles of 90° with the central Si$_2$E$_2$ plane.

The Si–N (8, 1.718(4) and 1.721(3) Å; 9 1.727(3) and 1.732(2) Å) bond lengths in the SiNCCN ring of the cyclodisilachalcogenide are reduced by ca. 0.02 Å compared with corresponding lengths in the parent silylene 3, see Table 3. A similar reduction of M–N bond lengths was noted when comparing [M{N(SiMe$_3$)$_2$}$_2$(μ-Te)]$_2$/M[N(SiMe$_3$)$_2$]$_2$ (M = Ge [16] or Sn [17]) pairs,

Table 4
Interatomic bond lengths (Å) and angles (deg) for compound 8

Se–Si	2.294(1)	Se–Si'	2.255(1)
Si–N(1)	1.721(3)	Si–N(2)	1.718(4)
N(1)–C(1)	1.402(5)	N(1)–C(7)	1.473(5)
N(2)–C(2)	1.415(5)	N(2)–C(12)	1.461(6)
C(1)–C(6)	1.387(6)	C(1)–C(2)	1.409(6)
C(2)–C(3)	1.376(6)	C(3)–C(4)	1.388(6)
C(4)–C(5)	1.370(6)	C(5)–C(6)	1.386(6)
C(7)–C(8)	1.543(6)	C(8)–C(9)	1.507(7)
C(8)–C(10)	1.526(6)	C(8)–C(11)	1.524(7)
C(12)–C(13)	1.541(7)	C(13)–C(14)	1.492(7)
C(13)–C(15)	1.490(10)	C(13)–C(16)	1.549(10)
Si–Se–Si'	83.02(5)	N(2)–Si–N(1)	93.6(2)
N(2)–Si–Se'	118.76(13)	N(1)–Si–Se'	118.69(13)
N(2)–Si–Se	115.37(14)	N(1)–Si–Se	115.04(13)
Se–Si–Se'	96.98(5)	C(1)–N(1)–C(7)	121.5(3)
C(1)–N(1)–Si	109.5(3)	C(7)–N(1)–Si	125.2(3)
C(2)–N(2)–C(12)	120.0(4)	C(2)–N(2)–Si	109.7(3)
C(12)–N(2)–Si	126.3(3)	C(6)–C(1)–N(1)	127.0(4)
C(6)–C(1)–C(2)	119.5(4)	N(1)–C(1)–C(2)	113.5(3)
C(3)–C(2)–N(2)	127.8(4)	C(3)–C(2)–C(1)	119.8(4)
N(2)–C(2)–C(1)	112.4(3)	C(2)–C(3)–C(4)	120.0(4)
C(5)–C(4)–C(3)	120.4(4)	C(4)–C(5)–C(6)	120.5(4)
C(5)–C(6)–C(1)	119.7(4)	N(1)–C(7)–C(8)	117.6(4)
C(9)–C(8)–C(10)	108.9(5)	C(9)–C(8)–C(7)	110.9(4)
C(10)–C(8)–C(7)	112.4(4)	C(9)–C(8)–C(11)	110.1(5)
C(10)–C(8)–C(11)	108.5(4)	C(7)–C(8)–C(11)	105.9(4)
N(2)–C(12)–C(13)	118.0(5)	C(14)–C(13)–C(15)	110.3(7)
C(14)–C(13)–C(12)	113.9(4)	C(15)–C(13)–C(12)	110.3(5)
C(14)–C(13)–C(16)	107.2(6)	C(15)–C(13)–C(16)	109.5(7)

Symmetry transformations used to generate equivalent atoms (denoted by primes): $-x,- y,- z$.

