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Synthesis, crystal structures and reactions of sila- and germa-β-diketiminates

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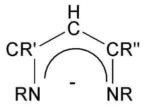
Addition of ArCN or PhCN to $LiSiR_3(thf)_n$ (n = 0 or 3) or $LiGeR_3(thf)_3$ gave the lithium 3-sila- or 3-germa-β-diketiminates $[Li\{(N(R)C(Ar))_2SiR\}D]$ **1** or $[Li\{(N(R)C(Ph))_2GeR\}]_2$ **2**, respectively [Ar = 2,6-$Me_2C_6H_3$; R = $SiMe_3$; D = $(thf)_2$ (**1a**), NCAr (**1b**), or $(NCAr)_2$ (**1c**)]. Compound **1a** with an equivalent portion of the heavier alkali metal *tert*-butoxide gave the appropriate dinuclear metal complex $[M\{(N(R)C(Ar))_2SiR\}]D]_2$ [M = Na, D absent (**3**), or M = Rb, D = NCAr (**5**)] or $[K\{\mu\text{-}(N(R)C(Ar))_2SiR\}]_2$ **4**; while **1a** with Hg_2Cl_2 gave $Hg[SiR\{C(Ar){=}NR\}_2]_2$ **6**. Thus, the ligand is (i) *N,N′*-chelating in the mononuclear lithium complexes **1a**–**1c**, (ii) *Si*-terminally bonding in the Hg(II) complex **6**, (iii) not only *N,N′*-chelating but also *Si*- (**3**, **5**) or *Ge*- (**2**) bridging in the Na, Rb or Li dinuclear complexes, and (iv) *N,N′,Si*-bridging in the K complex **4**. Treatment of the lithium 3-sila-β-diketiminate **1a** with H–C_5H_5, Cl–$TiCp_2Cl$, Br–CH_2CH_2Br or Br–HgBr, Me_3Si–Cl, or Me_3Sn–Cl yielded the appropriate silane $Si(R)X[C(Ar){=}NR]_2$ (X = H **7**, Cl **8**, Br **9**, $SiMe_3$ **10** or $SnMe_3$ **11**); whereas with two equivalents of methanol the product was $Si(R)OMe[C(Ar){=}NR][C(H)(Ar){-}N(H)R]$ **12**. The reaction between **2** and half an equivalent of $NiCl_2$ or $PdCl_2$ afforded the digermane $[Ge(R)\{C(Ph){=}NR\}_2]_2$ **13**. The X-ray structures of the crystalline compounds **1b**, **5**, **6**, **8**, **9**, **11** and **13** are reported; those for **1c**, **2**, **3** and **4** were described in preliminary publications. For the four latter, as well as **5**, it is evident that the alkali metal 3-sila- or 3-germa-β-diketiminates are zwitterionic (unlike the 3-carba-π-delocalised analogues) having significant negative charge localised at the 3-Si or 3-Ge atom and localised C=N double and E–N (E = Si or Ge) single bonds. Reaction pathways and solution NMR data are discussed.

Introduction

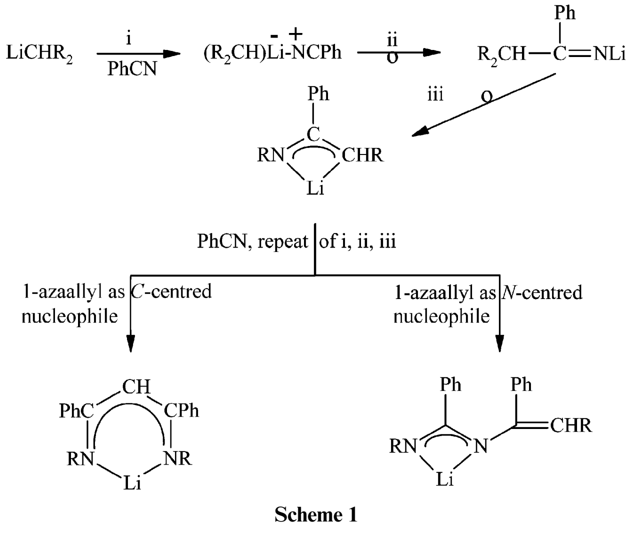
The chemistry of metal β-diketiminates is of much current interest.[1] The β-diketiminates have a useful role as spectator ligands, because of their strong binding to metals, their tuneable and varied steric and electronic demands and diversity of bonding modes. Our experimental contributions have in the main been restricted to complexes in which the ligand has the *N,N′*-bis(trimethylsilyl) formula **A** (shown for simplicity in a π-delocalised form), the *N,N′*-dihydro analogue or is $[\{N(Ar)C(R)\}_2CH]^-$ (R = $SiMe_3$ and Ar = $C_6H_3Me_2$-2,6 here and throughout this paper).



A

R' = R" = C_6H_4R'''-4
(R‴ = H, Me, OMe, Bu^t, Ph)
R' = Ph, R" = Bu^t
R' = C_6H_4Me-4, R" = 1-adamantyl

Thus, we have reported on the varied outcome of the reaction of an α-H-free nitrile R′CN or R″CN with a trimethylsilylmethyl reagent LiCH(R)R^1 (R^1 = H, R or Ph),[2] $C_6H_4[CH(R)Li]_2$-1,2,[2] or $LiCR_3$.[3] Depending on stoichiometry and absence or presence of a neutral donor D, the product from $LiCHR_2$ and PhCN was a lithium 1-azaallyl (*e.g.*, **B**), β-diketiminate (*e.g.* **C** or **D**) or the isomeric 1,3-diazaallyl (*e.g.* **E**).[2] The formation of such products was interpreted by the reaction sequence of Scheme 1 (for the case of the $LiCHR_2$/PhCN system), involving nucleophilic addition of the carbanion to the C≡N bond (C–C coupling) and 1,3-Me_3Si migration from C⟶N.[2]



Scheme 1

It was further shown that the reactions of the isocyanide ArNC with $LiCHR_2$ led to the related classes of products to **B** – **E**, namely the lithium 1-azaallyl **F**, β-diketiminate **G** and 1-aza-1,3-dienyl-3-amide **H**.[4] Results of the following systems have also been reported: $LiCHR_2/Bu^tNC$,[4] LiCH(R)Ph/ArNC,[4] and $C_6H_4[CH(R)Li]_2$-1,3/Bu^tNC.[5] A similar reaction sequence as that shown in Scheme 1 was proposed, involving (step ii) 1,1-addition of the Li-carbanion fragments to the isocyanide carbon and (step iii) 1,2-Me_3Si migration from C⟶C.[4]

This paper focuses on the reactions of the lithium silyl or germyl congeners $LiER_3$ of $LiCR_3$ towards PhCN (E = Ge) or ArCN (E = Si), and then on the behaviour of the $LiSiR_3$/ArCN products, the lithium 3-sila-β-diketiminates **1**, towards various

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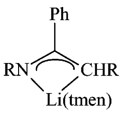
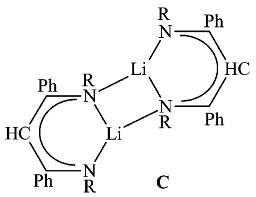
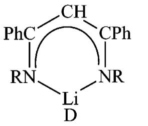


B

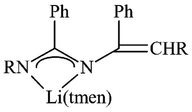


C

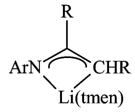


[D = tmen or (thf)$_2$]

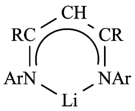
D



E



F



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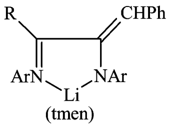
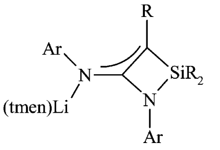


H

reagents. Comparisons of the structures, bonding and reactivity of **1** with their carbon analogues such as **C** or **D** (which generally behave as *N,N′*-centred nucleophiles[1]) was a principal aim of these studies.

In preliminary communications, we briefly reported (i) that Li(SiR$_3$)(thf)$_n$ (n = 0 or 3) and ArCN gave the lithium 3-sila-β-diketiminates [Li{(N(R)C(Ar))$_2$SiR}D] **1a**, **1b** and **1c**, (ii) that [Li(GeR$_3$)(thf)$_3$] and PhCN yielded the lithium 3-germa-β-diketiminate **2**, (iii) the X-ray molecular structures of **1c** and **2**,[6] and (iv) that **1a** and NaOBu^t or KOBu^t gave the X-ray characterised sodium **3** and potassium **4** 3-sila-β-diketiminates.[7] Full details of these experiments (apart from the X-ray data of **1c** and **2**–**4**) and further reactions of compound **1a**, as well as X-ray structures of seven compounds, are described in this paper.

We have also reported that [Li(SiR$_3$)(thf)$_3$] with the isocyanide ArNC in the presence of tmen gave the lithium amide **I**.[8] The latter is a structural isomer of [Li{(N(R)C(Ar))$_2$-SiR}(tmen)] **1d**. The compounds **1d** and **I** may be regarded as sila-analogues of the carba-compounds **D** and **E**, respectively.



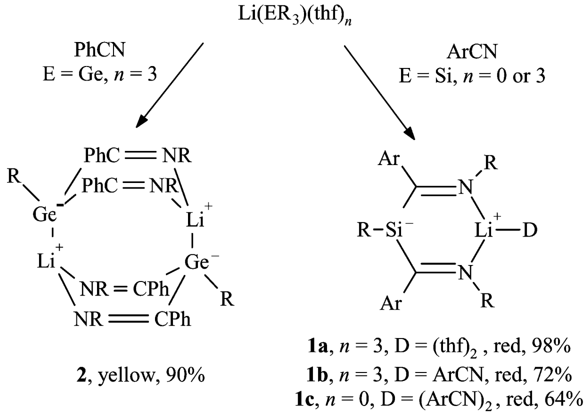
I

Results and discussion

Metal 3-sila-(or germa)-β-diketiminates

Crystalline products **1a**–**1c** were obtained from LiER$_3$(thf)$_n$ and 2 ArCN (E = Si) or 2 PhCN (E = Ge) in pentane at low temperature, Scheme 2.

From [Li(SiR$_3$)(thf)$_3$][9] and 2 ArCN the product was **1a** if thf was added prior to work-up, whereas **1b** was obtained if these reagents were mixed with 1,2-bis(dimethylamino)ethane (tmen) and volatiles removed *in vacuo*. Compound **1c** was prepared from LiSiR$_3$ and 3 ArCN. The lithium germyl [Li(GeR$_3$)-(thf)$_3$][10] was evidently less reactive towards ArCN than its silyl analogue, since under similarly mild conditions only partial displacement of coordinated thf occurred. However, PhCN readily underwent insertion into the Li–Ge bond yielding **2**. Using in place of ArCN the less sterically hindered PhCN or 2-MeC$_6$H$_4$CN, there was a rapid reaction with [Li(SiR$_3$)(thf)$_3$], but the mixtures of products have not yet been separated or identified; and with 1-adamantyl cyanide (AdCN), the ^{1}H NMR spectrum showed that the adduct Li(SiR$_3$)(NCAd) had formed. Compounds **1a**–**1c**, unlike **2**, were readily soluble in pentane. The dinuclear compound **2** was also sparingly soluble in benzene; it readily dissolved in Et$_2$O or thf to give red solutions. These may have contained mononuclear solvates, but attempts to isolate crystalline materials failed.



