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Syntheses and structures of structurally diverse potassium β-diketiminates derived from the ligand [{N(SiMe$_3$)C(Ph)}$_2$CH]$^-$†

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The compounds [K{(μ-N(SiMe$_3$)C(Ph))$_2$CH}(thf)$_2$]$_\infty$ 1, [K{μ-N(SiMe$_3$)C(Ph)C(H)C(Ph)NH}L]$_2$ [L = (thf)$_2$ 2, tmen 3], [K{μ-NSi(Me)$_2$C(Ph)C(H)C(Ph)N}(thf)$_3$]$_2$ 4 and [K{N(H)C(Ph)}$_2$CH](thf)$_{0.5}$ 5 have been prepared from K[{N(SiMe$_3$)C(Ph)}$_2$CH] and the X-ray structures of 1–4 are reported.

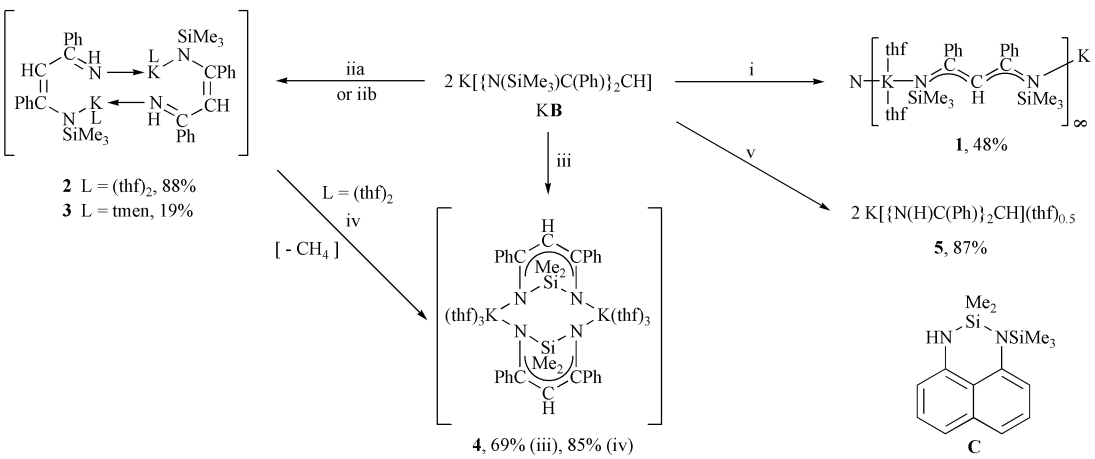
Metal β-diketiminates are attracting much current attention, as evident from the 38 papers on this topic published in 2001, and data now available on complexes of 43 metals.[1] A major synthetic route involves σ-bond metathesis between an alkali metal β-diketiminate and a metal chloride. In our hands, a sodium or potassium, rather than a lithium, β-ketiminate is the precursor of choice, because of the greater ease of separation of the heavier alkali metal chloride coproduct, as in the synthesis of lanthanide metal β-ketiminates.[2] Whereas structural data are available for several lithium β-diketiminates,[1,3] there is just a single published structure of a heavier group 1 metal analogue, namely K[{N(C$_6$H$_3$^{i}Pr$_2$-2,6)C(Me)}$_2$CH]·PhMe (K**A**).[4] We now report on five potassium β-diketiminates **1**–**5**, starting from the known K[{N(SiMe$_3$)C(Ph)}$_2$CH] (K**B**),[5] and the crystal structures of four of them **1**–**4**, in each of which the ligand unusually (*cf.*,[1,3] the chelated Li β-diketiminates) features in a bridging mode.

