Novel lithium 3-sila- and 3-germa-β-diketiminates†‡

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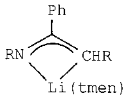
The novel 3-sila- and 3-germa-β-diketiminates $[Li\{N(R)C(Ar)E(R)C(Ar)N(R)\}(D)_n]$ (R = SiMe$_3$, Ar = C$_6$H$_3$Me$_2$-2,6 or Ph, E = Si or Ge, D = thf or ArCN and *n* = 1 or 2) were obtained from the reaction of [Li(ER$_3$)(thf)$_3$] with PhCN or ArCN; the X-ray crystal structures of two representatives of this new class of compounds were determined and shown to have, in contrast to related carbon analogues, the anionic charge localised at Si or Ge.

We have recently reported on the diverse outcome of the reaction of a trimethylsilylmethyllithium reagent, *e.g.* Li(CHR$_2$) or Li(CR$_3$), with an α-H-free nitrile (R = SiMe$_3$).[1] *E.g.* from Li(CHR$_2$) and PhCN, depending on stoichiometry and conditions the product was the crystalline lithium 1-azaallyl **1**,[2] β-diketiminate **2**[3] or **3**,[4] or the isomeric 1,3-diazaallyl **4**.[2]



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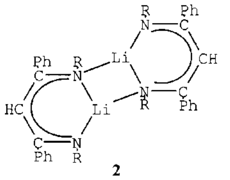

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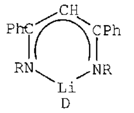
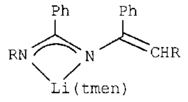


3 [D = tmen or (thf)$_2$]



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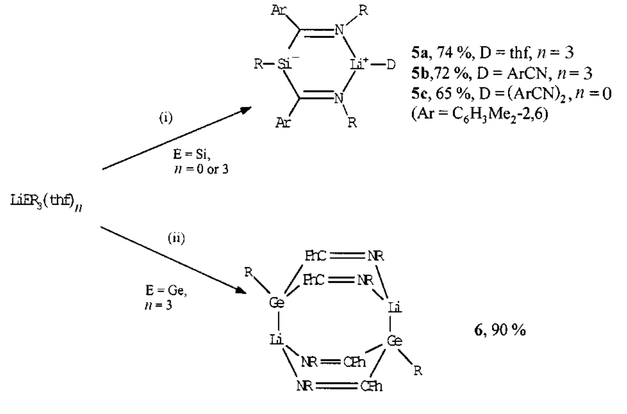
We now focus on the behaviour of the silicon or germanium congener Li(ER$_3$) of Li(CR$_3$) towards PhCN or ArCN (E = Si or Ge, Ar = 2,6-Me$_2$C$_6$H$_3$). This study has led to the isolation (Scheme 1) and characterisation of the novel crystalline compounds **5a–c** and **6**, which are 3-sila (**5a–c**) or 3-germa (**6**) analogues of the ketiminates **3** or **2**, respectively. Whereas the anionic ligands in **2** and **3** are N,N′-centred, in **5** and **6** they are E-centred.

While [Li(SiR$_3$)(thf)$_3$][5] in pentane with 1 or 2 equiv. of PhCN yielded a mixture, using the bulkier and less reactive ArCN afforded (i in Scheme 1) the red, crystalline lithium 3-sila-β-diketiminate $[Li\{N(R)C(Ar)Si(R)C(Ar)N(R)\}(D)_n]$ **5a** or **5b** in high yield. The exact nature of the product was strongly influenced by the choice of starting material and work-up procedure. When thf-free LiSiR$_3$ was treated with 3.5 equiv. of ArCN, **5c** [(D)$_n$ = (ArCN)$_2$] was isolated, whereas [Li(SiR$_3$)(thf)$_3$] with 2 equiv. of ArCN gave either **5b** [(D)$_n$ = ArCN; removal of volatiles prior to recrystallisation] or **5a** [(D)$_n$ = thf; product directly crystallised from the reaction mixture].