Table 5
Interatomic bond lengths (Å) and angles (deg) for compound 9

Te–Si	2.533(1)	Te–Si'	2.489(1)
Si–N(2)	1.727(3)	Si–N(1)	1.732(2)
N(1)–C(1)	1.408(3)	N(1)–C(7)	1.461(4)
N(2)–C(2)	1.412(4)	N(2)–C(12)	1.463(4)
C(1)–C(6)	1.384(4)	C(1)–C(2)	1.409(4)
C(2)–C(3)	1.384(4)	C(3)–C(4)	1.401(5)
C(4)–C(5)	1.373(6)	C(5)–C(6)	1.396(5)
C(7)–C(8)	1.548(5)	C(8)–C(9)	1.503(6)
C(8)–C(10)	1.514(5)	C(8)–C(11)	1.528(6)
C(12)–C(13)	1.532(5)	C(13)–C(15)	1.495(8)
C(13)–C(14)	1.505(6)	C(13)–C(16)	1.529(9)
Si'–Te–Si	82.13(3)	N(2)–Si–N(1)	93.67(12)
N(2)–Si–Te'	119.15(10)	N(1)–Si–Te'	118.78(10)
N(2)–Si–Te	114.57(10)	N(1)–Si–Te	114.14(9)
Te'–Si–Te	97.87(3)	C(1)–N(1)–C(7)	121.5(2)
C(1)–N(1)–Si	109.1(2)	C(7)–N(1)–Si	124.9(2)
C(2)–N(2)–C(12)	120.2(3)	C(2)–N(2)–Si	109.3(2)
C(12)–N(2)–Si	125.7(2)	C(6)–C(1)–N(1)	126.7(3)
C(6)–C(1)–C(2)	120.0(3)	N(1)–C(1)–C(2)	113.3(2)
C(3)–C(2)–C(1)	119.8(3)	C(3)–C(2)–N(2)	127.0(3)
C(1)–C(2)–N(2)	113.2(2)	C(2)–C(3)–C(4)	119.8(3)
C(5)–C(4)–C(3)	120.2(3)	C(4)–C(5)–C(6)	120.6(3)
C(1)–C(6)–C(5)	119.7(3)	N(1)–C(7)–C(8)	118.4(3)
C(9)–C(8)–C(10)	109.2(4)	C(9)–C(8)–C(11)	110.2(4)
C(10)–C(8)–C(11)	107.8(4)	C(9)–C(8)–C(7)	110.8(3)
C(10)–C(8)–C(7)	112.9(3)	C(11)–C(8)–C(7)	105.8(3)
N(2)–C(12)–C(13)	118.6(3)	C(15)–C(13)–C(14)	110.0(6)
C(15)–C(13)–C(16)	110.2(7)	C(14)–C(13)–C(16)	106.6(5)
C(15)–C(13)–C(12)	111.0(4)	C(14)–C(13)–C(12)	113.2(3)

Symmetry transformations used to generate equivalent atoms (denoted by primes): $-x$, $-y$, $-z$.

or $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}Se)]_2$ with $Sn[N(SiMe_3)_2]_2$ [14]. The geometric parameters relating to the immediate Group 14 element environment in four of these cyclodimetallatelluranes are available for comparison in

Fig. 3. In each compound the endocyclic bond angles are acute at E and obtuse at the Group 14 element.

The cyclodisilatellurane 9 appears to be the only one of three crystallographically characterised cyclic sili-

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound 8

	x	y	z	U_{eq}
Se	−716.8(4)	1919.7(7)	−167.6(3)	43(1)
Si	484.5(9)	342.9(17)	−688.1(6)	33(1)
N(1)	165(3)	−248(5)	−1606(2)	32(1)
N(2)	1493(2)	1630(5)	−861(2)	35(1)
C(1)	720(3)	810(6)	−2049(2)	30(1)
C(2)	1472(3)	1866(6)	−1636(2)	32(1)
C(3)	2065(3)	2998(6)	−1999(2)	41(1)
C(4)	1930(4)	3076(7)	−2769(3)	48(1)
C(5)	1184(3)	2086(7)	−3172(2)	43(1)
C(6)	572(3)	953(6)	−2818(2)	38(1)
C(7)	−774(3)	−1143(6)	−1919(2)	36(1)
C(8)	−723(3)	−3162(6)	−2173(2)	41(1)
C(9)	−347(5)	−4395(7)	−1529(3)	79(2)
C(10)	−60(4)	−3404(7)	−2783(3)	63(2)
C(11)	−1785(4)	−3693(9)	−2487(4)	83(2)
C(12)	2063(3)	2901(8)	−346(3)	55(1)
C(13)	3130(4)	2344(11)	−21(3)	75(2)
C(14)	3818(4)	2109(11)	−591(3)	79(2)
C(15)	3113(5)	640(16)	434(5)	175(6)
C(16)	3533(6)	3967(17)	485(5)	179(6)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for compound 9