Complex K**B** had been obtained from either [Li{(N(SiMe$_3$)C(Ph))$_2$CH}]$_2$ by treatment with KOBu^t, or KCH(SiMe$_3$)$_2$ and 2 PhCN.[5] Its conversion into the complexes **1**–**5** is illustrated in Scheme 1. Treatment of K**B** with thf yielded (i in Scheme 1) the polymeric acyclic bis(thf) adduct **1**. Using K**B** and potassium hydroxide pellets (which had been heated *in vacuo* at 100 °C) in appropriate stoichiometry in thf afforded the potassium β-diketiminate in which either one (**2**) or both (**5**) of the trimethylsilyl groups of the ligand was replaced by hydrogen, iia and v in Scheme 1, respectively. The tmen analogue **3** of **2** was obtained in low yield (iib in Scheme 1) from **B** and moist tmen. The dimeric potassium bicyclic β-diketiminate **4** was prepared under reflux in thf either (iii in Scheme 1) from K**B** and solid KOH, or (iv in Scheme 1) from **2**. By monitoring the former process in pyridine-d$_8$ in a sealed tube by ^{1}H NMR spectroscopy, it was established that **2** was an intermediate in the pathway from K**B** to **4**. The surprising implication is that Si–C, rather than Si–N, cleavage had occurred in a process involving an intramolecular N-Si(Me)$_3$MN → N-Si(Me)$_2$-N cyclometallation (M = H or K); a precedent is the conversion of 1,8-bis(trimethylsilylamino)naphthalene into **C**, by treatment with LiBu^n.[6]

Satisfactory microanalyses were obtained for complexes **1** and **3**–**5** (for **4** and **5** on thf-free materials; for **2** loss of thf *in vacuo* was accompanied by decomposition) and ^{1}H NMR spectra in C$_5$D$_5$N‡ which for **1**–**4** were consistent with their X-ray crystal structures,§ illustrated in Figs. 1 (**1**), 2 (**2**), and 3 (**4**) (the structure of **3** is closely similar to that of **2**). Selected geometrical parameters are listed in Table 1.

Crystalline **1** is a polymer. Each formally four-coordinate potassium ion has four additional K···C contacts to adjacent *ipso*- and *m*-carbon atoms, 3.213(5)–3.243(5) Å; there is significant electron π-delocalisation in the ligand. By contrast, this is less so in the centrosymmetric, dimeric, crystalline complexes **2** and **3**. In **2** the formally four-coordinate potassium ion has an additional inter-molecular K···N close contact of 3.231(2) Å, while **3** has K$^+$ in a distorted trigonal bipyramidal environment; there are three additional close K···C contacts [av. 3.146 Å for **2** and 2.993(5) Å for **3**]. The potassium ion in **3** lies *ca.* 2.5 Å outside the NCCCN plane. Crystalline **4** is a centrosymmetric dimer. Each of the two five-coordinate potassium ions lies in a distorted trigonal bipyramidal environment, being bound to three oxygen and two nitrogen atoms of adjacent, parallel and essentially planar NCCCN moieties, between which the potassium ions are sandwiched. There is substantial π-delocalisation in the NCCCN moiety; and the four nitrogen atoms of the pair of NCCCN rings are coplanar.

† Electronic supplementary information available: details of crystallography for **1**–**4** and further analytical data for **1**–**5**. See http://www.rsc.org/suppdata/cc/b2/b205296b/



Scheme 1

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Table 1 Selected bond lengths (Å) in **1**–**4** and **A**[4] (Ar = $C_6H_3{}^iPr_2$-2,6)

Bond	**1**	**2**	**3**	**4**	K**A**[4]
K-NSiMe$_2$	2.827(3), 2.833(3)	2.893(2)	2.889(4)	2.810(4), 2.811(4)	—
K-NH	—	2.746(2)	2.747(4)	—	—
K-NAr	—	—	—	—	2.6387(19), 2.7398(19)
PhC-NSiMe$_2$	1.322(5), 1.317(5)	1.325(3)	1.326(6)	1.330(5), 1.326(5)	—
PhC-NH	—	1.302(3)	1.303(6)	—	—
MeC-NAr	—	—	—	—	1.323(3), 1.317(3)
PhC-CH	1.406(5), 1.426(5)	1.400(3), 1.435(3)	1.381(6), 1.436(5)	1.408(6), 1.415(6)	—
MeC-CH	—	—	—	—	1.400(3), 1.414(3)

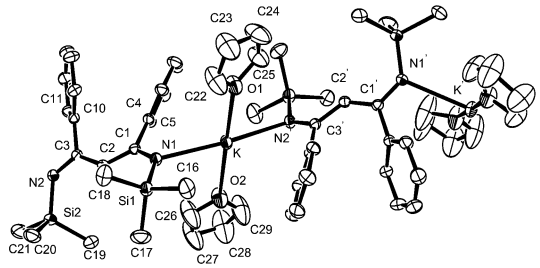

Fig. 1 Molecular structure of **1**.