Scheme 1 Some reactions of LiER$_3$ with aryl nitriles (R = SiMe$_3$). *Reagents* (ArCN for i or PhCN for ii) *and conditions*: reagents were mixed in C$_5$H$_{12}$ at −78 °C (i) or −50 °C (ii) and the mixture was then warmed to *ca.* 25 °C and stirred for 12 h.

The germyllithium compound [Li(GeR$_3$)(thf)$_3$][6] was less reactive than its silicon analogue, as evident from its different behaviour towards the two nitriles. Treatment with ArCN gave a stable Lewis acid/base adduct by partial replacement of thf by ArCN. The more reactive PhCN yielded (ii in Scheme 1) bright yellow, crystalline [LiGe(R){C(Ph)=NR}$_2$]$_2$ **6**.

Each of **5a**, **5b**, **5c** and **6** gave satisfactory microanalytical and NMR spectroscopic data.§ In order to investigate the nature of the bonding, and make comparisons with carbon analogues such as the β-diketiminates **2** and **3** and a series of alkali metal cyclopentadienyls M[η^5-C$_4$Me$_4$(ER)] (M = Na or K, E = Si or Ge),[7] the X-ray crystal structures of **5b** (which is structurally similar to **5c**, to be described in the full paper), **5c** (Fig. 1)¶ and **6** (Fig. 2)¶ were determined.

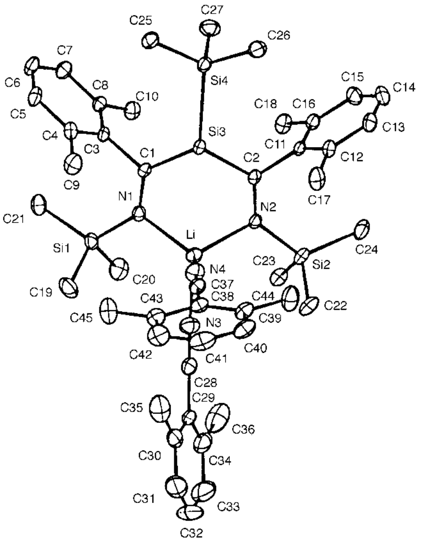


Fig. 1 Molecular structure of **5c** with selected bond distances (Å): Li–N(1) 2.000(7), Li–N(2) 1.995(7), Li–N(3) 2.106(8), Li–N(4) 2.106(9), Si(3)–Si(4) 2.334(5), Si(3)–C(1) 1.874(4), Si(3)–C(2) 1.878(5), N(1)–C(1) 1.303(5), N(2)–C(2) 1.308(5)

Crystalline **5c** is a monomer; the Li atom is surrounded in an approximately tetrahedral fashion by two nitrogens N(1) and N(2) from the ligand and two from the coordinated nitriles. The atoms Li, N(1), C(1), Si(3), C(2) and N(2) are arranged in a six-membered ring of boat conformation [the angles between the planes N(1)N(2)C(1)C(2) and LiN(1)N(2) or C(1)Si(3)C(2) are 44.3(3) or 28.2(3)°, respectively]. The negative charge is probably mainly localised at the silicon Si(3) [see also δ(^{29}Si{^{1}H}) −15.5 in **5b**], as is indicated by its pyramidal configuration [Σ°Si(3) 336.4(2)°] and the Si(3)–C(1) [1.874(4)

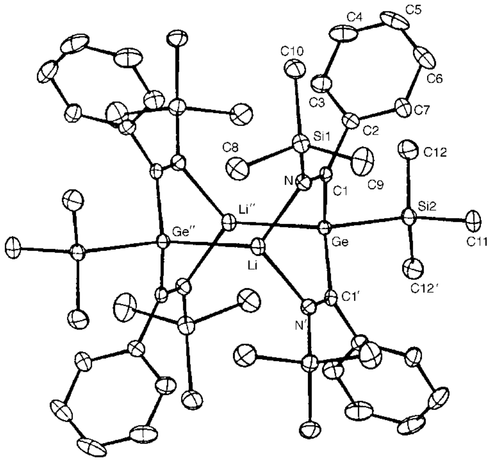


Fig. 2 Molecular structure of **6** with selected bond distances (Å): Li–N 1.954(5), Li–Ge″ 2.657(8), Ge–Si(2) 2.401(1), Ge–C(1) 2.008(3), N–C(1) 1.288(4)

