Organometallics **2000,** *19,* 4030−4035

Synthesis and Structures of the Crystalline Heavier Alkali Metal Alkyls: X-ray Structures of $[K(\mu\text{-}R)\{O(Me)Bu^t\}]_\infty$, $[(pmdeta)K(\mu\text{-}R)K(\mu\text{-}R)_2K(\mu\text{-}R)K(pmdeta)]$, and $[Cs(\mu\text{-}R)(tmeda)]_\infty$ ($R = CH(SiMe_3)_2$)

W. Marco Boesveld, Peter B. Hitchcock, Michael F. Lappert,*
Dian-Sheng Liu, and Shun Tian

The Chemistry Laboratory, University of Sussex, Brighton, U.K. BN1 9QJ

Received May 19, 2000

The crystalline hexane-soluble metal alkyls $[Na(\mu\text{-}R)]_\infty$ (**1**), $[K(\mu\text{-}R)\{O(Me)Bu^t\}]_\infty$ (**2**), $[(pmdeta)K(\mu\text{-}R)K(\mu\text{-}R)_2K(\mu\text{-}R)(pmdeta)]$ (**3**), $[Rb(\mu\text{-}R)(pmdeta)]_2$ (**4**), $[Cs(\mu\text{-}R)\{O(Me)Bu^t{}_2\}]_\infty$ (**5**), and $Cs(\mu\text{-}R)(tmeda)]_\infty$ (**6**) ($R = CH(SiMe_3)_2$, pmdeta = $(Me_2NCH_2CH_2)_2NMe$, tmeda = $Me_2NCH_2CH_2NMe_2$) have been prepared from LiR with an equimolar portion of $NaOBu^t$, $KOBu^t$, $RbOC_6H_2Bu^t{}_2$-2,6-Me-4, or $CsOCH_2CH(Et)Bu^n$ and for **2**−**6** the appropriate neutral ligand. X-ray crystal structures of the metal alkyls **2**, **3**, and **6** are presented; **1** and **4** were described in an earlier communication. Treatment of **5** with Bu^tCN afforded the cesium 1-azaallyl $Cs\{N(R)C(Bu^t)C(H)R\}$ (**7**).

Introduction

Interest in the chemistry of organometallic compounds of the alkali metals is steadily increasing.[1] Several comprehensive reviews exist relating to their synthesis and structures. The emphasis has been on organolithium compounds,[2] but attention is now also focusing on analogues of the heavier alkali metals sodium, potassium, rubidium, and cesium.[3]

The use of trimethylsilyl-substituted methyls was first recognized in a 1969 patent.[4] The ligands $[CH_{3-n}R'_n]^-$ ($R' = SiMe_3$, $n = 1-3$) confer certain useful properties on their metal complexes, including thermal stability, lipophilicity, crystallinity, and convenient NMR spectroscopic characteristics by virtue of their bulk, absence of β-hydrogen and -alkyl substituents, and multiplicity of methyl groups, respectively.[5] The syntheses and structures of the crystalline alkyls $[LiCH_2R']_6$,[6] $[Li(\mu\text{-}CHR'_2)]_\infty$ ($\equiv[Li(\mu\text{-}R)]_\infty$),[7] $[LiR(pmdeta)]$[8] (the tmeda analogue was also shown to be mononuclear by ebullioscopy),[8] $[Li(thf)_4][Li(CR'_3)_2]$,[9] and $[Li(\mu\text{-}CR'_3)]_2$[10] have been reported, while more recently the structures of $[Na(OEt_2)(tmeda)_2][Na(CR'_3)_2]$,[11] $[Na\{C(SiMe_2Ph)\}_3]$,[11] $[K(\mu\text{-}CR'_3)]_\infty$,[12] $[Rb(\mu\text{-}CR'_3)]_\infty$[12] and $[Cs(\mu\text{-}CR'_3)(\eta^6\text{-}C_6H_6)_3]_2\cdot C_6H_6$[13] were elucidated.

