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Sodium and potassium 3-sila-β-diketiminates show new coordination modes

James D. Farwell, Peter B. Hitchcock and Michael F. Lappert*
The Chemistry Laboratory, University of Sussex, Brighton, UK BN1 9QJ. E-mail: m.f.lappert@sussex.ac.uk

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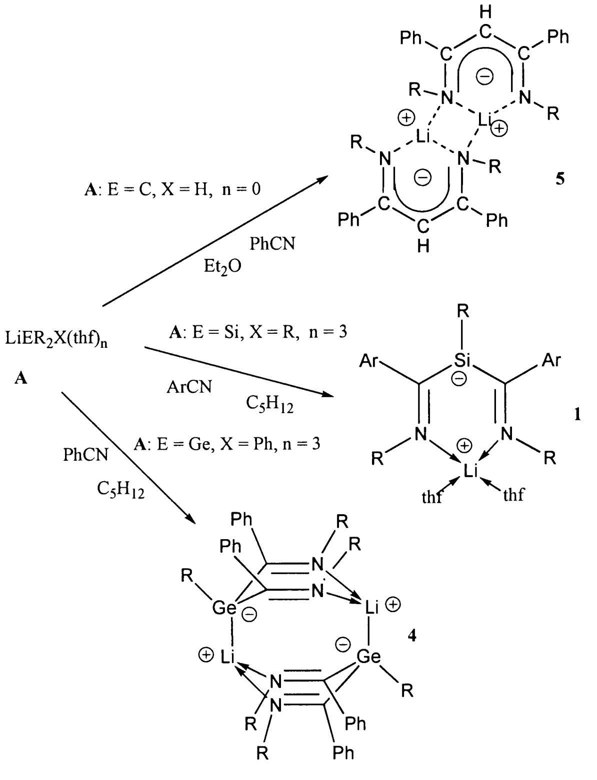
The reaction between the lithium 3-sila-β-diketiminate (1) and the appropriate MOBu^t yielded the crystalline sodium (2) or potassium (3) 3-sila-β-diketiminate in high yield; X-ray crystal data and NMR spectra show new coordination modes for the [N(R)C(Ar)Si(R)C(Ar)N(R)]$^-$ ligand (R = SiMe$_3$, Ar = C$_6$H$_3$Me$_2$-2,6).

We recently reported the synthesis of the new lithium 3-sila- (**1**) and 3-germa- (**4**) β-diketiminates by reaction between [Li(ER$_3$)(thf)$_3$] (E = Si or Ge) **A** and an appropriate nitrile PhCN/ArCN (Scheme 1, Ar = C$_6$H$_3$Me$_2$-2,6, R = SiMe$_3$).[1] Due to the reluctance of Si or Ge atoms to form double bonds, compounds **1** and **4** show a higher degree of charge localisation at the 3-position than previously noted for the carbon analogue the lithium β-diketiminate **5**.[2]

We now focus on the heavier alkali metal compounds of the 3-sila-β-diketiminato ligand [N(R)C(Ar)Si(R)C(Ar)N(R)]$^-$. To this end compound **1** was reacted with sodium or potassium *tert*-butoxide giving in high yield the appropriate alkali metal derivative, the neutral coligand-free compound **2** or **3**, respectively (Scheme 2).[†]

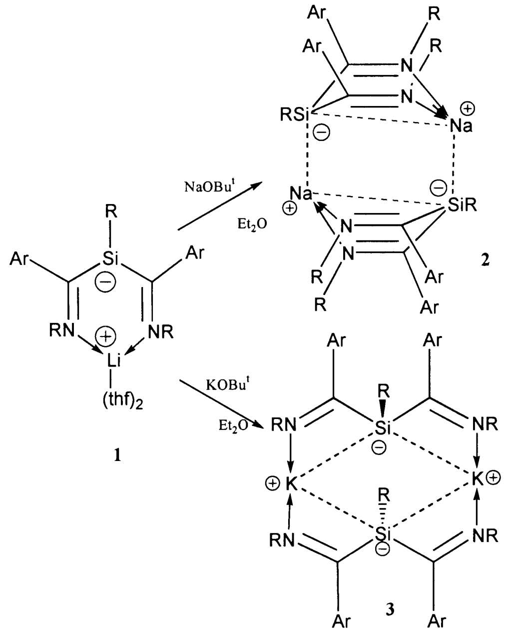
The yellow–orange sodium 3-sila-β-diketiminate **2** was only sparingly soluble in Et$_2$O but soluble in arenes or thf. The deep orange potassium 3-sila-β-diketiminate **3**, however, was even soluble in pentane.