Scheme 2

The heavier alkali metal crystalline 3-sila-β-diketiminates **3**–**5** were prepared by metathetical exchange reactions between **1a** and the appropriate metal *tert*-butoxide in pentane with (**3**) or without (**4**, **5**) diethyl ether at low temperature, Scheme 3. They were separated from the co-product LiOBu^t on the basis of their relative solubilities in hydrocarbons: **4** > LiOBu^t > **3** or **5** (which were only slightly soluble in benzene). The mercury(II) complex **6** was obtained by the disproportionation reaction of **1a** and Hg$_2$Cl$_2$ in a 2 : 1 molar ratio in diethyl ether, with mercury as the coproduct, Scheme 3; thus, it is likely that a mercury(I) analogue was first formed.

The molecular structures of the crystalline mononuclear metal 3-sila-β-diketiminates **1b** and **6** are illustrated in Figs. 1 and 2, respectively and selected geometric parameters together with those for **1c** are listed in Table 1. The bond length data for **1c** were cited in a preliminary publication,[6] from which it is clear that its structure is very similar to that of **1b**, except for the absence in **1b** of a second coordinated ArCN ligand.

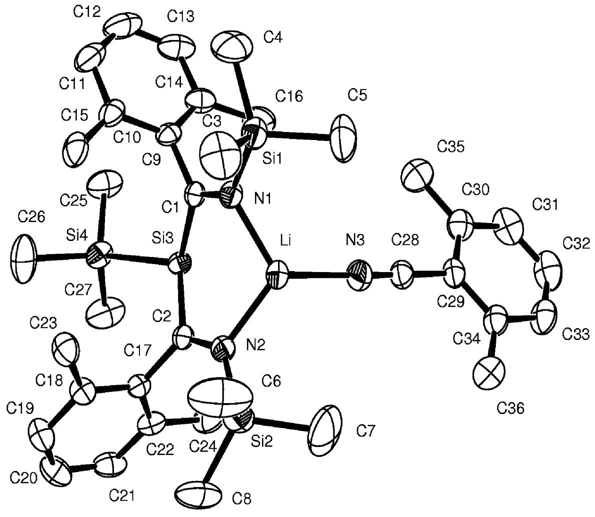


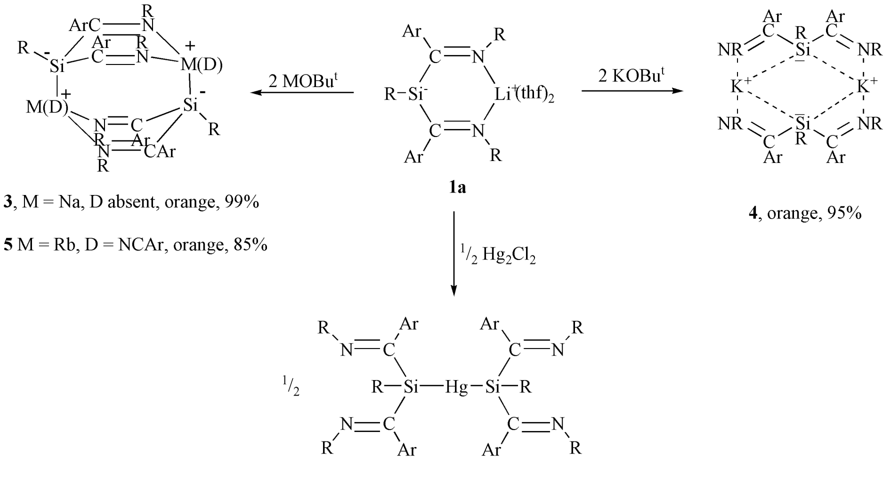
Fig. 1 The molecular structure of **1b**.

In both the lithium 3-sila-β-diketiminates **1b** and **1c** the ligand is *N,N′*-bonded in a chelating fashion to the lithium atom, which is in an approximately trigonal planar LiN$_3$ [**1b**, Σ 355.8(2)°] or tetrahedral LiN$_4$ (**1c**) environment. The atoms Li, N1, C1, Si3, C2 and N2 are arranged in a six-membered ring in

Table 1 Selected bond distances (Å) and angles (°) of mononuclear metal 3-sila-β-diketiminates **1b**, **1c** and **6**

	1b[a]	**1c**[6,b]	**6**		**1b**[a]	**1c**[6,b]	**6**
Li–N1	1.954(5)	2.000(7)	–	N1–Li–N2	111.4(2)	107.8(3)	–
Li–N2	1.950(5)	1.995(7)	–	Li–N1–C1	120.5(2)	110.8(3)	–
N1–C1	1.311(3)	1.303(5)	1.275(7)	N1–C1–Si3	124.3(2)	125.4(3)	114.4(5)
N2–C2	1.303(3)	1.308(5)	1.288(7)	C1–Si3–C2	108.8(1)	108.6(2)	118.0(3)
C1–Si3	1.881(2)	1.874(4)	1.920(6)	Si3–C2–N2	123.9(2)	124.1(3)	111.5(4)
C2–Si3	1.881(2)	1.878(5)	1.923(6)	C2–N2–Li	107.0(2)	111.9(3)	–
Si3–Si4	2.336(1)	2.334(5)	–	C2–Si3–Si4	114.75(8)	113.8(2)	110.9(2)
Li(or Hg)–Si3	2.940	3.125	2.485(2)	C1–Si3–Si4	115.60(8)	114.0(2)	106.3(2)
				Si3–Hg–Si3′	–	–	180.0
				C2–N2–Si2	132.8(2)	132.0(3)	133.9(4)
				C1–N1–Si1	132.7(2)	132.2(2)	132.1(5)

[a] Li–N3 1.995(5), N3–C28 1.141(3), C28–C29 1.437(4) Å; Li–N3–C28 173.7(3), N3–C28–C29 179.7(3)°. [b] Li–N3[N4] 2.106(8) [2.106(9)],[6] N3–C28 [N4–C37] 1.143(5) [1.141(5)], C28–C29 [C37–C38] [1.433(6) [1.442(6] Å; Li–N3–C28 [Li–N4–C37] 164.9(3) [172.5(3)], N3–C28–C29 [N4–C37–C38] 175.8(4) [178.3(4)]°; N1–Li–N3 121.4(2) [115.1(3)], N2–Li–N3 123.0(2) [116.2(3)], N3–Li–N4 94.5(3)°.



3, M = Na, D absent, orange, 99%

5 M = Rb, D = NCAr, orange, 85%

1a

4, orange, 95%

6, yellow, 67%

Scheme 3

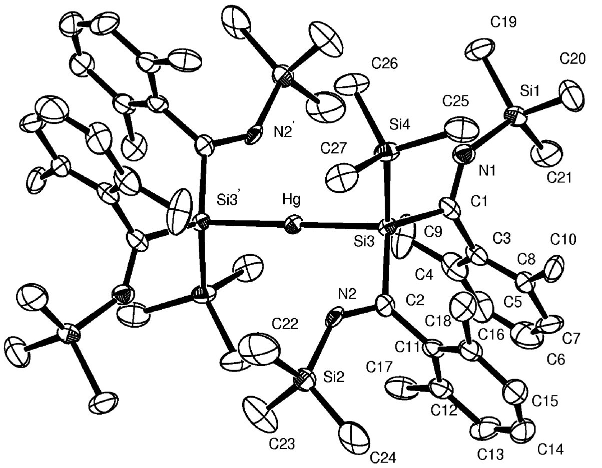


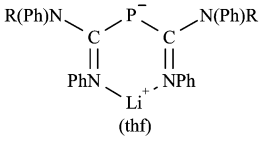
Fig. 2 The molecular structure of **6**.

boat conformation; the angles between the planes N1N2C1C2 and N1N2Li1 or C1Si3C2 are 53.7(1) or 28.4(1)° (**1b**) and 44.3(3) or 28.3(3)° (**1c**), respectively. The presence of a second ArCN co-ligand in **1c** compared to just one in **1b** has the effect of a longer Li · · · Si3 separation in the former (3.125 Å) than the latter, 2.940 Å. This is also reflected in the narrower NLiN′ angle in **1c** between the lithium atom and the two N atoms of the coordinated ArCN [94.5(3)°] than the other three NLiN′ angles which range from 107.8(3)° to 116.2(3)°. The two nitriles in **1c** are almost orthogonal to one another, the angle between the aromatic planes being 94.7°. The negative charge in both **1b** and **1c** is probably mainly localised at the silicon atom Si3 rather than at N1 and N2. This is indicated by (i) the pyramidicity at Si3 [Σ Si3: 339.2 (**1b**), 336.4° (**1c**)] and (ii), the C1(C2)–Si3 and N1(N2)–C1(C2) bond lengths of 1.87 to 1.89 Å and 1.30 to 1.31 Å, respectively, which approximate to C–Si single and N=C double bonds. There may be an element of π-delocalisation in **1b** and **1c** because these N–C bond lengths are somewhat longer than in **6** (av. 1.28 Å) and are only slighter shorter than in the close 3-carba-analogues **D** (av. 1.33 Å)[2] which also have longer Li–N bonds (av. 2.02 Å).[2] However, there is little evidence of C1(C2)–Si3 double bond character, since these bonds are (i) longer (1.874 to 1.881 Å) in **1b** or **1c** than the C(sp^2)–Si bonds in [Li{η^5-C$_5$H$_2$(SiMe$_3$)$_3$-1,2,4}(pmdien)] (pmdien = pentamethyldiethylenetriamine) [11] or [Li{η^5-C$_5$H$_3$(SiMe$_3$)$_2$-1,3}(tmen)][12] of av. 1.85 Å and 1.825 Å, and (ii) they are only slightly shorter than in **6** (av. 1.92 Å). Typical Li–Si bond distances are in the range of 2.6 to 2.8 Å, as in [Li(SiMe$_3$)(tmen)$_{1.5}$] [2.70(1) Å],[13] [{Li(μ-SiMe$_3$)}$_6$] [2.62(1) Å],[14] [Li(SiR$_3$)(thf)$_3$] [2.671(1) Å],[9] [Li(SiR$_3$)(dme)$_{1.5}$] [2.630(5) Å][15] and [(Li{μ-Si(Me)(SiMe$_2$-Ph)$_2$})$_2$], [2.778(7) Å].[16] Although the Li · · · Si3 contacts are considerably longer, particularly in **1c**, it is likely that in both **1b** and **1c** there is some electrostatic attraction between the two atoms; thus we conclude that these compounds have a zwitterionic structure. Similar boat shaped metallacycles have been reported for **J**[17] and **K**,[18] but only **J** has bond distances which correspond to P–C single and C=N double bonds, the bonding in **K** being better described as π-delocalised.