We now report on the synthesis of the crystalline alkali-metal alkyls MR ($R = CH(SiMe_3)_2$): $[Na(\mu\text{-}R)]_\infty$ (**1**), $[K(\mu\text{-}R)\{O(Me)Bu^t\}]_\infty$ (**2**), $[(pmdeta)K(\mu\text{-}R)K(\mu\text{-}R)_2K(\mu\text{-}R)K(pmdeta)]$ (**3**), $[Rb(\mu\text{-}R)(pmdeta)]_2$ (**4**), $[Cs(\mu\text{-}R)\{O(Me)Bu^t{}_2\}]_\infty$ (**5**), and $[Cs(\mu\text{-}R)(tmeda)]_\infty$ (**6**) and the structures of **2**, **3**, and **6**. The synthetic strategy was based on Lochmann−Schlosser LiR′/MOR″ systems.[14] A preliminary communication reporting the X-ray structures of **1** and **4** has appeared,[15] and their skeletal structures are illustrated in Chart 1.

Results and Discussion

Synthesis. The alkali-metal alkyls MR (M = Na, K, Rb, Cs; $R = CH(SiMe_3)_2$) were obtained by reacting the crystalline, lipophilic, and volatile lithium alkyl LiR[7] with the appropriate alkali-metal alkoxide or phenoxide (Scheme 1); they were extremely air- and moisture-sensitive, and characterization was often difficult due to their low solubility and high reactivity.

The coreagent for the compounds NaR and KR was the corresponding metal *tert*-butoxide, with hexane as

---

* To whom correspondence should be addressed. E-mail: M.F.Lappert@sussex.ac.uk.

(1) The Second International Conference on the Chemistry of the Alkali and Alkaline Earth Metals, Erlangen, Germany, Sept 1997.

(2) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169. Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. Sapse, A. M., Schleyer, P. v. R., Eds. *Lithium Chemistry*; Wiley: New York, 1994. Snieckus, V. *Chem. Rev.* **1990**, *90*, 879. Brandsma, L.; Verkruijsse, H. *Preparative Polar Organometallic Chemistry;* Springer: Berlin, 1987; Vol. 1.

(3) (a) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (b) Smith, J. D. *Adv. Organomet. Chem.* **1999**, *43*, 267.

(4) Collier, M. R.; Kingston, B. M.; Lappert, M. F.; Truelock, M. M. Brit. Patent 36021, 1969.

(5) Collier, M. R.; Lappert, M. F.; Truelock, M. M. *J. Organomet. Chem.* **1970**, *25,* C36.

(6) Tecle, B.; Rahmann, A. F. M. M.; Oliver, J. P. *J. Organomet. Chem.* **1986**, *317*, 267.

(7) Atwood, J. L.; Fjeldberg, T.; Lappert, M. F.; Luong-Thi, N. T.; Shakir, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1163.

(8) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323.

(9) Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827.

(10) Hiller, W.; Layh, M.; Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30,* 324.

(11) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Izod, K.; Mallien, M.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1268.

(12) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jaggar, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753.

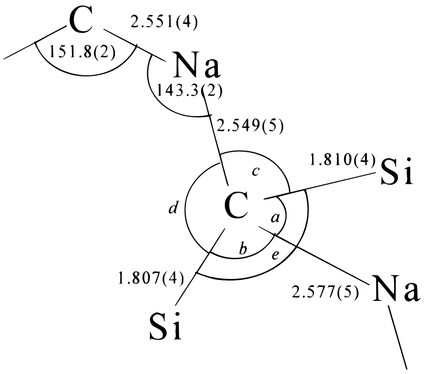
(13) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 687.

(14) Schlosser, M. J. In *Organometallics in Synthesis, a Manual*; Schlosser, M., Ed.; Wiley: New York, 1994, and references therein.

(15) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Diansheng, L.; Shun, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1386.