Å], Si(3)–C(2) [1.878(5) Å], C(1)–N(1) [1.303(5) Å] and C(2)–N(2) [1.308(5) Å] bond lengths which are appropriate for SiC single and CN double bonds. The distance between Si(3) and Li of 3.125 Å is much longer than the Si–Li bond in, for example, [LiSiMe$_3$)(tmen)$_{1.5}$] [2.70(1) Å],[8] [{Li(μ-SiMe$_3$)}$_6$] [2.62(1)–2.78(1) Å],[9] [Li(SiR$_3$)(thf)$_3$] [2.67(1) Å],[5] [Li(SiR$_3$)(dme)$_{1.5}$} [2.630(5) Å],[10] or [(Li{μ-Si(Me)(SiMe$_2$Ph)$_2$})$_2$] [2.664(5), 2.778(7) Å].[11] We conclude that **5c** has a zwitterionic structure with only a weak (hence boat) interaction between the anionic Si(3) and the cationic Li.

The germanium derivative **6**, in contrast to **5c**, is neutral donor-free. Crystalline **6** is a dimer, Fig. 2, in which two six-membered LiNC(1)GeC(1′)N′ rings in boat conformation are connected by a direct Ge–Li bond of 2.657(8) Å. Similar values are reported for [Li(GeR$_3$)(thf)$_3$] [2.666(6) Å] and [Li(GeR$_3$)(pmdeta)] [2.653(9) Å].[6] The Ge atoms are in an approximately tetrahedral environment and the Ge–C(1) and C(1)–N bond distances of 2.008(3) and 1.288(4) Å are typical for Ge$^{\text{II}}$–C single (*e.g.*[12] 2.042(8) Å in {Ge(CHR$_2$)$_2$}$_2$ or 1.961(8) and 2.007(9) Å in [Li(12-crown-4)$_2$][C$_4$Me$_4$GeC$_6$H$_2$Me$_5$-2,4,6][7]) and C=N double bonds.

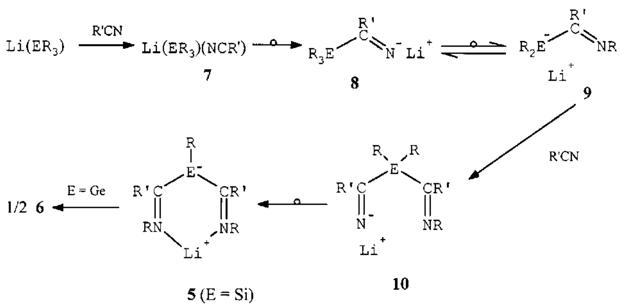
The presence of distinct E–C single and C=N double bonds in crystalline **5c** (E = Si) and **6** (E = Ge) contrasts with the situation in the carbon analogues such as **3**, which have an essentially planar central carbon [E(H), E = C]; this, and the E$\overset{-}{-}$C (E = C) and C$\overset{-}{-}$N distances of *ca.* 1.40 and 1.33 Å, respectively,[4] indicates that in **3** there is significant delocalisation in the β-diketiminate ligand.

Whereas studies on the Si and Ge analogues of cyclopentadienyls [E(R′)C$_4$Me$_4$]$^-$ in M{E(R′)C$_4$Me$_4$} (crown ether) (M = Li, Na or K; E = Si or Ge; R′ = Me, SiR$_3$ or C$_6$H$_2$Me$_3$-2,4,6) showed that in these systems Si and Ge are similarly reluctant to form delocalised aromatic anions, the monoanion of [Si(Bu^t)C$_4$Ph$_4$]$^-$ [13a] and the dianion [GeC$_4$Ph$_4$]$^{2-}$ [13b] are aromatic.