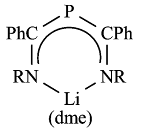
The inability of **1b** or **1c** to form significantly π-delocalised structures, in contrast to their 3-carba-analogue **D** is attributed to the general reluctance of silicon to engage in π-bonding. Likewise, the Si or Ge congeners of the cyclopentadienyls, as in [K(18-crown-6)][C$_4$Me$_4$ER′] (E = Si and R′ = SiR$_3$, or E = Ge and R′ = SiR$_3$ or C$_6$H$_2$Me$_3$-2,4,6), show localised structures and

Table 2 M–E and M–E′ bond distances (Å) and E–M–E′ and M–E–M′ bond angles (°) for the central $\overline{\mathrm{MEM'E'}}$ rhombus of compounds **2**–**5**

Compound, M, E	M–E	M–E′	E–M–E′	M–E–M′
2, Li, Ge	2.990(8)	2.657(8)	93.0(3)	87.0(3)
3, Na, Si	3.179(3)	3.192(4)	111.28(10)	68.7(1)
4, K, Si	3.305(2)	3.396(2)	92.19(5)	87.81(5)
5, Rb, Si	3.506(1)	3.757(2)	102.13(3)	77.87(3)



J



K

pyramidicity at the ring Si or Ge atom;[19] although evidence for delocalised aromatic structures has been found in $[\mathrm{Si(Bu^t)C_4Ph_4}]^{-}$[20] and the dianions $[\mathrm{GeC_4Ph_4}]^{2-}$[21] and $[\mathrm{GeC_4Et_4}]^{2-}$.[22]

Crystalline bis(3-sila-β-diketiminato)mercury **6** is centrosymmetric; the mercury atom is at the inversion centre and there is a linear Si3–Hg–Si3′ core. Thus the ligands, unlike in **1b** or **1c**, are silicon-centred and are in a staggered conformation, the silicon atoms being in a distorted tetrahedral environment. Both the Hg–Si bond lengths and the linearity at Hg(II) are unexceptional. Thus, the few examples of mercury(II) silyls also have a linear Si–Hg–Si′ backbone, the ligands in staggered conformation and Hg–Si bond distances ranging from 2.469(2) to 2.505(4) Å in $\mathrm{Hg(SiBu^t_3)_2}$,[23] $\mathrm{Hg(SiMe_3)_2}$,[24] $\mathrm{Hg(SiR_3)_2}$,[25] $\mathrm{Hg(SiPh_3)_2}$,[26] and $\mathrm{Li_2[Hg(SiMe_3)_4]}$.[27]

Whereas the mononuclear metal 3-sila-β-diketiminates **1b**, **1c** and **6** have the ligand bound to the metal in a terminal fashion, in the binuclear crystalline complexes **2** (the 3-germa analogue) and **3** and **5** each ligand is *N,N′*-chelating to one metal ion and is also *Ge*- (**2**) or *Si*- (**3**, **5**) bridging to the other. In **4**, a still different mode of ligand-to-metal bonding is observed: each ligand *N,N′*-bridges the two potassium ions although the central 3-silicon atom has relatively short K ··· Si contacts. Nevertheless, each of the compounds **2**–**5** has a central $\overline{\mathrm{MEM'E'}}$ rhombus having the M–E (*a*) and M–E′ (*b*) bond distances and E–M–E′ (*α*) and M–E–M′ (*β*) bond angles shown in Table 2. The former can be compared with the M–E bond distances found in the terminal lithium germyl $[\mathrm{Li(GeR_3)(thf)_3}]$ [2.666(6) Å][10] and the bridging heavier alkali metal silyls $[\mathrm{M(\mu\text{-}SiR_3)}]_2$ [M = Na: 2.996(1)–3.049(1), K: 3.368(1)–3.416(1), Rb: 3.522(4)–3.616(4) Å; their *α* and *β* values are 61.9 and 115.2, 73.2 and 106.7, and 74.2 and 96.9°, respectively.[9c]].

The bond lengths and endocyclic bond angles of $\overline{\mathrm{MNCECN}}$, the metallacycle for complexes **2**, **3** and **5**, are listed in Tables 3 and 4. The molecular structures of **2**,[6] **3**,[7] and **4**,[7] as well as some of the bond length data for each were cited in preliminary communications; full details are in the Cambridge Crystallographic Data Base. Hence, only a composite structural diagram is given in Fig. 3 for the related compounds **2** and **3**; data other than those in Table 2 for **4** are in Fig. 4. The molecular structure of the rubidium compound is illustrated in Fig. 5; selected geometric parameters are found in Tables 2, 3 and 4.

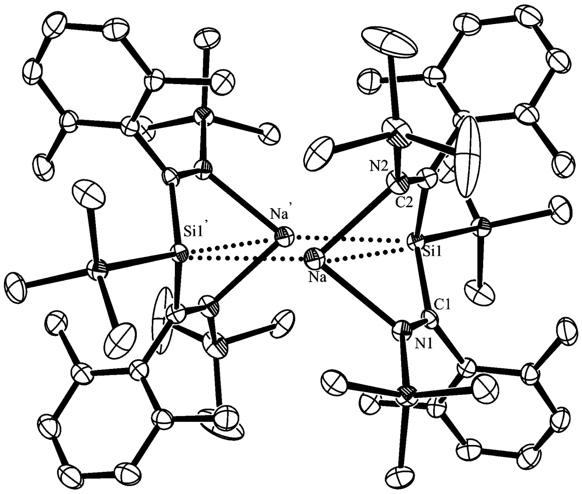


Fig. 3 The molecular structure of **3**[7] (**2**[6] is very similar with the Na replaced by Li and Si by Ge).

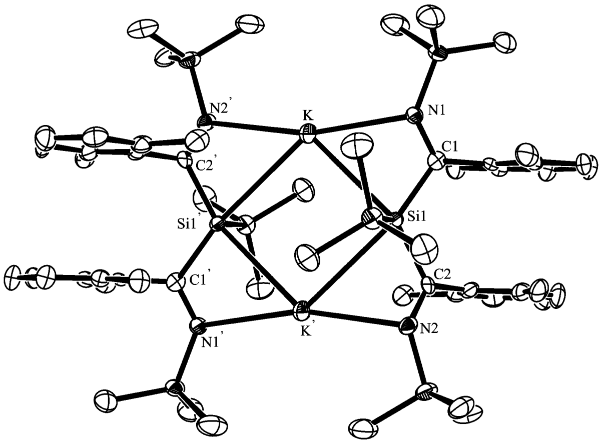


Fig. 4 The molecular structure of **4**.[7] Selected bond lengths (Å) and angles (°): K–N1 2.863(4), K–N2′ 2.857(4), N1–C1 1.307(6), N2–C2 1.295(6), C1–Si1 1.903(5), C2–Si1 1.904(5), Si1–Si4 2.343(2); N1–K–N2′ 164.27(13), K–N1–C1 105.5(3), N1–C1–Si1 77.91(16).

The C=N and C–Si bond lengths for **2** and **3** (Table 3), being closely similar to those for **6** (Table 1), are appropriate for double and single bonds respectively. The corresponding values for the potassium compound (Fig. 4) are slightly longer (CN) and shorter (CSi), which indicates that in **4** there is some slight π-delocalisation in the ligands, a situation similar to that in **1b** and **1c**. The M–N bond lengths in compounds **2**–**5** are unexceptional, as evident from comparison with such data for the compounds $[\mathrm{Li(\mu\text{-}NR_2)}]_3$ (1.98 to 2.02 Å),[28] and $[\mathrm{M(\mu\text{-}NR_2)}]_2$: M = Na 2.364(2) to 2.404(2) Å,[29] M = K 2.770(3) to 2.803(3) Å,[30] and M = Rb 2.878(2) to 2.956(2) Å.[31a] The C(sp²)–Ge distance in **2**, being 0.08 Å longer than the C–Si distance in **2** or **6**, is appropriate for a single bond, as may be judged by (i) the average C–E distances in $[\mathrm{Li(EPh_3)(thf)_3}]$ of 1.936 Å for E = Si[9b] and 2.010 Å for E = Ge[31b] and (ii) the av. 1.98 Å in $[\mathrm{Li(12\text{-}crown\text{-}4)}][\mathrm{Ge(SiR_3)C_4Me_4}]$.[19]

The structure of **4** may be compared with that of a close 3-carba-analogue **L**,[32] in which the ligand is *N,N′*-bridging.

Table 3 Bond distances (Å) for the $\overline{\mathrm{MNCECN}}$ metallacycle of compounds **2**–**5**

Compound, M, E	M–N1	M–N2	N1–C1	N2–C2	C1–E	C2–E	E–Si
2, Li, Ge	1.954(6)	1.954(5)	1.288(3)	1.288(3)	2.008(3)	2.008(3)	2.4007(14)
3, Na, Si	2.395(6)	2.370(6)	1.282(7)	1.295(7)	1.929(6)	1.928(6)	2.355(2)
5, Rb, Si[a]	2.892(4)	2.915(4)	1.296(5)	1.298(5)	1.908(5)	1.912(4)	2.355(2)

[a] Additional data for **5**: Rb–N3 2.972(5), N3–C28 1.444(6), C28–C29 1.435(7) Å.

Table 4 Endocyclic bond angles (°) for the MNCECN metallacycle of compounds **2**–**5**

Compound, M, E	N1–M–N2	M–N1–C1	M–N2–C2	N1–C1–E	N2–C2–E	C1–E–C2
2, Li, Ge	106.1(4)	106.5(3)	106.5(3)	123.9(2)	123.9(2)	101.3(2)
3, Na, Si	82.6(2)	110.8(4)	110.2(4)	119.3(5)	120,2(5)	104.3(3)
5, Rb, Si[a]	69.22(10)	106.1(3)	106.2(3)	123.3(3)	123.3(3)	106.71(19)

[a] Additional data for **5**: N1–Rb–Si3′ 133.56(8), N2–Rb–Si3′ 128.56(8), N3–Rb–Si3′ 103.45(10), Rb–N3–C28 163.2(4), N3–C28–C29 178.7(6)°.