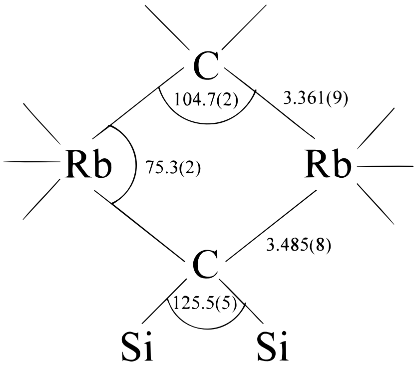
10.1021/om0004287 CCC: $19.00
Publication on Web 08/25/2000

Chart 1. Skeletal Structures



1

[*a* 92.8(2), *b* 105.2(2), *c* 91.7(2), *d* 94.4(2) *e* av. = 127.8(7)°] (ref. 15)



4 (ref. 15)

the solvent. Thus, $NaOBu^t$ with LiR gave the sodium alkyl $[Na(\mu\text{-}R)]_\infty$ (**1**) as a crystalline, colorless solid in 90% yield from hexane. Care had to be taken to isolate **1** before the coproduct, the somewhat more soluble $LiOBu^t$, began to crystallize. When the synthesis was performed on a larger scale, this posed some difficulties for the purification, $[Na(\mu\text{-}R)]_\infty$ (**1**) being contaminated with $LiOBu^t$. An alternative procedure, analogous to that used by Bickelhaupt and co-workers,[16] involving HgR_2 as the substrate for treatment with $NaBu^n$, was unsatisfactory due to the difficulty of separating **1** from $HgBu^n{}_2$.

The sodium alkyl **1** crystallized in two different crystal forms, both showing the same structural motif. The orthorhombic crystals, obtained from benzene, yielded good diffraction data,[15] in contrast with the monoclinic form which crystallized from hexane.

When LiR was treated with $KOBu^t$, the more soluble $LiOBu^t$ was simply removed by repeated washing with hexane, leaving the residual air-sensitive, white powder of KR (85%). Characterization of KR was not straightforward, because of its high reactivity and low solubility. It reacted with toluene as well as with tetrahydrofuran (thf) and was insoluble in benzene or aliphatic hydrocarbons. However, KR was crystallized from diethyl ether or methyl *tert*-butyl ether to yield its monoether adduct $[K(\mu\text{-}R)L]_\infty$ (L = OEt_2, $MeOBu^t$ (**2**)). Single crystals suitable for X-ray analysis were only readily obtained from the latter solvent.[17] Reacting KR with pmdeta (0.5 equiv) yielded the crystalline adduct [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)K(pmdeta)] (**3**).

The rubidium alkyl $[Rb(\mu\text{-}R)(pmdeta)]_2$ (**4**) was formed in 67% yield from LiR and RbOAr (Ar = 2,6-di-*tert*-butyl-4-methylphenyl) and the addition of pmdeta during workup.[15] The rubidium aryloxide was used as the starting material in this case, because of its solubility being greater than that of the *tert*-butoxide. This strategy was previously successful in tin(II)[18] and 4f element[19] chemistry.

By analogy with the procedure for the synthesis of $CsC(SiMe_3)_3$,[13] an excess of cesium 2-ethylhexoxide was reacted with LiR in hexane to give the colorless solid CsR (56%), which was insoluble in hydrocarbons but crystallized from a methyl *tert*-butyl ether/hexane mixture as extremely air-sensitive, thin needles. Single crystals suitable for X-ray analysis were obtained, but due to a mechanical failure during data collection only the unit cell parameters were determined.[20] Although many more attempts were made, we did not achieve full characterization of **5** by X-ray analysis due to decomposition during crystal mounting. ^1H NMR spectroscopy showed that CsR had formed a 1:2 adduct with the ether, $[Cs(\mu\text{-}R)\{O(Me)Bu^t\}_2]_\infty$ (**5**); the $^{133}Cs\{^1H\}$ NMR spectrum showed a broad signal at δ 97.5 ($\Delta w_{1/2} \approx 1.5$ kHz). When CsR was dissolved in a hot hexane solution of a ca. 10-fold excess of tmeda, filtered hot and the filtrate was cooled to ambient temperature, colorless needles of $[Cs(\mu\text{-}R)(tmeda)]_\infty$ (**6**) were obtained, which were soluble in benzene and revealed appropriate ^1H and ^{13}C NMR spectra.