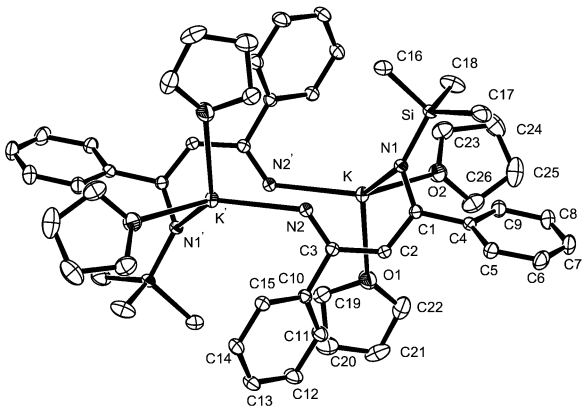

Fig. 2 Molecular structure of **2**.

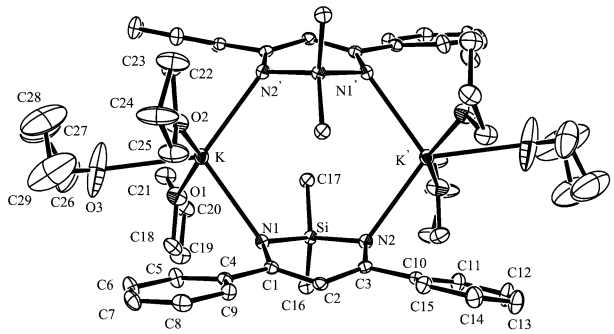

Fig. 3 Molecular structure of **4**.

In conclusion, we have synthesised some structurally diverse potassium β-diketiminates, each derived from the ligand [{N(SiMe$_3$)C(Ph)}$_2$CH]$^-$ **B**, and shown that one or both of the *N*-SiMe$_3$ groups may be hydrolysed yielding complexes based on N–H analogues containing [N(SiMe$_3$)C(Ph)C(H)C(Ph)NH]$^-$ or [{N(H)C(Ph)}$_2$CH]$^-$ ligands. Thus, the N-SiMe$_3$ groups in **B** are not only sterically significant, but this desilylation demonstrates their role as protected amino groups. Finally, the Si–C cleavage reaction yielding a complex containing the ligand [NSi(Me)$_2$C(Ph)C(H)C(Ph)N]$^-$ (**C**) is noteworthy. The use of these ligands, and especially **C**, is being vigorously pursued.

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Notes and references

‡ *Selected ^{1}H NMR spectral data (293 K, C_5D_5N, 300.1 MHz):* **1**(when separated from the mother liquor, crystals of **1** lost thf rapidly, as shown by the NMR data): δ 0.13 (s, 18 H, CHSi*Me*$_3$), 1.60 (m, 4 H, OCH$_2$C*H*$_2$), 3.64 (m, 4 H, OC*H*$_2$CH$_2$), 5.51 (s, 1 H, CH), 7.21-7.23 (m, 6 H, Ph), 7.55 (m, 4 H, Ph); **2**: δ 0.13 (s, 9 H, SiMe$_3$), 5.59 (s, 1 H, CH), 7.01-7.13 (m, 5 H, Ph), 7.49-7.53 (m, 3 H, Ph), 7.82 (m, 2 H, Ph), 11.64 (s, 1 H, NH); **3**: δ 0.22 (s, 9 H, NSiMe$_3$), 2.16 (s, 12 H, CH$_2$N*Me*$_2$), 2.37 (s, 4 H, C*H*$_2$NMe$_2$). 5.70 (s, 1 H, CH), 7.19-7.39 (m, 6 H, Ph), 7.71 (m, 2 H, Ph), 8.11 (m, 2 H, Ph); **4**: δ 0.49 (s, 6 H, SiMe$_2$), 6.64 (s, 1 H, CH), 7.10-7.20 (m, 6 H, Ph), 8.18 (d, 4 H, Ph); **5**: δ 1.58 (m, 2 H, thf), 3.63 (m, 2 H, thf), 5.57 (s, 1 H, CH), 7.23-7.33 (m, 6 H, Ph), 7.94 (d, 4 H, Ph), 10.8-11.4 (br, 2 H, NH).