	x	y	z	U_{eq}
Te	−803.1(2)	2097.3(3)	−195.1(1)	42(1)
Si	529.3(6)	374.0(11)	−735.2(4)	32(1)
N(1)	194(2)	−199(3)	−1653(1)	33(1)
N(2)	1532(2)	1677(4)	−896(1)	35(1)
C(1)	737(2)	886(4)	−2082(2)	31(1)
C(2)	1489(2)	1924(4)	−1661(2)	32(1)
C(3)	2071(3)	3085(5)	−2008(2)	43(1)
C(4)	1916(3)	3200(5)	−2777(2)	50(1)
C(5)	1174(3)	2200(5)	−3185(2)	48(1)
C(6)	574(2)	1043(5)	−2841(2)	40(1)
C(7)	−749(2)	−1046(4)	−1966(2)	37(1)
C(8)	−730(3)	−3026(5)	−2244(2)	44(1)
C(9)	−357(5)	−4295(6)	−1622(3)	89(2)
C(10)	−100(4)	−3255(6)	−2850(3)	68(1)
C(11)	−1808(4)	−3486(8)	−2564(3)	90(2)
C(12)	2077(3)	2971(5)	−380(2)	47(1)
C(13)	3148(3)	2513(7)	−32(2)	58(1)
C(14)	3840(4)	2242(9)	−589(3)	83(2)
C(15)	3171(5)	883(15)	453(5)	172(5)
C(16)	3527(5)	4180(15)	421(4)	151(4)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.
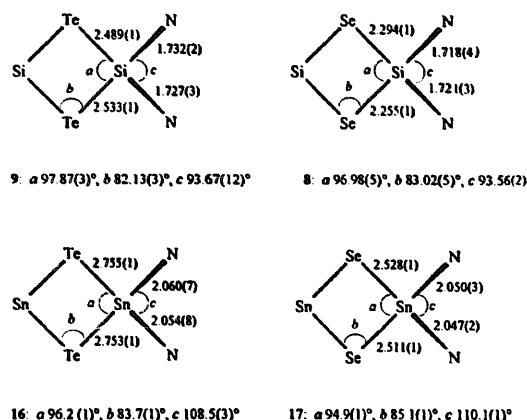
Fig. 3. Diagramatic representation of the geometry about the Group 14 metal atom in the cyciodimetallaselenanes and -telluranes 8, 9, 16 [14b] and 17 [14b].

con–tellurium compounds (and the first to have an SiTeSiTe ring), the others being [Si(η^5-C$_5$Me$_5$)$_2$]$_2$(μ-Te)(μ-Te$_2$) D [6] and [Si(C$_6$H$_2$Me$_3$-2,4,6)$_2$]$_2$(μ-Te) E [20], obtained from [Si(C$_6$H$_2$Me$_3$-2,4,6)$_2$]$_2$ and tellurium. The Si–Te bond lengths in the three compounds are very similar: 2.489(1) and 2.533(1) Å in 9, 2.529(2) Å in D [6] and 2.524(3) Å in E [20]. Among other Si–Te compounds, X-ray diffraction data are available for a number of complexes containing the TeSi(SiMe$_3$)$_3$ ligand, including trans-[Mg{TeSi(SiMe$_3$)$_3$}$_2$(THF)$_2$] with l(Si–Te) = 2.504(1) Å [21] and SiPh$_3$(TeH) with l(Si–Te) = 2.511(1) Å [22].

X-ray structures are known for two cyclodisilathianes [SiX$_2$(μ-S)]$_2$ (X = Me [23] or O^{t}Bu [24]), but apparently not for Se analogues, although compounds such as [(SiEt$_2$)(μ-Se)]$_2$ [25] and ASeASe [6] have been reported. The cyclodisilaselenane 8 appears to be the first compound having an SiSeSiSe ring for which structural data are available, although three other SiSe compounds have been thus characterised: [Si(C$_6$H$_2$Me$_3$-2,4,6)$_2$]$_2$-(μ-Se) F [20], [Si{C(SiMe$_3$)$_3$}]$_2$(μ-Se)$_2$(μ-Se$_2$) G [26] and [Si{C(SiMe$_3$)$_3$}]$_2$(μ-Se)$_3$ H [27]; the Si–Se bond lengths in 8 are 2.256(1) and 2.294(1) Å compared with mean values of 2.306(2) Å in F, 2.323(2) Å in G and ranging from 2.234 to 2.331 Å in H. In (SiH$_3$)$_2$Se, the Si–Se bond length was reported to be 2.27(2) Å [28].

Two further tetravalent silicon compounds derived from the ligand 10a were prepared: [Si{N(CH$_2$^{t}Bu)}$_2$-C$_6$H$_4$-1,2](X)Y (X = Me = Y, 18, and X = H, Y = Cl, 19); the reaction of the diamine 1,2-C$_6$H$_4$[N(CH$_2$-^{t}Bu)H]$_2$ with successively Li^{n}Bu and SiCl$_2$Me$_2$ or Si(H)Cl$_3$ gave 18 and 19 respectively.

3. Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. The NMR spectra were recorded in [^{2}H$_6$]-benzene at 298 K using Bruker instruments: Bruker AC-P 250 at 250 MHz (^{1}H) or 62.86 MHz (^{13}C) and AMX 500 at 99.33 MHz (^{29}Si) and referenced internally to residual solvent resonances (data in δ). Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. ^{15}N NMR spectral chemical shifts were determined by the INEPT method from $^3J[^1$H–^{15}N].

3.1. N,N'-Bis(neopentyl)-1,2-phenylenedi(amino)dichlorosilane 1

A solution of [HN(CH$_2$^{t}Bu)]$_2$C$_6$H$_4$-1,2 (20 g, 80.6 mmol) in hexane (400 ml) was dilithiated with Li^{n}Bu (100.75 ml of a 1.6 mol dm^{-3} n-hexane solution, 161.2 mmol) and the mixture was stirred overnight. The solvent was removed in vacuo and benzene (300 ml) was added to the residue to which SiCl$_4$ (11.1 ml, 97 mmol, 20% excess) was added with stirring. The mixture was refluxed for 4 h. The solid (LiCl) was filtered off and the precipitate was washed several times with benzene. The combined filtrate and washings were evaporated, leaving a viscous oil. Distillation yielded 1 (21.4 g; 77%) as a pale yellow, viscous oil, b.p. 116–117°C/10^{-4} Torr. ^{1}H NMR: δ 0.95 (CMe$_3$, 18 H, s), 3.17 (CH$_2$, 4 H, s) and 6.67–6.77 (phenyl, 4 H, m); ^{13}C{^{1}H} NMR: δ 29.02 (C Me$_3$), 33.67 (C Me$_3$), 55.57 (CH$_2$), 139.0, 110.53 and 119.36 (phenyl); ^{29}Si{^{1}H} NMR: δ –24.08. MS: m/z 344 (M$^+$, 38%).

3.2. 4-Methyl-N,N'-bis(neopentyl)-1,2-phenylenedi-(amino)dichlorosilane 2

Using a procedure similar to that described in Section 3.1., from [HN(CH$_2$^{t}Bu)]$_2$C$_6$H$_3$-1,2-Me-4 (8.9 g, 34 mmol), a Li^{n}Bu (68 mmol) hexane solution and SiCl$_4$ (4.3 ml, 37.4 mmol, 10% excess), there was obtained compound 2 (9.8 g, 80%) as a pale yellow, viscous oil, b.p. 116°C/10^{-4} Torr. ^{1}H NMR: δ 0.95 and 0.96 (CMe$_3$, 18 H, 2 s), 3.17 and 3.19 (CH$_2$, 4 H, 2 s), 2.27 (CH$_3$, 3 H, s) and 6.65 (phenyl, 3 H, s); ^{13}C{^{1}H} NMR: δ 28.82 and 28.88 (C Me$_3$), 33.61 and 33.64 (C Me$_3$), 55.45 and 55.6 (CH$_2$), 21.48 (CH$_3$), 110.44, 111.61, 119.55, 128.26, 136.87 and 139.02 (phenyl); ^{29}Si{^{1}H} NMR: δ –24.02. MS: m/z 358 (M$^+$, 35%).

3.3. N,N'-Bis(neopentyl)-1,2-phenylenedi(amino)silylene 3

A solution of 1 (15.5 g, 44.9 mmol) in THF (50 ml) was added to K (3.51 g, 89.9 mmol) in THF (200 ml) and the mixture was stirred at 70–80°C for 2 days. Filtration yielded a red-brown solution from which

volatiles were removed in vacuo. The residue was extracted into hexane, the extract was filtered and the filtrate was evaporated to leave a viscous red oil. Distillation yielded the silylene **3** (8.0 g, 65%), as an orange oil, b.p. 112–113°C/10^{-4} Torr. Further purification was achieved by sublimation, yielding **3** as a yellow solid, m.p. 61°C. ^{1}H NMR: δ 0.89 (CMe$_3$, 18 H, s), 3.58 (CH$_2$, 4 H, s), 7.01 (phenyl, 4H, s); ^{13}C{^{1}H} NMR: δ 28.72 (*C*Me$_3$), 33.17 (*C*Me$_3$), 54.91 (CH$_2$), 141.48, 110.67 and 118.48 (phenyl), ^{15}N NMR: δ −225.0; ^{29}Si{^{1}H} NMR: δ 96.92. MS: *m/z* 274 (M$^+$, 50%). Anal. Found: C, 69.7; H, 9.53; N, 10.13. C$_{16}$H$_{26}$N$_2$Si. Calc.: C, 70.0; H, 9.55; N, 10.21%. UV: λ_{max} in C$_6$H$_{14}$, 344 (w, sh), 296 and 249 nm.