In view of the fact that cesium alkyls and amides are rare, the cesium alkyl **5** was treated with Bu^tCN in pentane to afford the benzene-soluble, crystalline cesium 1-azaallyl $Cs\{N(R)C(Bu^t)C(H)R\}$ (**7**), involving a 1,2-addition of the metal alkyl to C≡N and a C → N trimethylsilyl shift; the analogous reaction of LiR with Bu^tCN has been described.[21] Compound **7** was characterized by its ^1H, ^{13}C, $^{29}Si\{^1H\}$, and ^{133}Cs NMR spectra but proved to be too sensitive for elemental analysis.

Crystal Structures. The molecular structures of crystalline $[K(\mu\text{-}R)\{O(Me)Bu^t\}]_\infty$ (**2**), [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)K(pmdeta)] (**3**), and $[Cs(\mu\text{-}R)(tmeda)]_\infty$ (**6**) are shown in Figures 1−3, and selected geometric parameters are listed in Tables 1−3, respectively. Some comparative data for compounds **1**−**4** and $[Li(\mu\text{-}R)]_\infty$ are shown in Table 4.

Crystalline $[K(\mu\text{-}R)\{O(Me)Bu^t\}]_\infty$ (**2**) (Figure 1), like $[Na(\mu\text{-}R)]_\infty$ (**1**)[15] and $[Li(\mu\text{-}R)]_\infty$,[7] consists of chains of alternating cations and anions. Although the hydrogens have not been located, we assume that the anions are planar, with average dimensions C−Si = 1.788(9) Å and Si−C−Si = 126.7(5)°. The two potassium cations on either side of the anion symmetrically complete a distorted bipyramid about the central carbon atom with average dimensions K−C = 3.000(8) Å and K−C−K″ =

---

(16) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1982**, *104*, 6848.

(17) Three other X-ray structures in alkali-metal chemistry with methyl *tert*-butyl ether as a neutral donor are known: (a) Knorr, R.; Behringer, C.; Nöth, H.; Schmidt, M.; Lattke, E.; Räpple, E. *Chem. Ber.* **1997**, *130*, 585. (b) Knizek, J.; Krossing, I.; Nöth, H.; Schwenk, H.; T. Seifert, T. *Chem. Ber.* **1997**, *130*, 1053. (c) Müller, G.; Lutz, M.; Waldkircher, M. *Acta Crystallogr., Sect. C* **1996**, *52*, 1182.

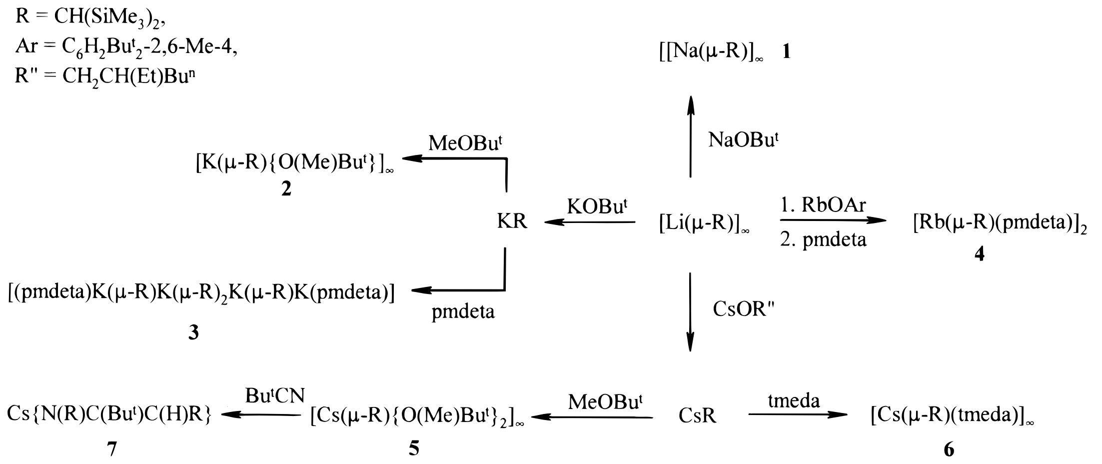
(18) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, *52*, 1551.

(19) Hitchcock, P. B.; Lappert, M. F.; Smith, R. G.; Bartlett, R. A.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1007.

(20) Pn_1/n, $a = 12.684(2)$ Å, $b = 11.184(1)$ Å, $c = 18.872(3)$ Å, and $\beta = 102.41°$.

