Synthesis and Structures of the Heavier Alkali Metal Alkyls; the X-ray Structures of [Na(μ-R)]∞ and [Rb(μ-R)(pmdeta)]2 [R = CH(SiMe3)2, pmdeta = (Me2NCH2CH2)2NMe]†

Peter B. Hitchcock, Michael F. Lappert, Wing-Por Leung, Liu Diansheng and Tian Shun

School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ

The crystalline, hexane-soluble metal alkyls [Na(μ-R)]∞ 1, [KR(pmedta)]m, and [Rb(μ-R)(pmdeta)]2 2 [R = CH(SiMe3)2, pmdeta = (Me2NCH2CH2)2NMe] have been prepared from LiR with equimolar portions of NaOBu^t, KOBu^t + pmdeta, and Rb(OC6H2Bu$^t_2$-2,6-Me-4) + pmdeta, respectively; 1 has chains of alternating cations and planar R⁻ anions which are approximately orthogonal to the chains, (Na–C)$_{av}$ 2.555(10) Å, (Na–C–H)$_{av}$ 76(3) and (Na–C–Na)$_{av}$ 152(1)°, whereas 2 consists of discrete dimers, (Rb–C)$_{av}$ 3.412(9) Å, Rb–C–Rb 75.3(2) and C–Rb–C 104.7(2)°.

As pointed out in a recent review, compared to organolithium compounds, much less attention has been paid to the analogues of the heavier Group 1 metals.[1]

We now report (*i*) the synthesis‡ (Scheme 1) of four crystalline heavier alkali metal bis(trimethylsilyl)methyls: [Na(μ-R)]∞ 1, [Rb(μ-R)(pmdeta)]2 2, [KR]n 3, and [KR(pmdeta)]m 4 [R = CH(SiMe3)2, pmdeta = (Me2NCH2CH2)2NMe]; (*ii*) NMR spectral data for the hexane-soluble compounds 1, 2 and 4;‡ and (*iii*) single crystal X-ray diffraction data for 1 (Fig. 1) and 2 (Fig. 2).§

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† No reprints available.

‡ *Preparation of* 1: Solid NaOBu^t (7.2 g, 75 mmol) was added in portions to a stirred solution of LiR (11.25 g, 67.7 mmol) in hexane (350 ml). The suspension was stirred for 2 days at *ca.* 25 °C and traces of insoluble material were filtered off. The filtrate was concentrated (to *ca.* 80 ml), then cooled (−30 °C) for several days yielding colourless crystals of almost pure 1, which were recrystallised from hexane, affording 1 (9.8 g, 80%), m.p. 130–132 °C, NMR (C6D6, 305 K) ¹H: δ 0.20 (Me), −2.04 (CH); ¹³C{¹H}: δ 6.99 (Me), 0.44 (CH); ²⁹Si{¹H}: δ 12.44. Crystalline LiR (91%) was prepared from RBr in Et2O and LiBu^n in hexane.

Preparation of 2: Solid LiR (0.71 g, 4.28 mmol) was added to a suspension of RbOAr (Ar = C6H2Bu$^t_2$-2,6-Me-4) (1.48 g, 4.27 mmol) in hexane (25 ml). The mixture was stirred for 10 h at *ca.* 25 °C. Tetrahydrofuran (thf) (10 ml) was added and the pale-yellow solution was concentrated and cooled at −30 °C; colourless, crystalline LiOAr(thf) (m.p. 256–258 °C)² was filtered off. Pmedta (0.74 g, 4.27 mmol) was added to the filtrate; the mixture was filtered, the filtrate concentrated and cooled to give pale-yellow crystals of 2 (1.2 g, 67%), m.p. 62–64 °C; ¹H NMR (C6D6, 305 K): δ 2.12 (m, CH2), 1.98 (s, NMe), 0.45 (s, SiMe3), −1.70 (CH). The RbOAr was prepared from Rb (1.0 g) and ArOH (2.55 g) in C6H14.

Preparation of 3 *and* 4: 3 was prepared from LiR (0.62 g, 3.73 mmol) and KOBu^t (0.40 g, 3.57 mmol) in a similar fashion to that described for 1, except that 3 (0.65 g, 93%) was the hexane-insoluble component. A solution of pmdeta (0.57 g, 3.3 mmol) and 3 (0.65 g, 3.3 mmol) in hexane (50 ml) at −20 °C yielded pale-yellow crystals of 4 (1.02 g, 84%), m.p. 58–60 °C; ¹H NMR (C6D6, 305 K): δ 2.36 (m, CH2), 2.21 (s, NMe), −0.10 (s, SiMe3), −2.11 (s, CH).