3.4. 4-Methyl-N,N'-bis(neopentyl)-1,2-phenylenedi-(amino)silylene 4

A solution of **2** (12.4 g, 34.5 mmol) in THF (50 ml) was added to K (2.7 g, 69.1 mmol) in THF (150 ml). After stirring the suspension at 70–80°C for 1 day, the precipitate was filtered off and the solvent was removed from the filtrate in vacuo. Sublimation of the residue at 10^{-5} Torr from a bath at 150°C gave the yellow solid silylene **4** (4.9 g, 50%), m.p. 88°C. ^{1}H NMR: δ 0.91 and 0.92 (CMe$_3$, 18 H, 2 s), 3.60 and 3.62 (CH$_2$, 4 H, 2 s), 2.39 (CH$_3$, 3 H, s), 6.82–6.96 (phenyl, 3 H, m); ^{13}C{^{1}H} NMR: δ 28.76 and 28.73 (*C*Me$_3$), 33.18 and 33.22 (*C*Me$_3$), 55.88 and 55.01 (CH$_2$), 21.53 (CH$_3$), 139.59, 141.64, 127.48, 110.39, 111.36 and 119.33 (phenyl); ^{29}Si{^{1}H} NMR: δ 97.72. MS: *m/z* 288 (M$^+$, 35%). Anal. Found: C, 70.2; H, 9.73; N, 9.5. C$_{17}$H$_{28}$N$_2$Si. Calc.: C, 70.8; H, 9.78; N, 9.71%.

3.5. N,N'-Bis(neopentyl)-1,2-phenylenedi(amino)(iodo)-(methyl)silane 5

Iodomethane (0.16 ml, 2.55 mmol) was added to a solution of the silylene **3** (0.7 g, 2.55 mmol) in benzene (10 ml). The yellow colour of **3** was immediately discharged. After stirring for 4 h, the solvent was removed in vacuo and the residual solid was recrystallised from pentane at −25°C, yielding **5** (1.0 g, 95%), m.p. 89°C. ^{1}H NMR: δ 0.84 (CMe$_3$, 18 H, s), 1.03 (CH$_3$, 3 H, s), 2.94, 3.00, 3.10 and 3.16 (CH$_2$, 4 H, *AB*-type) and 6.78–7.5 (phenyl, 4 H, m); ^{13}C{^{1}H} NMR: δ 11.94 (CH$_3$), 28.85 (*C*Me$_3$), 33.51 (*C*Me$_3$), 55.42 (CH$_2$), 110.68, 118.98 and 139.61 (phenyl); ^{29}Si{^{1}H} NMR: δ −8.9. MS: *m/z* 416 (M$^+$, 43%).

3.6. [N,N'-Bis(neopentyl)-1,2-phenylenedi(amino)]-(ethyl)silanol 6

Ethanol (0.13 ml, 2.19 mmol) was added to a solution of **3** (0.6 g, 2.19 mmol) in benzene (10 ml). The yellow colour of **3** was immediately discharged. After

stirring for 4 h, the solvent was removed in vacuo, the residual oil was distilled yielding **6** (0.66 g, 95%), b.p. 106–107°C/5 × 10^{-2} Torr. ^{1}H NMR: δ 0.93 (CMe$_3$, 18 H, s). 3.06, 3.11, 3.14 and 3.20 (CH$_2$, 4 H, *AB*-type), 1.05 (CH$_3$, 3 H, t), 3.45 (OCH$_2$, 2 H, q), 5.6 (H, 1 H, s) and 6.7–7.0 (phenyl, 4 H, m); ^{13}C{^{1}H} NMR: δ 28.97 (*C*Me$_3$), 34.35 (*C*Me$_3$), 54.9 (CH$_2$), 18.09 (CH$_3$), 58.1 (OCH$_2$), 108.81, 117.91 and 140.33 (phenyl); ^{29}Si{^{1}H} NMR: δ −31.3. MS: *m/z* 320 (M$^+$, 75%).