(21) Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *500*, 203.

Scheme 1



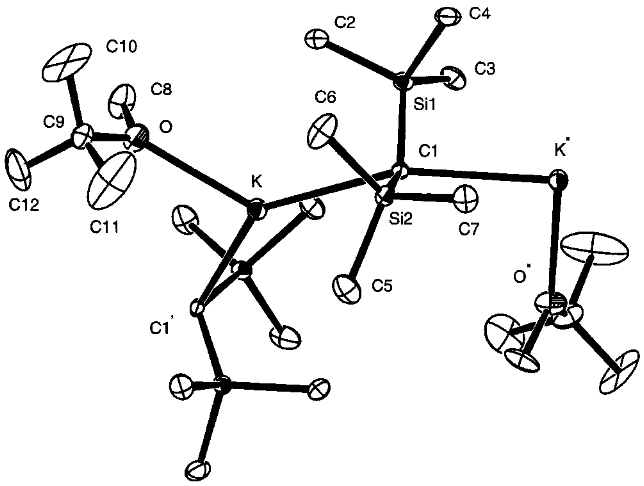


Figure 1. Molecular structure of [K(μ-R){O(Me)Bu^t}]$_\infty$ (**2**), with atom labeling.

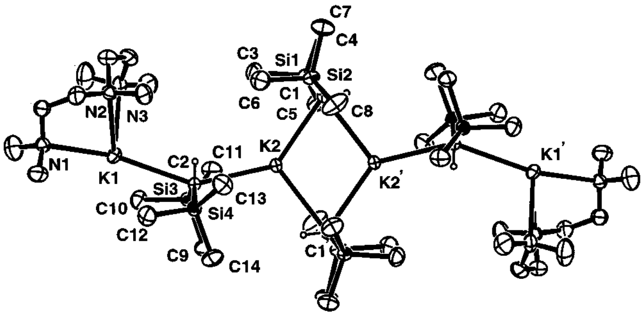


Figure 2. Molecular structure of [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)K(pmdeta)] (**3**), with atom labeling.

155.6(3)°. The three-coordinated potassium cation is additionally bound by a MeOBu^t donor molecule with K−O = 2.68(2) Å. The methyl groups of the donor molecule are severely disordered. Attempts to subject the extremely sensitive [K(μ-R)(OEt$_2$)]$_\infty$ adduct to an X-ray study yielded very poor diffraction data, which, however, showed that the general features are similar to those of **2**.

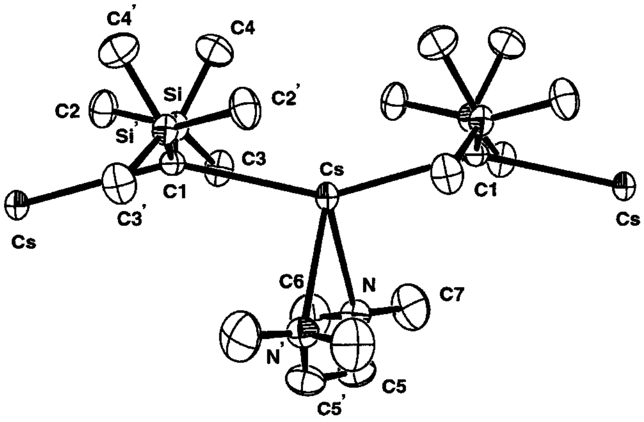


Figure 3. Molecular structure of [Cs(μ-R)(tmeda)]$_\infty$ (**6**), with atom labeling.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [K(μ-R){O(Me)Bu^t}]$_\infty$ (2)

K−O	2.676(9)	C(1)−Si(1)	1.794(9)
K−C(1)	2.988(8)	C(1)−Si(2)	1.782(9)
K−C(1)′	3.012(8)	Si(1)−C(3)	1.881(9)
O−K−C(1)′	89.7(3)	K−C(1)−K″	155.6(3)
C(1)−K−C(1)′	137.02(9)	Si(1)−C(1)−Si(2)	126.7(5)
O−K−C(1)	131.0(3)	C(1)−Si(1)−C(3)	111.8(4)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)K(pmdeta)] (3)