The ^{13}C{^{1}H} NMR chemical shifts of the skeletal carbon [E*C*(Ph)N] in **5c** (δ 219.4) and **6** (δ 238.0) differ considerably from those in the carbon analogues **2** (δ 177.5)[2] and **3** (D = tmen, δ 174.9),[4] which indicates that the bonding in the crystalline molecules is retained in solution. This is further supported by δ [^{29}Si{^{1}H}] −15.5 in **5b** [*cf.* refs. 7 and 13(*a*)].

Compounds **5**, unlike **6**, were soluble in aliphatic hydrocarbons. Attempts to convert the dimer **6** into a monomeric Lewis base (*e.g.* thf or py) adduct have not provided isolable products, but colour changes (red) indicated that reactions had occurred.

It is evident that in the formation of compounds **5** and **6** two successive E–C couplings, followed by unprecedented 1,3-Me$_3$Si migrations from E to N, are implicated. We propose that the reactions involve intermediates **7**–**10** of Scheme 2.



Scheme 2

Anionic 1,3-Me$_3$Si shifts from N → N,[14] C → N,[1–3] and P → N[15] in reactions with nitriles were previously documented.

Complexes **5** and **6** are of interest for the novelty of their formation and their structures and have potential as ligand transfer reagents.

We thank EPSRC for a fellowship for M. L.

Notes and References

† No reprints available.

‡ Dedicated to Professor Warren Roper as a mark of respect (by M. S. L.) and friendship.

§ *Selected spectroscopic data* [^{7}Li{^{1}H} at 116.6, ^{13}C{^{1}H} at 75.5 and ^{29}Si at 99.4 MHz]. **5b** (C$_6$D$_6$): ^{7}Li{^{1}H} δ 1.65; ^{13}C{^{1}H} δ 219.5 (CN, s), ^{29}Si{^{1}H} δ −15.5 (SiR, s). **5c** (C$_6$D$_6$): ^{7}Li{^{1}H} δ 1.64; ^{13}C{^{1}H} δ 219.4 (CN, s). **6** (C$_6$D$_6$, C$_5$D$_5$N): ^{7}Li{^{1}H} δ 0.73; ^{13}C{^{1}H} δ 238.0 (CN, s).

¶ *Crystallographic data* for **5c**/**6**: C$_{45}$H$_{63}$LiN$_4$Si$_4$/C$_{46}$H$_{74}$Ge$_2$Li$_2$N$_2$Si$_6$(C$_5$H$_{12}$)$_2$, M = 779.3/1127.0, triclinic, space group $P\bar{1}$ (no. 2), a = 11.78(2), b = 12.90(2), c = 16.82(2) Å, α = 82.8(2), β = 72.8(2), γ = 88.9(2)°/monoclinic, space group $C2/m$ (no. 12), a = 18.482(2), b = 16.552(2), c = 12.221(1) Å, β = 112.31(1)°, U = 2423(6)/3460.7(6) Å^3, Z = 2/2, D_c = 1.07/1.08 Mg m^{-3}, F(000) = 840/1204, λ(Mo-Kα) = 0.71073 Å, μ = 0.16/1.00 mm^{-1}. Data were collected at 173(2) K on a Enraf Nonius CAD4 diffractometer in the ω–2θ mode for the range of 2 < θ < 23° (**5c**) or 2 < θ < 25° (**6**). The structures were solved by direct methods (SHELXS86) and refined with full matrix least-squares on all F^2 (SHELXL93). Final residuals for 6738/3160 independent reflections were R_1 = 0.079/0.059, wR_2 = 0.153/0.119 and for the 5083/2590 with $I > 2\sigma(I)$, R_1 = 0.056/0.044, wR_2 = 0.136/0.110. CCDC 182/999.

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