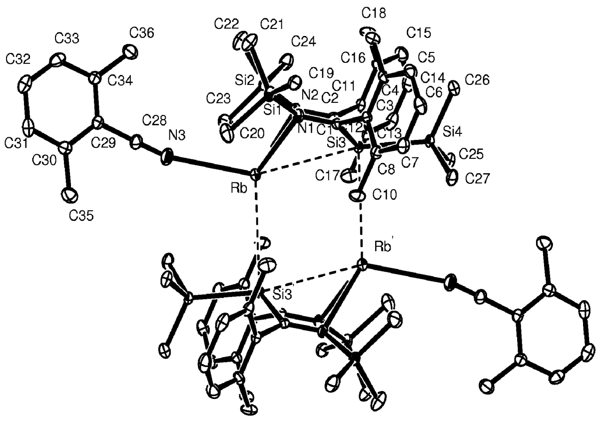
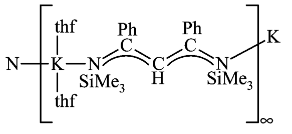


Fig. 5 The molecular structure of **5**.



L

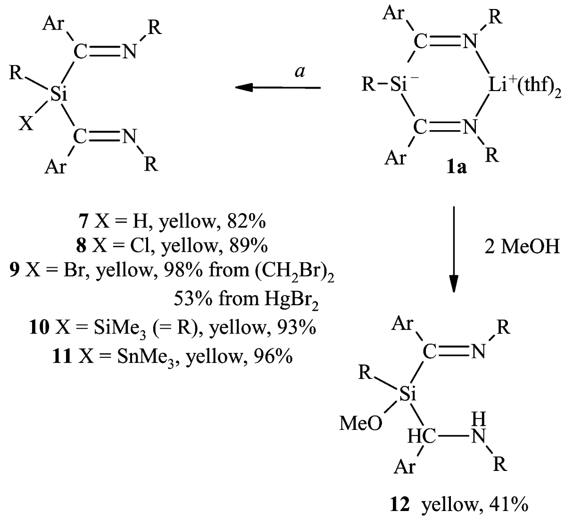
Further reactions of the lithium 3-sila-β-diketiminate 1a and the 3-germa-analogue 2

As shown in Scheme 3, compound **1a** was found to act as a ligand transfer agent generating the heavier alkali metal (**3**–**5**) and mercury(II) (**6**) 3-sila-β-diketiminates by reaction with the appropriate MOBu^t (M = Na, K, Rb) or Hg_2Cl_2. However, this behaviour is not general, as evident from the outcome of treating **1a** with $SiMe_3Cl$, $[TiCp_2Cl_2]$, $SnMe_3Cl$ or $HgBr_2$, as summarised in Scheme 4. Also included in Scheme 4 are the results of reactions of **1a** with cyclopentadiene, 1,2-dibromoethane, or methanol.

Each of the reactions of Scheme 4 was carried out at or below room temperature in pentane, toluene (**8**) or diethyl ether (**9**, using $HgBr_2$) in a 1 : 1 molar proportion of reagents, except for the $HgBr_2$ and $[TiCp_2Cl_2]$ systems in which a 2 : 1 ratio of **1a** : metal halide was employed. The structures of **7**, **10** and **12** are assigned on the basis of their ^1H, ^{13}C and ^{29}Si (not **10**) solution NMR and EI mass spectra (not **10**), and for **10** and **12** also elemental analysis and for **12** the IR spectrum. The structures of the crystalline complexes **8** and **9** (Fig. 6 and Table 5) and **11** (Fig. 7 and Table 6) were further confirmed by X-ray diffraction data.

Complexes **8** and **9** are isostructural and differ only in the positions of the methyls of the $SiMe_3$ group attached to the central silicon atom Si1, as a consequence of the disorder in these groups, Fig. 8. The angles subtended at Si1 are essentially tetrahedral, varying from 104.77(11) to 114.21(12)° in **8** and 104.5(1) to 113.9(2)° in **9**. The Si–Cl (**8**) and Si–Br (**9**) distances are unexceptional, as evident by comparison with those in $Si(Cl)Ph_3$ [2.075(5) Å][33] or $[Si(Br)(H)_2CH_2\text{-}]_2$ [2.2362(12)].[34]

The lithium 3-sila-β-diketiminate **1a** evidently behaved as a *Si*-rather than an *N,N′*-centred nucleophile in its reactions with the X–A reagents H–C_5H_5, Cl–$TiCp_2Cl$, Br–CH_2CH_2Br, Br–HgBr, $SiMe_3$–Cl or $SnMe_3$–Cl. A plausible reaction pathway is shown in eqn. (1).



Scheme 4 Reactions of **1a** with reagents *a* yielding compounds **7**–**11** or MeOH affording **12**. Reagents *a*: C_5H_7 **7**, $[TiCp_2Cl_2]$ **8**, $(CH_2Br)_2$ or $HgBr_2$ **9**, $SiMe_3Cl$ **10**, $SnMe_3Cl$ **11**.

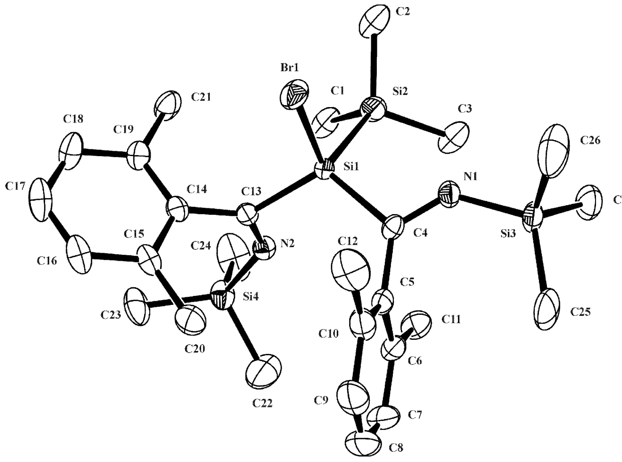


Fig. 6 The molecular structure of **9** is closely similar to that of **8** (Cl1 in place of Br1).

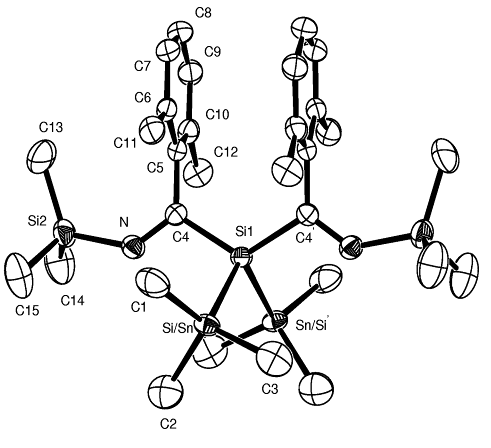


Fig. 7 The molecular structure of **11**.

Table 5 Selected bond lengths (Å) and angles (°) for the halogenosilanes Si(R)X[C(Ar)NR]$_2$ **8** (X = Cl) and **9** (X = Br)

	8	**9**		**8**	**9**
Si1–X	2.0997(13)	2.266(1)	Si1–Si2	2.356(2)	2.365(2)
Si1–C4	1.902(3)	1.924(4)	Si1–C13	1.924(4)	1.899(4)
N1–C4	1.269(4)	1.280(5)	N2–C13	1.274(4)	1.282(5)
X–Si1–Si2	108.53(6)	108.36(5)	Si2–Si1–C4	114.2(1)	108.0(1)
X–Si1–C4	107.93(11)	104.5(1)	Si2–Si1–C13	107.2(1)	113.8(1)
X–Si1–C13	104.77(11)	107.8(1)	C4–Si1–C13	113.7(2)	113.9(2)

Table 6 Selected bond lengths (Å) and angles (°) for the silane Si(R)(SnMe$_3$)[C(Ar)NR]$_2$ **11**

Si1–Si/Sn[a]	2.4880(4)	N–C4	1.2761(18)
C1–C4	1.929(14)	C4–C5	1.757(13)
C4–Si–C4′	119.33(9)	Si1–C4–C5	122.85(10)
C4–Si1–Si/Sn[a]	105.09(4)	Si1–C4–N	112.29(11)
Si/Sn[a]–Si1–Si′/Sn′	105.42(2)	C4–N–Si2	132.66(11)

[a] The SnMe$_3$ and SiMe$_3$ (≡ R) groups are disordered about the crystallographic C_2 axis.

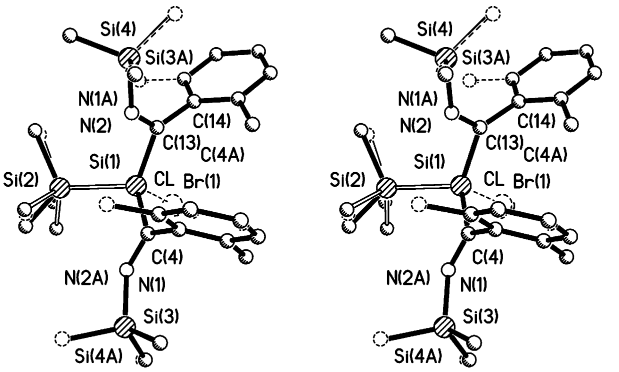
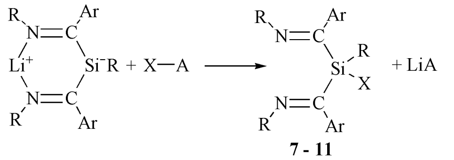


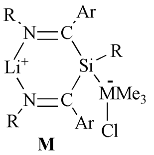
Fig. 8 Stereochemical view of the superposition of complexes **8** and **9**.



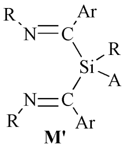
(1)

7 - 11

For the case of the latter two, an intermediate may be **M**; while **M′** may be implicated for A = TiCp$_2$Cl, CH$_2$CH$_2$Br or HgBr, which yields the final product SiR(X)[C(Ar)NR]$_2$ (X = Cl, Br or Br) by elimination of TiCp$_2$, C$_2$H$_4$, or HgBr, respectively. It is noteworthy that the HgBr$_2$ reaction did not give rise to the Hg(II) compound **6**.

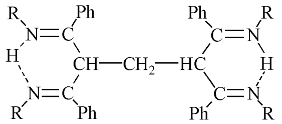


M



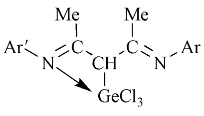
M′

That the lithium 3-sila-β-diketiminate **1a** has a significant range of *Si*-centred nucleophilic reactivity is consistent with the X-ray data presented earlier for the related compounds **1b**, **1c**, and **3**–**5**. It also contrasts with the structure and reactivity of the 3-carba-analogues. Thus, although metal β-diketiminates display a diversity of bonding and reactivity patterns, almost all are *N,N′*-centred.[1] Structural data which show the exceptional *N,C*-metal bonding mode are restricted to the products of the reactions of $K[\{N(R)C(Ph)\}_2CH]$ with CH$_2$Br$_2$ which gave **N**,[35] and $Li[\{N(C_6H_3Pr^i_2\text{-}2,6)C(Me)\}_2CH]$ with GeCl$_4$ which yielded **O** (Ar′ = $C_6H_3Pr^i_2$-2,6).[36] Examples of the *N,N′*-centred reactivity, particularly relevant to the present discussion are the reactions of **D** with C$_5$H$_6$ or SnMe$_3$Cl which gave **P** and LiCp,[37] or **Q**,[35] respectively.