Scheme 1

Both **2** and **3** gave satisfactory microanalytical and ^{1}H NMR spectroscopic data, which were consistent with their molecular structures, established by single crystal X-ray diffraction.[‡]

Attempts have been made, thus far unsuccessful, to convert the lithium complex **1** into its thf-free complex. Each of crystalline **2** (Fig. 1) and **3** (Fig. 2), in contrast to **1**, are neutral donor-free. Complex **2** is a centrosymmetric dimer, comprising two intramolecular boat-shaped six-membered metallacycles held together by the two intermolecular close Na···Si contacts



Scheme 2

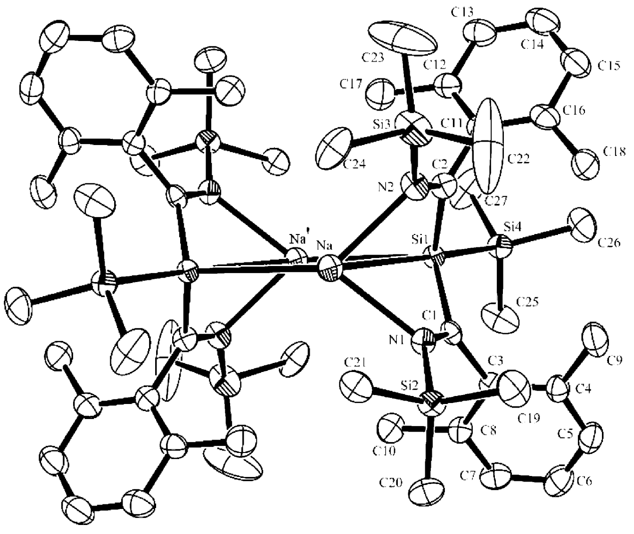


Fig. 1 Molecular structure of **2**.

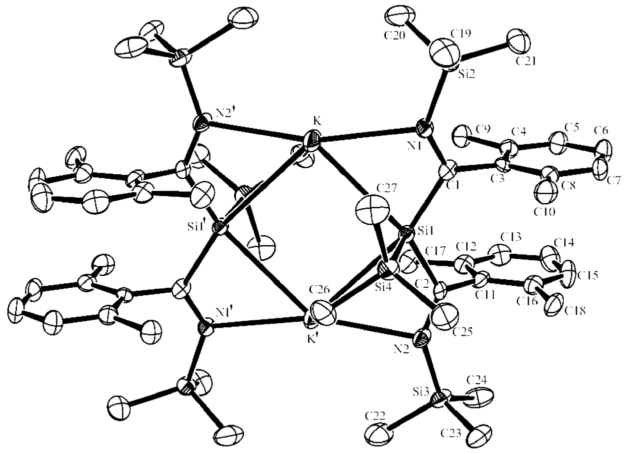


Fig. 2 Molecular structure of **3**.

(a similar arrangement was found in the lithium 3-germa-β-diketiminate **4**[1]). The central planar Si1,Na,Si1′,Na′ rhombus has almost equidistant Na–Si1 and Na–Si1′ bonds 3.179(3) and 3.192(4) Å, respectively, but very different bond angles of 111.28(10) and 68.7(2)° subtended at the Na and Si atoms, respectively.

Complex **3** is likewise a centrosymmetric dimer, containing a central almost square Si1,K,Si1′,K′ ring: K–Si1 3.305(2) Å, K–Si1′ 3.396(2) Å; K–Si1–K′ 87.81(5)°, Si1–K–Si1′ 92.19(5)°. Unlike in **2**, each 3-sila-β-diketiminato ligand additionally acts as an *N*,*N*′-bridging ligand with respect to each of the two potassium ions.

The geometry about each K ion in **3** is distorted square planar (sum of angles, 360°), with close contacts not only to the two Si atoms but also to one N atom from each ligand. The angles between the donor atoms vary between an average of 51.8° for N(1 or 2″)–K–Si(1 or 1′) and 164.27(13)° for N1′–K–N2′. There are also short contacts between the K ions and the methyl groups of the trimethylsilyls pendant to the Si1 or Si1′ atoms [*e.g.* C26···K′ 3.234 Å.] The endocyclic Si atoms Si and Si1′ are therefore penta-coordinate, each having three bonds to other atoms of the ligand, and an interaction with each of the K ions.

In the dimeric lithium β-diketiminate **5** the negative charge is not resident at the 3-position, nor is it totally delocalised around the skeleton, as in many other metal β-diketiminates.[3] This is evident from the difference in the pairs of C–N and M–N bond lengths, Table 1. The lithium 3-sila-β-diketiminate **1** has charge more localised at the 3-position, the pairs of Si–C and C–N distances being essentially identical.[1] For compounds **2** and **3**, the charge is even less delocalised than for **1**, as shown by the shorter C–N and longer Si–C bond lengths.

Comparison of **2** with $[\mathrm{Na}\{\mathrm{N(SiMe_3)_2}\}]_{\infty(\text{or } 3)}$ **6**[4] and $[\mathrm{Na}\{\mathrm{Si(SiMe_3)_3}\}]_2$ **7**[5] shows that the Na-Si distances in **2** are longer than that in **7**, while the Na-N distances in **2** and **6** are similar. Comparing compound **3** with $[\mathrm{K}\{\mathrm{Si(SiMe_3)_3}\}]_2$ **8** one of the K–Si distances in **3** is shorter than in **8**, while the other is almost identical; the K–N distances in **3** are significantly longer than those in $[\mathrm{K}\{\mathrm{N(SiMe_3)_2}\}]_2$ **9**.[6] Also included in Table 1 is the metal–ligand N–C bond length for $[\mathrm{Ni}\{\overline{\mathrm{N(H)C(CN)C(CN)N}}\mathrm{(H)}\}_2]$[7] **10**, which is longer than in any of **1**–**9**.