§ Crystallographic data were collected on an Enraf-Nonius Kappa CCD at 173(2) K (**2**, **4**) or CAD4 at 253(2) K (**1**) or 173(3) K (**3**)(ESI†).

1: $C_{29}H_{45}KN_2O_2Si_2$, *M* = 548.9, monoclinic, space group *P*2$_1$/*n* (no. 14), *a* = 11.217(3), *b* = 19.020(3), *c* = 15.524(3) Å, β = 93.05(2)°, *U* = 3308(1) Å^3, *Z* = 4, μ(Mo-Kα) = 2.29 mm^{-1}. Final residual was R_1 = 0.069 for the 3500 reflections with $I > 2\sigma(I)$ and wR_2 = 0.206 for all the 5756 reflections. CCDC 187158. **2**: $C_{52}H_{74}K_2N_4O_4Si_2{\cdot}C_4H_8O$, *M* = 1097.74, triclinic, space group *P*1 (no. 2), *a* = 9.8158(3), *b* = 10.7458(3), *c* = 15.2080(5) Å, α = 83.771(2), ß = 88.730(2), γ = 89.386(2)°, *U* = 1597.2(1) Å^3, *Z* = 1, μ(Mo-Kα) = 0.23 mm^{-1}. Final residual was R_1 = 0.057 for the 4813 reflections with $I > 2\sigma(I)$ and wR_2 = 0.161 for all the 5491 reflections. CCDC 187159. **3**: $C_{48}H_{74}K_2N_8Si_2$, *M* = 897.5, monoclinic, space group *P*2$_1$/*n* (no. 14), *a* = 12.361(3), *b* = 16.470(4), *c* = 13.008(3) Å, β = 94.54(2)°, *U* = 2656.2(11) Å^3, *Z* = 2, μ(Mo-Kα) = 0.26 mm^{-1}. Final residual was R_1 = 0.060 for the 2030 reflections with $I > 2\sigma(I)$ and wR_2 = 0.143 for all the 3249 reflections. CCDC 187160. **4**: $C_{58}H_{82}K_2N_4O_6Si_2$, *M* = 1065.66, monoclinic, space group *P*2$_1$/*n* (no. 14), *a* = 11.5035(4), *b* = 18.0757(7), *c* = 14.5585(6) Å, β = 100.978(2)°, *U* = 2971.8(2) Å^3, *Z* = 2, μ(Mo-Kα) = 0.25 mm^{-1}. Final residual was R_1 = 0.078 for the 3421 reflections with $I > 2\sigma(I)$ and wR_2 = 0.205 for all the 5226 reflections. CCDC 187161. See http://www.rsc.org/suppdata/cc/b2/b205296b/ for crystallographic files in .cif or other electronic format.

1 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.* in press.
2 P. B. Hitchcock, M. F. Lappert and S. Tian, *J. Chem. Soc., Dalton Trans.*, 1997, 1945.
3 P. B. Hitchcock, M. F. Lappert, M. Layh, D.-S. Liu, R. Sablong and S. Tian, *J. Chem. Soc., Dalton Trans.*, 2000, 2301.
4 W. Clegg, E. K. Cope, A. J. Edwards and F. S. Mair, *Inorg. Chem.*, 1998, **37**, 2317.
5 P. B. Hitchcock, M. F. Lappert and D.-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1994, 1699.
6 S. Daniele, C. Drost, B. Gehrhus, S. M. Hawkins, P. B. Hitchcock, M. F. Lappert, P. G. Merle and S. G. Bott, *J. Chem. Soc., Dalton Trans.*, 2001, 3179.