3.7. Di[N,N'-bis(neopentyl)-1,2-phenylenediamino]cy-clodisilathiane 7

A solution of the silylene **3** (1.5 g, 5.47 mmol) in toluene (30 ml) was added to a suspension of sulphur (0.175 g, 5.47 mmol) in toluene (50 ml) at −78°C. After stirring at this temperature for 1 h, the solution was allowed to warm up to room temperature. The solvent was removed in vacuo to about half of its volume, the precipitate was redissolved by heating and the suspension was filtered hot. After 1 day, colourless crystals of **7** (1.2 g, 72%), m.p. 295°C, were obtained. ^{1}H NMR: δ 1.1 (CMe$_3$, 18 H, s), 3.45 (CH$_2$, 4 H, s, broad) and 6.87–6.92 (phenyl, 4 H, m); ^{13}C{^{1}H} NMR: δ 29.79 (*C*Me$_3$), 34.31 (*C*Me$_3$), 53.79 (CH$_2$), 110.77, 118.73 and 138.53 (phenyl); ^{29}Si{^{1}H} NMR: δ −21.66. MS: *m/z* 612 (M$^+$, 55%). Anal. Found: C, 62.6; H, 8.49; N, 8.95. C$_{32}$H$_{52}$N$_4$S$_2$Si$_2$. Calc.: C, 62.7; H, 8.55; N, 9.14%.

3.8. Di[N,N'-bis(neopentyl)-1,2-phenylenediamino]cy-clodisilaselenane 8

The silylene **3** (0.7 g, 2.55 mmol) in toluene (30 ml) was added to a suspension of selenium (0.2 g, 2.55 mmol) in toluene (30 ml). After stirring for 1 h at room temperature and then for 2 h at 80°C, the hot suspension was filtered. Cooling to room temperature gave colourless crystals of **8** (0.8 g, 89%), m.p. > 300°C (decomp.). ^{1}H NMR: δ 1.13 (CMe$_3$, 18 H, s), 3.48 (CH$_2$, 4 H, s), 6.91 (phenyl, 4 H, s); ^{13}C{^{1}H} NMR: δ 30.07 (*C*Me$_3$), 34.22 (*C*Me$_3$), 54.10 (CH$_2$), 111.09, 118.82 and 138.76 (phenyl); ^{29}Si{^{1}H} NMR: δ −40.44. MS: *m/z* 708 (M$^+$, 47%). Anal. Found: C, 54.7; H, 7.46; N, 7.63. C$_{32}$H$_{52}$N$_4$Se$_2$Si$_2$. Calc.: C, 54.4; H, 7.41; N, 7.93%.

3.9. Di[N,N'-bis(neopentyl)-1,2-phenylenediamino]cy-clodisilatellurane 9

The silylene **3** (0.5 g, 1.82 mmol) in toluene (30 ml) was added to a suspension of tellurium (0.23 g, 1.82 mmol) in toluene (30 ml). The mixture was kept at 100°C for 30 h. The resulting olive suspension was filtered, the filtrate was reduced in volume, then filtered hot. The filtrate was cooled to room temperature, yielding yellow plates of **9** (0.6 g, 82%), m.p. > 180°C

(decomp.). ^{1}H NMR ([^{2}H$_8$]toluene): δ 1.21 (CMe$_3$, 18 H, s), 3.54 (CH$_2$, 4 H, s) and 6.88–6.89 (phenyl, 4 H, m); ^{13}C{^{1}H} NMR ([^{2}H$_8$]toluene): δ 29.39 (CMe$_3$), 32.98 (CMe$_3$), 53.63 (CH$_2$), 110.36, 117.75 (phenyl). MS: m/z 804 (M$^+$, 13%). Anal. Found: C, 47.7; H, 6.56; N, 6.91. C$_{32}$H$_{52}$N$_4$Si$_2$Te$_2$. Calc.: C, 47.8, H, 6.52; N, 6.97%.

3.10. Di[N,N'-bis(neopentyl)-1,2-phenyldiamino]di-(methyl)silane 18

A solution of [HN(CH$_2^t$Bu)]$_2$C$_6$H$_4$-1,2 (4.0 g, 16.1 mmol) in hexane (50 ml) was dilithiated with Li^{n}Bu (22 ml of a 1.5 mol dm^{-3} hexane solution, 33 mmol) at 0°C, and SiCl$_2$Me$_2$ (2.1 g, 16.2 mmol) was added. The mixture was stirred for 5 days at 20°C, then filtered. The solvent was evaporated from the filtrate. Distillation of the residue afforded compound 18 (2.7 g, 55%), b.p. 90–100°C/0.08 Torr. ^{1}H NMR: δ 0.24 (Me, 6 H, s), 0.91 (CMe$_3$, 18 H, s), 2.98 (CH$_2$, 4 H, s), 6.76 (phenyl, 2 H, m) and 6.88 (phenyl, 2 H, m); ^{13}C{^{1}H} NMR: δ 1.76 (Me), 29.8 (CMe$_3$), 34.6 (CMe$_3$), 56.8 (CH$_2$), 109.0, 118.3 and 143.5 (phenyl); ^{29}Si{^{1}H} NMR: δ 15.8; ^{15}N NMR: δ −317.9.