§ *Crystal data*: For each structure data were measured for 2 < θ < 25° using monochromated Mo-Kα radiation (λ = 0.71069 Å) on an Enraf-Nonius CAD4 diffractometer. Structure solution was by heavy atom methods for the Rb alkyl 2 or direct methods for the Na alkyl 1 using SHELXS86.

(*i*) Na alkyl 1 (orthorhombic form). C7H19NaSi2, *M* = 182.4, orthorhombic, *P*2₁2₁2₁, *a* = 11.397(4), *b* = 12.207(3), *c* = 34.962(11) Å, *U* = 4863.9 Å³, *Z* = 16, *D*c = 1.00 g cm⁻³, μ = 2.6 cm⁻¹, *F*(000) = 1600, *T* = 173 K. 4805 Unique reflections, 3881 observed for *I* > 2σ(*I*), *R* = 0.044, *R*w = 0.048, *S* = 1.3, 377 variables. Methyl H atoms fixed, others located and refined.

(*ii*) Na alkyl 1 (monoclinic form). C7H19NaSi2, *M* = 182.4, monoclinic, *P*2₁/n, *a* = 10.373(2), *b* = 12.871(3), *c* = 19.204(9) Å, β = 97.13(3)°, *U* = 2544.0 Å³, *Z* = 8, *D*c = 0.95 g cm⁻³, μ = 2.5 cm⁻¹, *F*(000) = 800, *T* = 293 K. 4939 Unique reflections, 1422 observed for *I* > σ(*I*), *R* = 0.110, *R*w = 0.125, *S* = 3.2, 181 variables. All H atoms omitted.

(*iii*) Rb alkyl 2. C32H84N6Rb2Si4, *M* = 836.4, monoclinic, *P*2₁/n, *a* = 11.871(6), *b* = 11.936(3), *c* = 18.275(5) Å, β = 100.87(3)°, *U* = 2542.8 Å³, *Z* = 2, *D*c = 1.09 g cm⁻³, μ = 19.9 cm⁻¹, *F*(000) = 896, *T* = 293 K. 4694 Unique reflections, 1603 observed for *I* > 3σ(*I*), *R* = 0.050, *R*w = 0.065, *S* = 1.9, 199 variables. Methyl H atoms fixed, rest omitted.

The alkylating agent for each of 1–4 was the crystalline, lipophilic, and volatile lithium alkyl LiR.³ For the homoleptic compounds 1 and 3, the co-reagent was the appropriate metal *tert*-butoxide with hexane as solvent. The key to the synthesis was the somewhat greater hexane-solubility of the lithium *tert*-butoxide co-product, which permitted the less soluble 1 to be readily separated. For the insoluble [KR]n 3, repeated removal by extraction of the sparingly soluble KOBu^t with C6H14 led to its purification. For [Rb(μ-R)(pmdeta)]2 2, we turned to an ⁻OAr/R⁻ (Ar = a 2,6-di-*tert*-butylphenyl group) rather than the ⁻OBu^t/R⁻ displacement reaction, the Rb starting aryloxide being somewhat more soluble than the *tert*-butoxide. That strategy had previously been introduced by us into tin(ii)⁴ and 4f element⁵ chemistry; for example Li(OC6H3Bu$^t_2$-2,6), unlike [LnR3] or [Ln(OAr)3] (Ln = La or Sm), is hexane-insoluble.⁵ The isoleptic potassium analogue of 2, [K(R)(pmdeta)]m 4, obtained from 3 + pmdeta, had similar NMR spectral characteristics to 2,‡ and hence 2 and 4 are probably isostructural.

The sodium alkyl [Na(μ-R)]∞ 1 crystallises in two different crystal forms, with both showing the same structural motif of chains of the compound. For the monoclinic form the diffraction data are poor; hence only the crystal data are listed.§ The orthorhombic form gave excellent diffraction data and the resulting structure is shown in Fig. 1.