Table 1 Selected bond lengths (Å) for compounds **2** and **3** and related examples

Compound	M–Si	M–N	Si–C	C–N
5[3]		1.97(2)		1.33(1)
		2.01(2)		1.27(1)
1[1]		2.000(7)	1.874(4)	1.303(5)
		1.995(7)	1.878(5)	1.308(5)
2	3.179(3)	2.370(6)	1.282(7)	
	3.192(4)	2.395(6)	1.929(6)	1.295(7)
6[4]		2.376(8)	1.876(4)	
7[5]	2.983			
3	3.305(2)	2.863(4)	1.903(5)	1.307(6)
	3.396(2)	2.857(4)	1.904(5)	1.295(6)
9[6]		2.786(8)	1.876(4)	
8[5]	3.391			
10[7]				1.3305(4)

The $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR chemical shifts for *C*=N in compounds **2** and **3** are δ 204.3 and 213.1, respectively. These unusual shifts for olefinic carbon atoms are in good agreement with that of δ 219.4 for **1**.[1]

The $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR resonance for the skeletal Si atom has shifts for compounds **2** and **3** of δ −45.20 and −56.86, respectively. The $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ chemical shifts for **7** and **8**, at δ 179.8 and −185.7, respectively, show that while the Si atoms of **2** and **3** are at a significantly lower frequency than the normal range for *Si*Me$_3$X groups of δ 0 to −20, they are not as shielded as those of compounds **7** and **8**.

Complexes **2** and especially **3** are of interest because they demonstrate that the extra localisation of charge at the 3 position, due to the Si atom, allows the β-diketiminato ligand extra flexibility to coordinate in new ways.

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Notes and references

† *Synthesis* of **2** and **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 **1** (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* and, after extracting with pentane (150 cm^3), a saturated solution of the filtrate in toluene (*ca.* 3 cm^3) was cooled at −30 °C yielding orange crystals of **2** (0.66 g, 99%). ^{1}H NMR (C$_6$D$_6$, 298 K): δ 0.04 (s, 9H, Si{SiMe$_3$}), 0.12 (s, 18H, N{SiMe$_3$}), 2.72 (s, 12H, C$_6$H$_3$*Me*$_2$), 7.05–7.32 (m, C$_6$*H*$_3$Me$_2$). ^{29}Si NMR (C$_6$D$_6$): δ −1.32 (s, N{SiMe$_3$}), −17.11 (s, Si{*Si*Me$_3$}), −45.20 (s, *Si*{SiMe$_3$}). Similarly, from potassium *tert*-butoxide (0.08 g, 0.71 mmol) and **1** (0.49 g, 0.58 mmol) in pentane (30 cm^3) at −80 °C, deep orange crystals of **3** (0.28 g, 95%) were obtained. ^{1}H NMR (C$_6$D$_6$): δ 0.04 (s, 9H, Si{SiMe$_3$}), 0.12 (s, 18H, N{SiMe$_3$}), 2.72 (s, 12H, C$_6$H$_3$*Me*$_2$), 7.05–7.32 (m, C$_6$*H*$_3$Me$_2$). ^{29}Si NMR (C$_6$D$_6$): δ −3.09 (s, Si{*Si*Me$_3$}), −19.60 (s, N{*Si*Me$_3$}), −56.86 (s, *Si*{SiMe$_3$}).

‡ *Crystal data* for **2**: $\mathrm{C_{54}H_{90}N_4Na_2Si_8 \cdot 2C_7H_8}$, M = 1250.3, monoclinic, space group $P2_1/c$, a = 14.372(7), b = 15.689(4), c = 18.281(7) Å, β = 111.69(4)°, V = 3830(3) Å^3, T = 173 K, Z = 2, μ(Mo-Kα) = 0.18 mm^{-1}, 6998 reflections measured, 6721 unique (R_{int} = 0.050). Refinement on all F^2, final $R1$ = 0.090 (for 3389 reflections with $I > 2\sigma(I)$), wR_2 = 0.266 (for all data).

Crystal data for **3**: $\mathrm{C_{54}H_{90}K_4Na_2Si_8}$, M = 1098.2, monoclinic, space group $P2_1/c$, a = 10.539(5), b = 22.920(9), c = 13.200(6) Å, β = 93.26(4)°, V = 3183(2) Å^3, T = 173 K, Z = 2, μ(Mo-Kα) = 0.34 mm^{-1}, 4685 reflections measured, 4418 unique (R_{int} = 0.065). Refinement on all F^2, final $R1$ = 0.060 (for 2808 reflections with $I > 2\sigma(I)$), $wR2$ = 0.153 (for all data).

CCDC reference numbers 174516 and 174517. See http://www.rsc.org/suppdata/cc/b1/b10443h/ for crystallographic data in CIF or other electronic format.

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