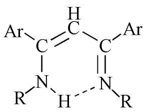


2

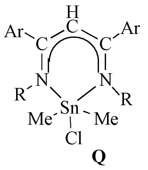
N



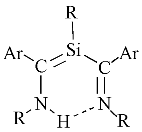
O



P



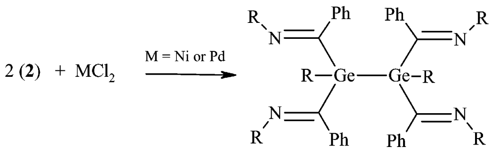
Q



R

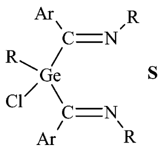
The reaction of **D** with a controlled amount of water gave the β-diketimine **P**.[35] The 3-sila-analogue **R** of **P** may likewise have been a labile intermediate in the reaction of **1a** with MeOH, which with a further equimolar portion of methanol gave the isolated product **12**.

The reaction of two equivalents of the lithium 3-germa-β-diketiminate **2** with nickel(II) or palladium(II) chloride gave the digermane **13** in modest yield, eqn. (2).



13, yellow, 43% (Pd)
or 30% (Ni)

(2)



S

A plausible reaction pathway implicates the chlorogermane **S** (the Ge analogue of the silane **8**) and finely divided Ni or Pd. The latter may then have acted as reagent for the reductive coupling of **S** to provide **13**, a process analogous to the coupling of organic halides by such metals (see, for example, ref. 38).

The crystalline digermane molecule has an inversion centre at the mid-point of the Ge–Ge bond, Fig. 9; selected geometric parameters are in Table 7. The substituents at the carbon and nitrogen atoms adopt a staggered conformation. Bond angles at the four-coordinate germanium atoms range from 105.29(7) to 114.64(7)°. The Ge–Ge′ bond length is at the shorter end of values recorded for digermanes: 2.42(1) in $[GeCl_2(SiR_3)]_2$[39] and 2.710(5) Å in $(GeBu^t_3)_2$.[40]

The behaviour of the lithium 3-germa-β-diketiminate **2** towards NiCl$_2$ or PdCl$_2$ is quite different from that reported for the related alkali metal β-diketiminates, which afforded the

Table 7 Selected bond lengths (Å) and angles (°) for the digermane **13**

Ge1–Ge1′	2.4340(5)	Ge1–Si1	2.4043(8)
Ge1–C4	2.004(3)	Ge1–C14	2.014(3)
N1–C4	1.275(3)	N2–C14	1.266(4)
Si1–Ge1–Ge1′	110.91(2)	Si1–Ge1–C4	105.29(7)
C4–Ge1–Ge1′	106.29(7)	Si1–Ge1–C14	114.64(7)
C14–Ge1–Ge1′	112.08(7)	C4–Ge1–C14	107.0(1)

Primed atoms are related to unprimed by the symmetry transformations: $x + 1, y + 2, z + 2$.

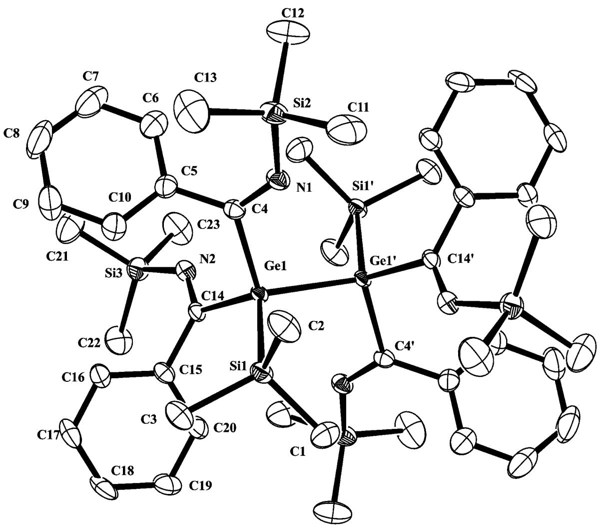


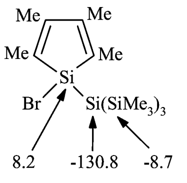
Fig. 9 The molecular structure of **13**.

homoleptic metal(II) compounds [M{(N(R)C(Ph))$_2$CH}$_2$], in which the d^8 Ni(II)[41] or Pd(II)[37] atom was in a square planar MN$_4$ environment.

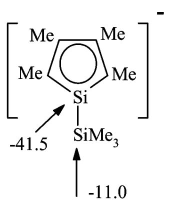
NMR (and IR) spectral data for compounds 1–13

Each of the compounds **1**–**13** showed two clearly separated signals both in the ^{1}H- and the ^{29}Si-NMR solution spectra for the E*Si*Me$_3$ and NSiMe$_3$ groups, in a ratio of 1 : 2; the corresponding ^{13}C chemical shifts were very close together. The relative positions of the two ^{1}H signals to one another appears (except for **5**) to be diagnostic as a probe as to whether the E atom is bonded to an electropositive or electronegative atom. Thus, for **1**–**4** δ[ESi(CH$_3$)$_3$] was observed at lower frequency than δ[NSi(CH$_3$)$_3$]; for **6**–**11** and **13**, a reversal of this pattern was noted, Table 8. Surprisingly the δ[^{29}*Si*SiMe$_3$] data showed no obvious trend; for comparison, data for **T** and **U**[19] and **V** and **W**[20] are available {the counter cation for **U** or **W** is [K(18-crown-6)]$^+$ and K$^+$, respectively}.

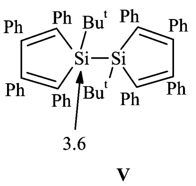
The δ[^{13} C(Ar)] values for the ^{13}CNAr nucleus was at significantly higher frequency in **1**–**13** (203 to 238 ppm, Table 8) than in metal β-diketiminates, *e.g.* for **D**: δ = 174.9 (D = tmen) or 175.7 [D = (thf)$_2$]^2 and δ = 170.8 for **L**.[32] This is consistent with the notion that in **1**–**13**, the carbon atom of the CNAr moiety is multiply bonded to the nitrogen atom, whereas in the metal β-diketiminates such as **D** or **L** there is only partial double bond character because of the π-delocalisation.



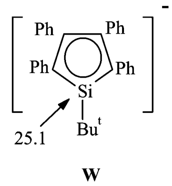
T



U



V



W

The structures of compounds **7** and **12** were established solely from spectroscopic data. The presence of a Si–H bond in **7** was deduced from (i) the δ[^{1}H] value of 4.88, which is typical for such a bond; (ii) the ^1J(^{29}Si–H) of 175.8 Hz, *cf.* ref. 42; and (iii) the strong IR spectral ν(Si–H) band at 2084 cm^{-1}. The structure of **12** was based on a series of NMR spectroscopic experiments. The presence of adjacent CH and NH groups was consistent with the ^3J(^{1}H–^{1}H) value of 9.2 Hz for both CH and NH protons and the IR spectral band at 3403 cm^{-1} was appropriate for the N–H group. NOE experiments identified the particular SiMe$_3$ group attached to NH. Finally a 2D ^{1}H–^{29}Si NMR spectral correlation experiment (Fig. 10) enabled us to assign the ^{29}Si chemical shift to appropriate Si atoms.

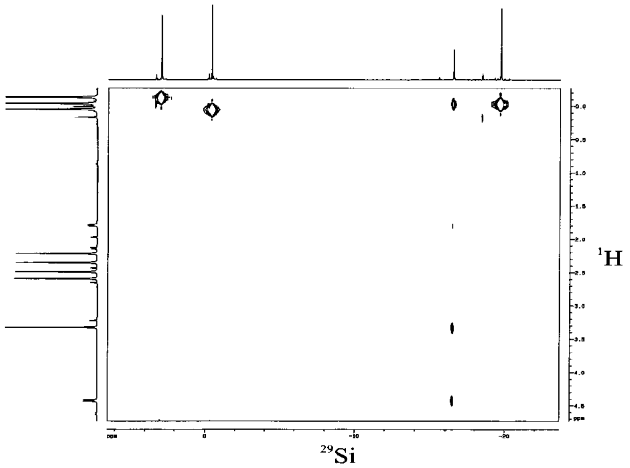


Fig. 10 2D ^{1}H–^{29}Si NMR spectral correlation data.

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 C$_6$D$_6$ or C$_7$D$_8$ at 298 K using the following Bruker instruments: DPX 300 (^{1}H, 300.1; ^{7}Li 116.6; ^{13}C 75.5 MHz) and AMX 500 (^{1}H, 500.1; ^{13}C, 125.7 ^{29}Si 99.4, ^{199}Hg 89.1 MHz) and referenced internally to residual solvent resonances (data in δ) in the case of ^{1}H and ^{13}C spectra. The ^{7}Li, ^{29}Si and ^{199}Hg spectra were referenced externally to LiCl, SiMe$_4$ or HgMe$_2$, respectively. Unless otherwise stated, all NMR spectra other than ^{1}H were proton-decoupled. Electron impact mass spectra were from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, UK.