The orthorhombic form of Na[CH(SiMe3)2] 1, crystallised from benzene, consists of chains of alternating cations and anions. The anions are planar with average dimensions C–Si 1.806(3), C–H 0.81(1) Å, Si–C–Si 129(1) and Si–C–H 115(2)°. The planes of the anions are roughly perpendicular to the chains with average Na–C distances of 2.555(10) Å for the symmetrically bridging Na cations. The two Na cations on either side of the R⁻ anion complete a distorted trigonal bipyramidal geometry about the central C atoms with Na–C–H averaging 76(3)° and Na–C–Na 152(1)°. The coordination at Na is bent two-coordinate with C–Na–C averaging 143(6)°. In addition, there are methyl groups close to the Na cations giving rise to short Na···H contacts: Na(1)···H(5b) 2.62, Na(1)···H(5c) 2.60, Na(2)···H(7b) 2.43, Na(2)···H(8b) 2.57, Na(2)···H(13b) 2.40, Na(2)···H(15b) 2.50, Na(3)···H(12c) 2.54, Na(3)···H(19b) 2.65, Na(4)···H(17b) 2.56, Na(4)···H(17c) 2.52, Na(4)···H(25b) 2.46 and Na(4)···H(27c) 2.65 Å.
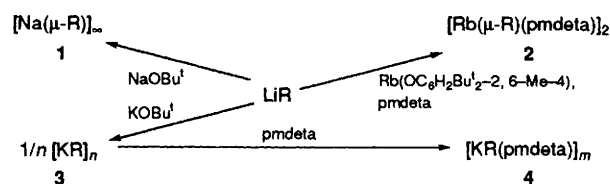
Scheme 1 Synthesis of alkyls of Na, K and Rb: complexes 1–4 [R = CH(SiMe3)2, pmdeta = (Me2NCH2CH2)2NMe]‡

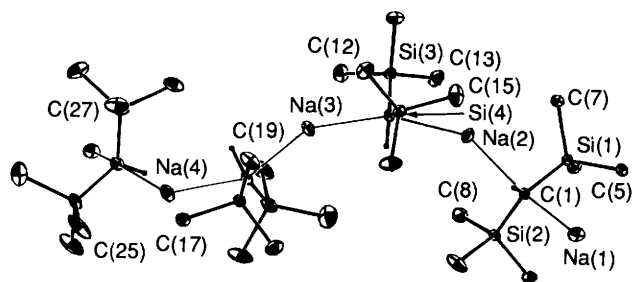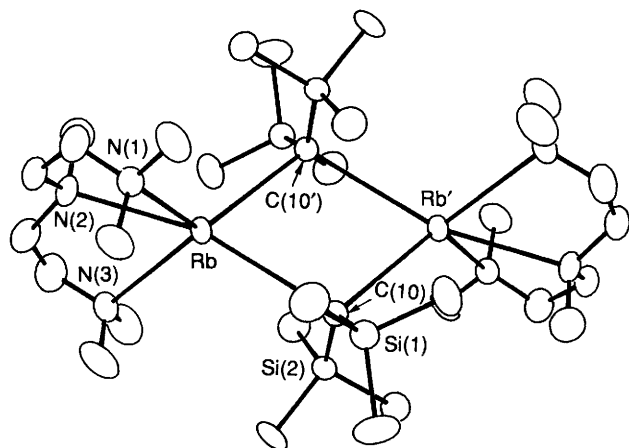
Fig. 1. The X-ray structure and atom labelling for [Na(μ-R)]∞ 1

Fig. 2. The X-ray structure and atom labelling for [Rb(μ-R)-(pmdeta)]₂ 2

The monoclinic form of 1, crystallised from hexane, contains similar chains of alternating cations and anions with essentially the same geometry.

In the rubidium alkyl [Rb(μ-R)(pmdeta)]₂ 2 there are discrete dimers with the Rb atoms bridged by the two alkyl groups. Although the H atoms on the bridging C atoms have not been located, it seems likely that the alkyl anions are planar. The Si–C–Si angle is 125.5(5)°, with Si–C 1.744(9) and 1.829(8) Å. The endocyclic ring angles are 104.7(2)° at C(10) and 75.3(2)° at Rb. The coordination at Rb is completed by the three Rb–N bonds averaging 3.11(1) Å, with Rb–C(10) 3.361(9) and Rb–C(10') 3.485(8) Å.

The low coordination number of two for sodium in crystalline [Na(μ-R)]∞ 1 has a single precedent: the isoelectronic crystalline [Na{μ-N(SiMe₃)₂}]∞[6] is isostructural with 1. Both compounds are hexane-soluble and volatile below 150 °C at 10⁻² Torr, and thus probably are of low molecular mass in the gas phase (their structures by gas phase electron diffraction are under investigation; the Na compound was believed to be largely monomeric in the gas phase). By contrast, lithium bis(trimethylsilyl)amide is a trimer in the crystal,[8] but a dimer in the vapour;[9] crystalline [K{μ-N(SiMe₃)₂}]₂ is hexane-soluble and in view of its low electrical conductivity has been described as having strong ion-pairing.[10] The rubidium and caesium analogues have been X-ray-characterised as their dioxane adducts, the polymeric dioxane-linked dimers [M({μ-N(SiMe₃)₂}(OC₄H₈O))₂(O₂C₄H₈)]∞,[11] each Rb or Cs atom (M) being four-coordinate, unlike the five-coordinate Rb in [Rb(μ-R)(pmdeta)]₂ 2, [Rb–N(1) 3.112(7), Rb–N(2) 3.093(7), Rb–N(3) 3.131(7) Å].