3.11. Di[N,N'-bis(neopentyl)-1,2-phenylenediamino]-chlorosilane 19

A solution of [HN(CH$_2^t$Bu)]$_2$C$_6$H$_4$-1,2 (5.0 g, 20 mmol) in hexane (100 ml) was dilithiated with Li^{n}Bu (26 ml of a 1.53 mol dm^{-3} hexane solution, 40 ml) at

0°C, and Si(H)Cl$_3$ (3.4 g, 25 mmol) was added drop-wise. The mixture was stirred for 5 days at 20°C, then filtered and the precipitate was washed with diethyl ether. Volatiles were evaporated from the combined filtrate and washings. Distillation of the residue afforded compound 19 (3.0 g, 48%), b.p. 83–85°C/0.03 Torr, which solidified after about 1 week, m.p. 54–55°C. ^{1}H NMR: δ 0.85 (CMe$_3$, 18 H, s), 3.09 (CH$_2$, 4 H, s), 6.41 (SiH, 1 H, s), 6.73 and 6.87 (phenyl, 4 H, m); ^{13}C{^{1}H} NMR: δ 28.4 (CMe$_3$), 34.04 (CMe$_3$), 54.5 (CH$_2$), 109.8, 118.7 and 139.5 (phenyl); ^{29}Si{^{1}H} NMR: δ −19.45. MS: m/z 312 (M$^+$, 11%). Anal. Found: C, 61.6; H, 9.23; N, 8.8. C$_{16}$H$_{27}$ClN$_2$Si. Calc.: C, 61.8; H, 8.75; N, 9.01%.

3.12. X-ray structure determination for 3, 8 and 9

Unique data sets were collected at 293(2) K on a Siemens P4 (3, at Essen) or an Enraf–Nonius CAD4 (8 and 9, Sussex) diffractometer with monochromated Mo K α radiation, λ = 0.7107 Å, using a crystal sealed in a Lindemann capillary under argon. Data were corrected for absorption based on ψ scans for 8 and 9, but not for 3. For 3, refinement was based on F and reflections with I > 2σ(I), using SHELXTL-PLUS; refinement of the Rodgers η parameter could not unambiguously define the absolute structure because of the very small anomalous dispersion contributions of the Si atoms. For 8 and 9, refinement was based on F^2 and all reflections, using SHELXL-93. Hydrogen atoms were included in a riding mode.

Table 8
X-ray crystal structure details for compounds 3, 8 and 9

Parameter	3	8	9
Formula	C$_{10}$H$_{26}$N$_2$Si	C$_{32}$H$_{52}$N$_4$Se$_2$Si$_2$	C$_{32}$H$_{52}$N$_4$Si$_2$Te$_2$
M$_r$		706.9	804.2
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2	P2$_1$/n	P2$_1$/n
a (Å)	21.219(5)	13.545(1)	13.555(2)
b (Å)	5.332(3)	7.265(1)	7.371(3)
c (Å)	13.633(4)	18.165(3)	18.406(5)
β (deg)	104.32(2)	97.64(1)	98.84(2)
V (Å^3)	1663.0(6)	1771.6(4)	1817.2(9)
T (K)	293	293	293
Z	4	2	2
D (g cm^{-3})	1.10	1.33	1.47
μ (Mo|K α)(mm^{-1})	0.13	2.18	1.70
2Θ$_{max}$. for data (deg)	25	28	30
Total reflections measured	3287	4428	5480
Unique reflections	3148	4264	5289
Reflections with I > 2σ(I)	2097	2512	4201
R1 (I > 2σ(I))	0.047	0.053	0.041
Rw [I > 2σ(I)]	0.048	—	—
I (all data)	—	0.122	0.111
No. of parameters	174	181	181
Max. residual density (e Å^{-3})	0.41	0.36	1.15

Further details are given in Table 8. Tables of atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

References

[1] M. Weidenbruch, Coord. Chem. Rev., 130 (1994) 275, and references cited therein.