Preparations

[Li{N(R)C(Ar)Si(R)C(Ar)NR}](thf)$_2$] 1a. A solution of [Li(SiR$_3$)(thf)$_3$] (3.54 g, 7.53 mmol) in pentane (100 cm^3) was added slowly to a stirred suspension of 2,6-dimethylbenzonitrile (ArCN) (1.97 g, 15.06 mmol) also in pentane (50 cm^3) at −40 °C. A red product was immediately formed; the mixture was allowed to warm to room temperature and then stirred for 20 h. Thf (5 cm^3) was added and the reaction mixture stirred for a further 17 h. Solvent was removed *in vacuo* and the product was extracted into pentane; the pentane solution was concentrated and dark red crystals of the pure product **1a** (4.94 g, 7.48 mmol, 98%) were obtained; ^{1}H-NMR (C$_6$D$_6$): δ −0.15 (s, 9 H,

Table 8 Selected NMR spectral shifts (δ) for compounds **1**–**13**

Compound	ESiMe$_3$ ^{1}H|^{13}C|^{29}Si	NSiMe$_3$ ^{1}H|^{13}C|^{29}Si	*Si*SiMe$_3$ ^{29}Si	*C*NAr ^{13}C
1a	−0.15|1.7|[a]	0.03|1.5|[a]	[a]	219.8
1b	−0.13|1.7|−7.7	0.13|1.7|−6.8	−15.5	219.5
1c	−0.14|1.7|[a]	0.14|1.7|[a]	[a]	219.4
2	−0.12|2.3|−4.0	−0.07|2.8|−5.1	[a]	238.0
3	0.04|[a]|−17.1	0.12|[a]|−1.3	−45.2	[a]
4	0.04|1.7|−3.1	0.12|1.5|−19.6	−56.9	219.5
5	0.20|1.7|−19.4	−0.05|1.5|−1.5	−51.1	235.3
6	0.44|2.1|6.7*	−0.01|0.6|−2.6	−8.9*	210.3
7	0.03|0.2|−14.3	−0.05|0.0|−1.5	−57.0	204.3
8	0.36|−0.3|−11.4	−0.03|−0.1|0.9	−43.8	205.3
9	0.35|−0.4|−11.3	−0.01|−0.1|0.4	−40.4	203.4
10	0.42|1.4|[a]	−0.04|0.5|[a]	[a]	206.2
11	0.40|1.4|[a]	−0.05|0.5|[a]	[a]	206.4
12	−0.04|0.1|−19.7	−0.15,[b] 0.04[c]|0.2|2.9,[b] −0.5[c]	−16.5	210.9
13	0.45|1.6|[a]	0.21|1.7|[a]	[a]	205.5

*Tentative assignment. [a] Not recorded. [b] N(H)Si*Me*$_3$. [c] NSiMe$_3$.

SiSiMe$_3$), 0.03 (s, 18 H, NSiMe$_3$), 1.32 (m, 8 H, thf), 2.55 (s, 12 H, Me), 3.62 (m, 8 H, thf), 6.9–7.1 (m, 6 H, Ph); ^{7}Li-NMR (C$_6$D$_6$) δ 1.64; ^{13}C NMR (C$_6$D$_6$): δ 1.5 (s, NSiMe$_3$), 1.7 (s, SiSiMe$_3$), 20.5 (s, Me, nitrile), 25.9 (s, thf), 67.97 (s, thf), 113.2, 118.9, 127.1, 127.4, 132.7 and 133.5 (s, Ph), 142.6 [s, *ipso*-C(Me), nitrile], 219.8 (s, CN).

[Li[Si(R){C(Ar)=NR}$_2$](NCAr)] 1b. ArCN (0.26 g, 2.05 mmol) was added at −78 °C to a solution of [Li(SiR$_3$)(thf)$_3$] (0.48g, 1.03 mmol) in pentane (30 cm^3) and tmen (0.15 cm^3). The reaction mixture was allowed to warm slowly to room temperature and was stirred for 12 h. The volatiles were removed *in vacuo* and the residue extracted with pentane (40 cm^3). The extract was filtered. Concentration of the filtrate and cooling gave **1b** as red crystals (0.32 g, 72%), mp 98 °C (decomp.); mass spectrum [*m*/*z* (%)]: 516 (58 [M]$^+$), 443 (24 [M − SiMe$_3$]$^+$); ^{1}H NMR (C$_6$D$_6$): δ −0.13 (s, 9 H, SiSiMe$_3$), 0.13 (s, 18 H, NSiMe$_3$), 2.13 (s, 6 H, Me, nitrile), 2.63 (s, 12 H, Me, ligand), 6.47 [d, 2 H, Ph,], 6.77 [t, 1 H, Ph], 6.95 [m, 6 H, Ph]; ^{7}Li-NMR (C$_6$D$_6$): δ 1.65; ^{29}Si-NMR (C$_6$D$_6$): δ −6.8 (s, N*Si*Me$_3$), −7.7 (s, Si*Si*Me$_3$), −15.5 (s, *Si*SiMe$_3$); ^{13}C NMR (C$_6$D$_6$): δ 1.7 (s, SiMe$_3$), 20.4 (s, Me, nitrile), 20.8 (s, Me, ligand), 111.4, 118.2 (s, Ph, nitrile), 126.7, 127.5, 127.8, 133.1, 133.5 (s, Ph), 143.1 [s, *ipso*-C(Me), nitrile], 149.1 [s, *ipso*-C(Me), ligand], 219.5 (s, CN); IR (cm^{-1}): ν(C≡N, ArCN) 2238 (s) [*cf.* free nitrile ν(C≡N) 2216 (s)]; UV-spectrum (0.34 mmol in pentane, λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 354.4 (5150), 405.6 (5520), 502.5 (8500).

[Li[Si(R){C(Ar)=NR}$_2$](NCAr)$_2$] 1c. ArCN (0.75 g, 5.74 mmol) was added at −78 °C to a solution of LiSiR$_3$ (0.46 g, 1.81 mmol) in pentane (20 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred for 36 h. The volatiles were removed *in vacuo* and the residue extracted with pentane (30 cm^3). The red extract was filtered (from a small amount of colourless precipitate) and concentrated to give on cooling dark red crystals of **1c** (0.88 g, 64%) (Found: C, 69.7; H, 8.50; N, 7.43. C$_{45}$H$_{63}$LiN$_4$Si$_4$ requires C, 71.9; H, 8.45; N, 7.45%). ^{1}H NMR (C$_6$D$_6$): δ −0.14 (s, 9 H, SiSiMe$_3$), 0.14 (s, 18 H, NSiMe$_3$), 2.15 (s, 12 H, Me, nitrile), 2.63 (s, 12 H, Me, ligand), 6.52 [d, 2 H, Ph, ^3J(^{1}H–^{1}H) 7.7], 6.80 [t, 1 H, Ph, ^3J(^{1}H–^{1}H) 7.7 Hz], 6.92–7.02 [m, 9 H, Ph]; ^{7}Li-NMR (C$_6$D$_6$): δ 1.64; ^{13}C NMR (C$_6$D$_6$): δ 1.7 (s, SiMe$_3$), 20.5 (s, Me, nitrile), 20.8 (s, Me, ligand), 112.6, 117.7, 126.7, 127.4, 132.5 and 133.5 (s, Ph), 142.6 [s, *ipso*-C(Me), nitrile], 149.1 [s, *ipso*-C(Me), ligand], 219.4 (s, CN).

[Li[Ge(R){C(Ph)=NR}$_2$]$_2$ 2. PhCN (0.23 cm^3, 2.28 mmol) was added at −50 °C to a solution of [Li(GeR$_3$)(thf)$_3$] (0.60 g, 1.14 mmol) in pentane (30 cm^3) and the reaction mixture was allowed to warm to room temperature and stirred overnight to give a red solution with a yellow precipitate. Filtration and drying of the yellow precipitate *in vacuo* gave **2** (0.35 g, 61%). Concentrating the filtrate and cooling it gave a second fraction of **2** as yellow crystals (0.17 g, 29%) (Found: C, 52.8; H, 7.26; N, 5.43. C$_{23}$H$_{37}$GeLiN$_2$Si$_3$ requires C, 54.7; H, 7.38; N, 5.54%), mp 180 °C (decomp.), mass spectrum [*m*/*z* (%)]: 500 (35 [LLH]$^+$), 426 (32 [LL − SiMe$_3$]$^+$) (LL represents the ligand); ^{1}H NMR (C$_6$D$_6$/C$_5$D$_5$N): δ −0.12 (s, 9 H, SiSiMe$_3$), −0.07 (s, 18 H, NSiMe$_3$), 7.01–7.11 [3 H, Ph], 7.34 [d, 2 H, Ph, *J*(^{1}H–^{1}H) 8.0 Hz]; ^{7}Li-NMR (C$_6$D$_6$/ C$_5$D$_5$N): δ 0.73; ^{29}Si-NMR (C$_6$D$_6$/C$_5$D$_5$N): δ −5.1 (s, N*Si*Me$_3$), −4.0 (s, Ge*Si*Me$_3$); ^{13}C NMR (C$_6$D$_6$/C$_5$D$_5$N): δ 2.3 (s, NSiMe$_3$), 2.8 (s, SiSiMe$_3$), 124.8, 127.8, 127.6 (s, Ph), 152.0 (s, *ipso*-C), 238.0 (s, CN).

[Na(Si(R){C(Ph)=NR}$_2$)]$_2$ 3. Sodium *tert*-butoxide (0.177 g, 1.8 mmol), as a suspension in diethyl ether (30 cm^3), was added to a stirred solution of **1a** (1.0 g, 1.4 mmol) in pentane (60 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. All volatiles were removed *in vacuo*. The residue was extracted with pentane (150 cm^3) and the extract was filtered. A saturated solution of the filtrate in toluene (*ca.* 3 cm^3) was cooled at −30 °C yielding orange crystals of **3** (0.66 g, 99%). ^{1}H NMR (C$_6$D$_6$): δ 0.04 (s, 9 H, SiSiMe$_3$), 0.12 (s, 18 H, NSiMe$_3$), 2.72 (s, 12 H, C$_6$H$_3$*Me*$_2$), 7.05–7.32 (m, 6 H, C$_6$*H*$_3$Me$_2$); ^{29}Si NMR (C$_6$D$_6$): δ −1.3 (s, N*Si*Me$_3$), −17.1 (s, Si*Si*Me$_3$), −45.2 (s, *Si*SiMe$_3$); ^{13}C NMR (C$_6$D$_6$): δ 1.5 (s, NSiMe$_3$), 1.7 (s, SiSiMe$_3$), 20.5 (s, Me, nitrile), 112.3, 117.9, 126.9, 127.2, 133.1 and 133.5 (s, Ph), 141.3 [s, *ipso*-C(Me), nitrile], 218.6 (s, CN).

[K(Si(R){C(Ph)=NR}$_2$)]$_2$ 4. Similarly, from potassium *tert*-butoxide (0.08 g, 0.71 mmol) and **1a** (0.49 g, 0.58 mmol) in pentane (30 cm^3) at −78 °C, deep orange crystals of **4** (0.28 g, 95%) were obtained. ^{1}H NMR (C$_6$D$_6$): δ 0.04 (s, 9 H, SiSiMe$_3$), 0.12 (s, 18 H, NSiMe$_3$), 2.72 (s, 12 H, C$_6$H$_3$*Me*$_2$), 7.05–7.32 (m, 6 H, C$_6$*H*$_3$Me$_2$); ^{29}Si NMR (C$_6$D$_6$): δ −3.1 (s, Si*Si*Me$_3$), −19.6 (s, N*Si*Me$_3$), −56.9 (s, *Si*SiMe$_3$); ^{13}C NMR (C$_6$D$_6$): δ 1.5 (s, NSiMe$_3$), 1.7 (s, SiSiMe$_3$), 20.5 (s, Me, nitrile), 112.3, 117.9, 126.9, 127.2, 133.1 and 133.5 (s, Ph), 141.3 [s, *ipso*-C(Me), nitrile], 219.5 (s, CN).