Crystalline [Na(μ-R)]∞ 1 and the lithium analogue are isostructural; the latter is a monomer in the vapour (at 100 °C and 10⁻² Torr).[3] The dimeric structure of crystalline 2 has some similarity in its bis(alkyl)-bridging and five-coordinate α-carbon with the well-known and archetypal electron-deficient compounds [AlMe₂(μ-Me)]₂ or [Be(μ-Me)₂]∞. By contrast, the crystalline lithium compound isoleptic with 2 is a monomer, [LiR(pmdeta)], having four-coordination for both the metal and the ligating carbon.[12]

The structural data here presented for compounds 1 and 2 are available for comparison with those for others in the literature.[1] For homoleptic alkyls, data are available for NaMe, NaEt, KMe and CsMe; e.g., [(NaMe)₄]∞ has four-coordinate sodium with Na–C 2.58–2.64 Å and intermolecular contacts of 2.76 Å;[13] while each metal and carbon is six-coordinate in the heavier Group 1 metal methyls.[14] One example of a heavier alkali metal σ-hydrocarbyl containing double bridges had been established prior to 2: [Na(μ-Ph)(pmdeta)]₂ has (Na–C)ₐᵥ 2.670(7), Na–NMe₂ 2.661(1), and Na–NMe 3.237(3) Å.[15] In the latter, unlike in 2, it appears that pmdeta behaves as a bi- and not as a tri- (as in 2)-dentate ligand.

The results here presented on the heavier alkali metal bis(trimethylsilyl)methyls provide further illustrations of the versatility of the ⁻CH(SiMe₃)₂ ligand.[16]

References

1 C. Schade and P. v. R. Schleyer, Adv. Organomet. Chem., 1987, 27, 169.

2 B. Çetinkaya, I. Gümrükçü, M. F. Lappert, J. L. Atwood, R. D. Rogers and M. J. Zaworotko, J. Am. Chem. Soc., 1980, 102, 2088.

3 J. L. Atwood, T. Fjeldberg, M. F. Lappert, N. T. Luong-Thi, R. Shakir and A. J. Thorne, J. Chem. Soc., Chem. Commun., 1984, 1163.

4 T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, J. Chem. Soc., Dalton Trans., 1986, 1551.

5 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, J. Chem. Soc., Chem. Commun., 1988, 1007.

6 R. Grüning and J. L. Atwood, J. Organomet. Chem., 1977, 137, 101.

7 J. C. Green, M. Payne, E. A. Seddon and R. A. Andersen, J. Chem. Soc., Dalton Trans., 1982, 887.

8 R. D. Rogers, J. L. Atwood and R. Grüning, J. Organomet. Chem., 1978, 157, 229.

9 T. Fjeldberg, M. F. Lappert and A. J. Thorne, J. Mol. Struct., 1984, 125, 265.

10 K. F. Tesh, T. P. Hanusa and J. C. Huffman, Inorg. Chem., 1990, 29, 1584.

11 F. T. Edelmann, F. Pauer, M. Wedler and D. Stalke, Inorg. Chem., 1992, 31, 4143.

12 M. F. Lappert, L. M. Engelhardt, C. L. Raston and A. H. White, J. Chem. Soc., Chem. Commun., 1982, 1323.

13 E. Weiss, S. Corbelin, J. K. Cockcroft and A. N. Fitch, Chem. Ber., 1990, 123, 1629.

14 E.g. KCD₃: E. Weiss, T. Lambertsen, B. Schubert and J. K. Cockcroft, J. Organomet. Chem., 1988, 358, 1 (like NaCD₃: neutron diffraction on powder; for NaCD₃ also using synchrotron radiation).

15 U. Schümann, U. Behrens and E. Weiss, Angew. Chem., Int. Ed. Engl., 1989, 28, 476.

16 M. F. Lappert, Proceedings of the IXth International Symposium on Organosilicon Chemistry, ed. A. R. Bassindale and P. G. Gaspar. The Royal Society of Chemistry, Cambridge 1991, pp. 231–252.