[2] P. Jutzi, U. Holtmann, D. Kanne, C. Krüger, R. Blom, R. Gleiter and I. Hyla-Kryspin, Chem. Ber., 122 (1989) 1629, and references cited therein.

[3] H.H. Karsch, U. Keller, S. Gamper and G. Müller, Angew. Chem. Int. Ed. Engl., 29 (1990) 295.

[4] M. Denk, R. Lennon, R. Hayashi, R. West, A.V. Belyakov, H.P. Verne, A. Haaland, M. Wagner and N. Metzler, J. Am. Chem. Soc., 116 (1994) 2691.

[5] M. Veith, E. Werle, R. Lisowsky, R. Löppe and H. Schnöckel, Chem. Ber., 125 (1992) 1375.

[6] P. Jutzi, A. Möhrke, A. Müller and H. Bögge, Angew. Chem. Int. Ed. Engl., 28 (1989) 1518.

[7] P. Jutzi, E.-A. Bunte, U. Holtmann, B. Neumann and H.G. Stammler, J. Organomet. Chem., 446 (1993) 139.

[8] M. Denk, R. Hayashi and R. West, J. Am. Chem. Soc., 116 (1994) 10813.

[9] B. Gehrhus, M.F. Lappert, J. Heinicke, R. Boese and D. Bläser, J. Chem. Soc. Chem. Commun., (1995) 1931.

[10] H. Braunschweig, B. Gehrhus, P.B. Hitchcock and M.F. Lappert, Z. Anorg. Allg. Chem., 621 (1995) 1922.

[11] J. Pfeiffer, M. Maringelle, M. Noltemeyer and A. Meller, Chem. Ber., 122 (1989) 245.

[12] E. Çetinkaya, P.B. Hitchcock, H. Küçükbay, M.F. Lappert and S. Al-Juaid, J. Organomet. Chem., 481 (1994) 89.

[13] M.J.S. Gynane, M.F. Lappert, S.J. Miles and P.P. Power, J. Chem. Soc. Chem. Commun., (1978) 192.

[14] (a) P.B. Hitchcock, H.A. Jasim, M.F. Lappert, W.-P. Leung, A.K. Rai and R.E. Taylor, Polyhedron, 10 (1991) 1203; (b) P.B. Hitchcock, E.S. Jang and M.F. Lappert, J. Chem. Soc. Dalton Trans., (1995) 3179.

[15] M. Veith, M. Nötzel, L. Stahl and V. Huch, Z. Anorg. Allg. Chem., 620 (1994) 1264.

[16] M. Veith, S. Becker and V. Huch, Angew. Chem. Int. Ed. Engl., 28 (1989) 1237.

[17] M.F. Lappert, S.J. Miles, J.L. Atwood, M.J. Zaworotko and A.J. Carty, J. Organomet. Chem., 212 (1981) C4.

[18] A.J. Arduengo, H. Bock, H. Chen, M. Denk, D.A. Dixon, J.C. Green, W.A. Herrmann, N.J. Jones, M. Wagner and R. West, J. Am. Chem. Soc., 116 (1994) 6641.

[19] P. Blakeman, B. Gehrhus, J.C. Green, J. Heinicke, M. Kindermann, M.F. Lappert and T. Veszpremi, J. Chem. Soc. Dalton Trans., (1996) 1475.

[20] R.P.-K. Tan, G.R. Gillette, D.R. Powell and R. West, Organometallics, 10 (1991) 546.

[21] D.E. Grindelberger and J. Arnold, Inorg. Chem., 33 (1994) 6293.

[22] D.E. Grindelberger and J. Arnold, Organometallics, 13 (1994) 4462.

[23] W.E. Schklower, Yu.T. Struchkov, L.E. Guselnikov, W.W. Wolkowa and W.G. Awahyan, Z. Anorg. Allg. Chem., 501 (1983) 153.

[24] W. Wojnowski, K. Peters, D. Weber and H.G. von Schnering, Z. Anorg. Allg. Chem., 519 (1984) 134.

[25] D.P. Thompson and P. Boudjouk, J. Chem. Soc. Chem. Commun., (1987) 1466.

[26] H. Yoshida, Y. Kabe and W. Ando, Organometallics, 10 (1991) 27.

[27] H. Yoshida, Y. Takahara, T. Erata and W. Ando, J. Am. Chem. Soc., 114 (1992) 1098.

[28] M.J. Barrow and E.A.V. Ebsworth, J. Chem. Soc. Dalton Trans., (1982) 211.