[Rb(Si(R){C(Ph)=NR}$_2$)(ArCN)]$_2$ 5. Similarly, from rubidium *tert*-butoxide (1.48 g, 0.94 mmol) and **1a** (0.61 g, 0.94 mmol) in pentane (30 cm^3) at −78 °C, deep orange crystals of **5** (0.58 g, 85%) were obtained (Found: C, 58.5; H, 7.56; N, 5.69. C$_{36}$H$_{54}$N$_3$RbSi$_4$ requires C, 59.5; H, 7.49; N, 5.78%); ^{1}H-NMR (C$_6$D$_6$): δ −0.05 (s, 18 H, NSiMe$_3$), 0.20 (s, 9 H, SiSiMe$_3$), 2.45 (s, 12 H, C$_6$H$_3$*Me*$_2$), 2.15 (s, 6 H, coord-C$_6$H$_3$*Me*$_2$), 6.5–7.15 (m, 9 H, aromatic); ^{29}Si NMR (C_6D_6): δ 1.5 (s, N*Si*Me$_3$), −19.4 (s, Si*Si*Me$_3$), −51.1 (s, *Si*SiMe$_3$); ^{13}C NMR (C_6D_6): δ 1.5 (s, NSiMe$_3$), 1.7 (s, SiSiMe$_3$), 20.5 (s, Me, nitrile), 20.8 (s, Me, ligand), 112.3, 117.9, 126.9, 127.2, 133.1 and 133.5 (s, Ph), 142.3 [s, *ipso*-C(Me), nitrile], 149.1 [s, *ipso*-C(Me), ligand], 235.3 (s, CN).

[Hg[Si(R){C(Ar)}=ANR}$_2$]$_2$] 6. Hg_2Cl_2 (0.25 g, 0.51 mmol) was added at −60 °C to a solution of **1a** (0.60 g, 1.02 mmol) in Et_2O (30 cm^3). At −30 °C the solution had changed colour from red to yellow and a black precipitate had formed. After allowing the reaction mixture to warm to room temperature and stirring for 1 h the solvent was removed *in vacuo* and the residue was extracted with pentane (60 cm^3). Filtration of the extract and cooling the filtrate gave slightly contaminated crystals (0.53 g). Recrystallising these from pentane gave yellow crystals of **6** (0.42 g, 67%) (Found: C, 53.1; H, 7.66; N, 4.62. $C_{54}H_{90}HgN_4Si_8$ requires C, 53.1; H, 7.43; N, 4.56%), mass spectrum [*m*/*z* (%)]: 1016 (1 [M − ArC=NR]$^+$), 814 (1 [M − ArC=NR − Hg]$^+$), 509 (87 [LL]$^+$), 204 (100 [ArC=NR]$^+$); ^{1}H NMR (C_6D_6): δ −0.01 (s, 18 H, NSiMe$_3$), 0.44 (s, 9 H, SiSiMe$_3$), 2.05 and 2.21 (s, 12 H, Me), 6.67 [d, 2 H, $^3J(^1H–^1H)$ 7.5, *m*-Ph], 6.71 [d, 2 H, $^3J(^1H–^1H)$ 7.5, *m*-Ph], 6.88 [t, 2 H, $^3J(^1H–^1H)$ 7.5 Hz, *p*-Ph]; ^{199}Hg-NMR (C_6D_6): δ −49.1; ^{29}Si-NMR (C_6D_6): δ −8.9 (s, *Si*-SiMe$_3$), −2.6 (s, *N*SiMe$_3$), 6.7 (s, Si*Si*Me$_3$); ^{13}C NMR (C_6D_6): δ 0.6 (s, NSiMe$_3$), 2.1 (s, SiSiMe$_3$), 20.4 and 20.8 (s, Me), 127.0, 127.8, 127.9 (s, *m*, *p*-Ph), 131.6 and 131.8 [s, *ipso*-C(Me)], 147.8 (s, *ipso*-C), 210.3 (s, CN); IR (Nujol): ν(C=N) 1581 (m).

[HSi(R){C(Ar))=NR}$_2$] 7. A solution of freshly distilled CpH (0.10 g, 1.56 mmol) in pentane (10 cm^3) was added at −30 °C dropwise to a solution of **1a** (1.0 g, 1.56 mmol) in pentane (20 cm^3). The reaction mixture was allowed to warm to room temperature to give a yellow solution with a white precipitate, which was stirred for 3 h at room temperature. The volatiles were removed *in vacuo*, the residue extracted with pentane (30 cm^3) and the extract filtered. Concentration of the filtrate and cooling gave ArCN (0.2 g). All volatiles were removed from the mother liquor to give **7** (0.65 g, 82%) as a yellow oil. Mass spectrum [*m*/*z* (%)]: 510 (47 [M]$^+$), 495 (7 [M − Me]$^+$), 437 (8 [M − SiMe$_3$]$^+$); ^{1}H NMR (C_6D_6): δ −0.05 (s, 18 H, NSiMe$_3$), 0.03 (s, 9 H, SiSiMe$_3$), 1.98 and 2.10 (s, 12 H, Me), 4.88 (s, 1 H, SiH), 6.73 [d, 4 H, $^3J(^1H–^1H)$ 7.5, *m*-Ph], 6.89 [t, 2 H, $^3J(^1H–^1H)$ 7.5, *p*-Ph]; ^{29}Si-NMR (C_6D_6): δ −57.0 [s, $^1J(^{29}Si–^1H)$ 175.8, *Si*H], −14.3 (s, Si*Si*Me$_3$), −1.5 (s, N*Si*Me$_3$); ^{13}C NMR (C_6D_6): δ 0.0 (s, NSiMe$_3$), 0.2 (s, SiSiMe$_3$), 19.8 and 20.1 (s, Me), 127.3, 127.75, 127.84 (s, *m*, *p*-Ph), 131.9 and 132.3 [s, *ipso*-C(Me)], 147.1 (s, *ipso*-C), 204.3 (s, CN); IR (Nujol, cm^{-1}): ν(Si–H) 2084 (s), ν(C=N) 1607 (vs).

[{RN=C(Ar)}$_2$Si(R)Cl] 8. Compound **1a** (1.46 g, 2.21 mmol) in toluene (30 cm^3) was added to a stirred suspension of [$TiCp_2Cl_2$] (0.33 g, 1.11 mmol) in toluene (50 cm^3). The mixture was stirred for 16 h; a black precipitate had formed and the colour of the solution changed from red to yellow. The mixture was filtered and the filtrate was concentrated (to *ca.* 10 cm^3) and stored at −30 °C for 1 d yielding yellow crystals of compound **8** (1.07 g, 89%). Mass spectrum [*m*/*z* (%)]: 340 [8 M − $C_6H_3Me_2CNSiMe_3$]$^+$, 204 [100 $C_6H_3Me_2CNSiMe_3$]$^+$ (100). ^{1}H-NMR (C_6D_6): δ −0.03 (s, 18 H, NSiMe$_3$), 0.36 (s, 9 H, SiSiMe$_3$), 2.02 (s, 6 H, Me), 2.21 (s, 6 H, Me), 6.74–6.82 [d, 4 H, ^3J ($^1H–^1H$) 8.6, *m*-Ph], 6.88–6.91 [t, 2 H, ^3J ($^1H–^1H$) 7.6 Hz, *p*-Ph)] ^{29}Si-NMR (C_6D_6): δ −43.8 (s, *Si*SiMe$_3$), −11.4 (s, Si*Si*Me$_3$), 0.9 (N*Si*Me$_3$); ^{13}C-NMR (C_6D_6): δ −0.3 (s, SiSiMe$_3$), −0.1 (s, NSiMe$_3$), 20.5 (s, Me), 21.2 (s, Me), 126.3 (s, *ipso*-C), 132.9 (s, *o*-C), 133.7 (s, *m*-C), 145.0 (s, *p*-C), 205.3 (s, *C*=N).

[{RN=C(Ar)}$_2$Si(R)Br] 9. *From* **1a** *and* $HgBr_2$. A solution of **1a** (0.53 g, 0.80 mmol) in diethyl ether was added to a suspension of $HgBr_2$ (0.15 g, 0.42 mmol) in diethyl ether (10 cm^3) at −60 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 16 h. The solvent was removed *in vacuo* and the yellow residue was extracted with hexane (40 cm^3). The extract was filtered and the filtrate concentrated and cooled. After a day at −20 °C yellow crystals of **9** (0.25 g, 53%) were obtained (Found: C, 54.8; H, 7.60; N, 4.78. $C_{27}H_{45}BrN_2Si_4$ requires C, 55.0; H, 7.69; N, 4.75 %); mp 78 °C. Mass spectrum [*m*/*z* (%)]: 204 [100 $C_6H_3Me_2CNSiMe_3$]$^+$; ^{1}H NMR (C_6D_6): δ −0.01 [s, 18 H, NSiMe$_3$], 0.35 (s, 9 H, SiSiMe$_3$), 2.06 and 2.24 [s, 12 H, CH$_3$], 6.78 [t, 2 H, $^3J(^1H–^1H)$ 7.2, *p*-Ph], 6.92 [d, 4 H, $^3J(^1H–^1H)$ 7.2 Hz, *m*-Ph]; ^{29}Si-NMR (C_6D_6): δ −40.4 (s, *Si*-*Si*Me$_3$), −11.3 (s, Si*Si*Me$_3$), δ 0.4 (N*Si*Me$_3$); ^{13}C NMR (C_6D_6): δ −0.4 (s, SiSiMe$_3$), −0.1 (s, NSiMe$_3$), 20.5 and 21.2 (s, Me), 127.9 and 128.8 (s, *m*-C), 128.3 (s, *p*-C), 132.9 and 133.2 [*ipso*-C (Me)], 145.0 (s, *ipso*-C), 203.4 (s, CN).

From **1a** *and* $BrCH_2CH_2Br_2$. $BrCH_2CH_2Br$ (0.28 g, 1.53 mmol) was added to **1a** (1.00 g, 1.53 mmol) in pentane (30 cm^3). The red solution immediately turned yellow with concomitant evolution of CH_2CH_2. All volatiles were removed *in vacuo;* the residue was redissolved in hot light petroleum (bp 60–80 °C, *ca.* 5 cm^3); the solution was concentrated (to *ca.* 2 cm^3) and stored at −30 °C for 4 h yielding yellow crystals of compound **9** (0.88 g, 98%).