K(1)−N(1)	2.907(4)	C(1)−Si(1)	1.796(5)
K(1)−N(2)	2.818(4)	C(1)−Si(2)	1.800(5)
K(1)−N(3)	2.891(4)	Si(1)−C(3)	1.881(5)
K(1)−C(2)	3.095(5)	C(1)−H(1)	0.85(3)
K(2)···K(2)′	3.576(2)	C(2)−Si(3)	1.783(5)
K(2)−C(1)	3.040(4)	C(2)−Si(4)	1.792(5)
K(2)−C(2)	3.017(4)	Si(3)−C(10)	1.886(5)
K(2)−C(1)′	3.059(5)	C(2)−H(2)	0.83(3)
N(1)−K(1)−C(2)	155.1(1)	Si(1)−C(1)−Si(2)	121.6(2)
C(2)−K(1)−N(2)	112.5(1)	C(1)−K(2)−C(2)	137.0(2)
K(1)−C(2)−K(2)	147.2(2)	K(2)−C(1)−K(2)′	71.8(1)
Si(3)−C(2)−Si(4)	131.4(3)		

The structure of crystalline [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)K(pmdeta)] (**3**) (Figure 2) showed it to be tetranuclear, lying on a crystallographic inversion center. The two inner potassium cations K(2) and K′(2) are bridged symmetrically by two μ-alkyl groups, forming a four-membered ring with an average K−C distance of 3.050(4) Å. The endocyclic ring angles are 71.8(1)° at C(1) and 108.2(1)° at K(2). The K(2)···K′(2) distance is 3.576(2) Å. Each central potassium cation is additionally exocyclically coordinated by a μ-alkyl group with a K(2)−C(2) distance of 3.017(4) Å. The coordination at the two terminal potassium atoms K(1) is completed by three K−N bonds averaging 2.872(4) Å, while K(1)−C(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Cs(μ-R)(tmeda)]$_\infty$ (6)

Cs−C(1)	3.425(2)	C(1)−Si	1.791(4)
Cs−N	3.200(5)	C(2)−Si	1.906(6)
C(3)−Si	1.877(6)	C(4)−Si	1.882(7)
Cs−C(1)−Cs′	151.7(3)	Si−C(1)−Si′	129.2(5)
N−Cs−N′	56.78(16)	Si−C(1)−Cs	98.19(5)

is 3.095(4) Å. The geometry of each μ-alkyl anion is planar at the α-carbon with average dimensions C−Si = 1.788(5) Å, Si−C−Si′ = 131.4(3)°, and Si−C−H = 114(2)°, while each μ-alkyl anion has C(1) at the center of a distorted trigonal bipyramid.

The structure determination of crystalline [Cs(μ-R){O(Me)Bu^t}$_2$]$_\infty$ (**5**) was incomplete; the preliminary data were adequate to show that it is probably similar to that of the potassium analogue **2**; i.e., comprising a polymeric chain consisting of alternating alkyls and metal atoms, each Cs atom being coordinated by two neutral donor molecules. The structure of crystalline [Cs(μ-R)(tmeda)]$_\infty$ (**6**) (Figure 3) showed it to be a polymer containing a central infinite chain of alternating Cs and C atoms, both lying on a 2-fold rotation axis, the C−Cs−C′ angles being 151.7(3)°. The Cs−C distance is 3.425(2) Å, which may be compared with 3.325(12) Å in [Cs(μ-C(SiMe$_3$)$_3$}(η^6-C$_6$H$_6$)$_3$]·0.5C$_6$H$_6$,[13] 3.245(13) and 3.220(15) Å in [{Cs(η-C$_6$H$_6$)$_3$C(SiMe$_3$)$_2$SiMe$_2$CH$_2$}$_2$],[22] and 3.348(4) Å in [Cs(μ-CPh$_3$)(pmdeta)]$_\infty$.[23] The Cs−N distances in **6** are 3.200(4) Å; cf. the 3.26 Å average in the trityl compound.[23]

Although the hydrogen atoms have only been located for the sodium and potassium alkyls **1** and **3**, it seems likely that in the case of the singly bridging bis(trimethylsilyl)methyls of Li, K (**2** or **3**), or Cs (**6**), the R$^-$ anions are also planar. This is indicated by the wide Si−C−Si′ angle in **2**, **3**, and **6** of ca. 130°, whereas for the doubly bridging alkyls in **3** and **4**, this angle is narrower. In particular, the X-ray structure of **3** shows the effect of a linear versus bridging coordination mode, resulting for the latter in narrower angles for Si−C−Si′ and M−C−M′ and shorter M−C distances.