[R_2Si{C(Ar)=NR}$_2$] 10. SiMe$_3$Cl (0.15 g, 0.18 cm^3, 1.38 mmol) was added with stirring to **1a** (0.91 g, 1.37 mmol) in pentane (60 cm^3). The appearance of the solution quickly changed from dark red to light yellow and a white precipitate had formed. After stirring for 1 h, volatiles were removed *in vacuo*. The residue was extracted into pentane (2 × 60 cm^3). The extract was concentrated (to *ca.* 5 cm^3) and stored at −30 °C for 1 d, yielding yellow crystals of **10** (0.75 g, 93%) (Found: C, 61.0; H, 9.69; N, 4.65. $C_{30}H_{54}N_2Si_5$ requires C, 61.8; H, 9.33; N, 4.80%); ^{1}H-NMR (C_6D_6): δ −0.04 (s, 18 H, NSiMe$_3$), 0.42 (s, 18 H, Si{SiMe$_3$}$_2$), 1.97 (s, 12 H, Me), 6.56 (d, 4 H, *m*-Ph), 6.81 (t, 2 H, *p*-Ph); ^{13}C NMR (C_6D_6): δ 0.5 (s, NSiMe$_3$), 1.4 (s, SiSiMe$_3$), 20.7 and 20.8 (s, Me), 127.3, 127.76, 128.2 (s, *m*, *p*-Ph), 132.5 and 132.2 [s, *ipso*-C(Me)], 146.5 (s, *ipso*-C), 206.2 (s, CN).

[Me$_3$SnSi(R){C(Ar)=NR}$_2$] 11. SnMe$_3$Cl (0.31 g, 1.55 mmol) was added with stirring to **1a** (1.03 g, 1.55 mmol) in pentane (60 cm^3). The appearance of the solution quickly changed from dark red to light yellow and a white precipitate had formed. After stirring for 1 h, volatiles were removed *in vacuo*. The residue was extracted into pentane (2 × 60 cm^3). The extract was concentrated (to *ca.* 5 cm^3) and stored at −30 °C for 1 d, yielding yellow crystals of **11** (1.07 g, 96%) (Found: C, 52.5; H, 8.29; N, 4.39. $C_{30}H_{54}N_2Si_4Sn$ requires C, 53.5; H, 8.08; N, 4.16%); ^{1}H-NMR (C_6D_6): δ −0.05 (s, 18 H, NSiMe$_3$), 0.40 (s, 9 H, Si-SiMe$_3$), 0.42 (s, 9 H, SiSnMe$_3$), 1.96 (s, 6 H, Me), 1.98 (s, 6 H, Me), 6.58 (d, 4 H, *m*-Ph), 6.82 (t, 2 H, *p*-Ph); ^{13}C NMR (C_6D_6): δ 0.5 (s, NSiMe$_3$), 1.4 (s, SiSiMe$_3$), δ 1.5 (s, SiSnMe$_3$), 20.6 and 20.9 (s, Me), 127.3, 127.9, 128.5 (s, *m*, *p*-Ph), 132.7 and 132.2 [s, *ipso*-C(Me)], 146.6 (s, *ipso*-C), 206.4 (s, CN).

[{RN=C(Ar)}Si(R)(OMe){C(H)(Ar)N(H)R}] 12. A mixture of MeOH (0.06 cm^3, 1.48 mmol) and pentane (2 cm^3) was added at −30 °C dropwise to a solution of **1a** (0.86 g, 1.34 mmol) in pentane (30 cm^3). An immediate colour change from red to yellow was observed. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Removal of volatiles *in vacuo* and extraction of the residue with pentane (30 cm^3) and cooling gave colourless crystals of ArCN (0.16 g). From the mother liquor yellow crystals of **12** (0.30 g, 41%) were obtained (Found: C, 60.7; H, 9.15; N, 5.47. $C_{28}H_{50}N_2OSi_4$ requires C, 61.9; H, 9.28; N, 5.16%), mp 80–95 °C (decomp.). Mass spectrum [*m*/*z* (%)]: 542 (15 [M]$^+$), 527 (25 [M − Me]$^+$); ^{1}H NMR (C_6D_6) [minor isomer in square brackets]: δ −0.14 [−0.15] [s, 9 H, SiMe$_3$, (NH)], −0.04 [0.00] (s, 9 H, SiSiMe$_3$), 0.04 [0.16] (s, 9 H, NSiMe$_3$), 1.80 [2.11] [d, 2 H, $^3J(^1H–^1H)$ 9.2, CH], 2.21, 2.35, 2.49, 2.58 [2.0, 2.4, 2.6, 1 Me group not observed] (s, 12 H, Me), 3.32 [3.2] (s, 3 H, OMe), 4.20 [4.6] [d, 1 H, $^3J(^1\text{H}–^1\text{H})$ 9.2, NH], 6.83–6.98 (m, 6 H, Ph); ^{29}Si-NMR (C_6D_6): δ −19.7 (s, Si*Si*Me$_3$), −16.5 (s, *Si*SiMe$_3$), −0.5 (C=N*Si*Me$_3$), 2.9 (s, NH*Si*Me$_3$); ^{13}C NMR (C_6D_6): δ 0.1 [q, $^2J(^{13}\text{C}–^1\text{H})$ 125.6, SiSiMe$_3$], 0.2 [q, $^2J(^{13}\text{C}–^1\text{H})$ 119.0, NSiMe$_3$], 20.67, 20.70, 21.9, 22.3 (q, Me), 44.4 [d, $^2J(^{13}\text{C}–^1\text{H})$ 126.3, CH], 52.4 [q, $^2J(^{13}\text{C}-^1\text{H})$ 142.3, OMe], 125.9, 127.5, 127.9, 128.7, 130.4 (d, Ph), 132.0, 132.9, 134.6, 138.3, 143.5, 146.5 (s, *ipso*-C), 210.9 (s, CN); IR (Nujol, cm^{-1}): ν(N–H) 3403 (m), ν(C=N) 1605 (s).

[N(R)=C(Ph)]$_2$(R)Ge–Ge(R)[C(Ph)=NR]$_2$ 13. Solid PdCl$_2$ (0.09 g, 0.52 mmol) was added to a solution of **2** (0.52 g, 1.0 mmol) in diethyl ether (25 cm^3) at −40 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h to give a red solution with a black precipitate, which were separated by filtration. The filtrate was concentrated *in vacuo* to give a brown solid, which was extracted with hexane. The extract was filtered; concentration of the filtrate and cooling to −60°C gave yellow crystals of **13** (0.22 g, 43%). ^{1}H NMR (C_6D_6): δ 0.21 (s, 18 H, NSiMe$_3$), 0.45 (s, 9 H, GeSiMe$_3$), 6.97–7.09 (10 H, Ph); ^{13}C NMR (C_6D_6): δ 1.6 (GeSiMe$_3$), 1.7 (s, NSiMe$_3$), 125.4 (s, *o*/*m*-C), 127.6 (s, *p*-C), 127.9 (s, *o*/*m*-C), 149.1 (s, *ipso*-C), 205.5 (s, CN).

The reaction of **2** (0.37 g, 0.73 mmol) with NiCl$_2$ (0.05 g, 0.37 mmol) in diethyl ether (20 cm^3) at −70 °C led in an analogous manner to **13** (0.11 g, 30%).

Crystallography

Data sets for compounds **1b** and **6**, were collected on an Enraf-Nonius CAD4 diffractometer, those for **9** and **13** on a Bruker Smart 1K CCD area detector, and **5**, **8** and **11** on a Kappa CCD diffractometer using monochromated Mo-Kα radiation. Single crystals were enclosed in mineral oil and cooled in a stream of nitrogen gas to 173(2) K. Refinement was based on F^2 with hydrogen atoms in riding mode, Further details for **1b**, **5**, **6**, **8**, **9**, **11** and **13** are found in Table 9; such data on **1c**,[6] **2**,[6] **3**[7] and **4**[7] have been published.

CCDC reference numbers: 199536 (**1b**), 199537 (**5**), 199538 (**6**), 199539 (**8**), 199037 (**9**), 199540 (**11**) and 199038 (**13**).

See http://www.rsc.org/suppdata/dt/b3/b300817g/ for crystallographic data in CIF or other electronic format.

Table 9 Crystal data and refinement for complexes **1b**, **5**, **6**, **8**, **9**, **11** and **13**

	1b	**5**	**6**	**8**	**9**	**11**	**13**
Formula	$C_{36}H_{54}LiN_3Si_4(0.5C_5H_{12})$	$C_{72}H_{108}N_6Rb_2Si_8(C_6H_6)_2$	$C_{54}H_{90}HgN_4Si_8$	$C_{27}H_{45}ClN_2Si_4$	$C_{27}H_{45}BrN_2Si_4$	$C_{30}H_{54}N_2Si_4Sn$	$C_{46}H_{74}Ge_2N_4Si_6$
Formula weight	682.18	1609.52	1220.6	545.46	598.9	637.80	996.81
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a/Å	12.324(3)	12.4463(10)	11.651(3)	10.4495(5)	10.531(2)	17.2307(4)	10.220(1)
b/Å	12.837(4)	12.8577(6)	13.661(5)	11.3914(6)	11.326(2)	11.5761(3)	12.035(2)
c/Å	15.253(4)	15.1885(12)	20.070(7)	14.9617(7)	15.066(2)	19.7605(5)	13.325(2)
α/°	80.74(3)	70.970(4)	90	73.957(3)	73.829(3)	90	114.225(2)
β/°	81.55(2)	88.410(3)	94.72(3)	71.919(2)	71.999(2)	109.685(2)	109.868(2)
γ/°	67.29(2)	86.368(5)	90	86.173(3)	86.555(3)	90	92.296(2)
U/Å^3	2187(1)	2293.1(3)	3184(2)	1626.7(1)	1640.8(4)	3711.2(2)	1374.6(3)
μ/mm^{-1}	0.16	1.21	2.60	0.28	1.42	0.84	1.26
Z	2	1	2	2	2	4	1
Unique refl., R_{int}	7672	7865, 0.062	5598, 0.045	5667, 0.081	7063, 0.047	5415, 0.039	5346, 0.029
Refl. with $I > 2\sigma(I)$	5897	4958	4048	3953	5975	4581	4640
Final R indices (for $I > 2\sigma(I)$)	$R_1 = 0.047$, $wR_2 = 0.119$	$R_1 = 0.066$, $wR_2 = 0.107$	$R_1 = 0.043$, $wR_2 = 0.102$	$R_1 = 0.065$, $wR_2 = 0.159$	$R_1 = 0.075$, $wR_2 = 0.193$	$R_1 = 0.029$, $wR_2 = 0.069$	$R_1 = 0.043$, $wR_2 = 109$
R indices (all data)	$R_1 = 0.067$, $wR_2 = 0.132$	$R_1 = 0.126$, $wR_2 = 0.128$	$R_1 = 0.073$, $wR_2 = 0.137$	$R_1 = 0.100$, $wR_2 = 0.183$	$R_1 = 0.083$, $wR_2 = 0.201$	$R_1 = 0.038$, $wR_2 = 0.073$	$R_1 = 0.047$, $wR_2 = 0.110$

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