It is interesting to compare the structures of the alkali-metal bis(trimethylsilyl)methyls M[CH(SiMe$_3$)$_2$] with those of the isoelectronic bis(trimethylsilyl)amides M[N(SiMe$_3$)$_2$]. As for the latter, it has recently been shown that crystalline derivatives of the neutral coligand-free complexes even of the heaviest alkali metals are accessible; they are binuclear, [M{μ-N(SiMe$_3$)$_2$}]$_2$ (M = K,[24] Rb[25] or Cs[25]), soluble in toluene and even sparingly so in cyclopentane. A further comparison should also be made with the alkali-metal trisyls MR″ (R″ = C(SiMe$_3$)$_3$).[3b] Among the heavier alkali-metal trisyls, X-ray data are available for [K(μ-R″)]$_\infty$ and [Rb(μ-R″)]$_\infty$, both of which have linear [M−C]$_\infty$ chains and planar carbanions,[12] [Cs(μ-R″)(η^6-C$_6$H$_6$)$_3$]·0.5C$_6$H$_6$,[13] and the less well defined [K(μ-R″)(tmeda)]$_\infty$.[26]

Conclusion

The X-ray structures of [Li(μ-R)]$_\infty$, [Na(μ-R)]$_\infty$ (**1**), [K(μ-R){O(Me)Bu^t}]$_\infty$ (**2**), and [Cs(μ_1-R)(tmeda)]$_\infty$ (**6**) show that their preferred structures have an (MC)$_\infty$ chain and comprise a polymeric array of ion pairs containing a singly bridging and probably planar carbanion. Only strongly chelating donors such as tmeda and pmdeta, but not diethyl or methyl *tert*-butyl ether, were able to break up this polymeric network for each (MR)$_n$, except **6**, with tmeda. In the case of potassium, the addition of pmdeta yielded [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)(pmdeta)] (**3**), having an unprecedented tetranuclear structure which may be regarded as a dimer of a dinuclear fragment, the two dinuclear moieties joined by a double μ-R bridge. The latter feature was also found in the rubidium compound [Rb(μ-R)(pmdeta)]$_2$ (**4**), containing distinct dimers, superficially resembling the structure of the electron-deficient [AlMe$_2$(μ-Me)]$_2$.

Experimental Section

General Considerations. All experiments were performed under argon using standard Schlenk and vacuum line techniques. Pentane, Et$_2$O, MeOBu^t, benzene, and benzene-d_6 were distilled from Na/K alloy and degassed prior to use. Tetrahydrofuran was distilled twice from Na/benzophenone. The compound LiR was prepared from RBr in Et$_2$O and LiBu^n in hexane and purified by sublimation.[7] The alkoxides NaOBu^t and KOBu^t were obtained from Aldrich and purified by sublimation. Cesium 2-ethylhexoxide was freshly prepared, by reacting an ingot of cesium with 2-EtC$_6$H$_{13}$OH in hexane. Microanalyses were carried out by Medac Ltd., Uxbridge, Middlesex, U.K. Melting points were determined in sealed capillaries under argon on an electrothermal apparatus and are uncorrected. The NMR spectra were recorded using a WM-300 Bruker instrument at 300.13 (^{1}H) and 75.42 (^{13}C) MHz or an AMX-500 Bruker spectrometer at 500.1 (^{1}H), 125.72 (^{13}C), 99.36 (^{29}Si{^{1}H}), and 65.60 (^{133}Cs) MHz, at ambient probe temperature in benzene-d_6 and referenced internally to residual solvent resonances unless stated otherwise.

Synthesis of [Na(μ-R)]$_\infty$ (1). Solid NaOBu^t (1.31 g, 13.6 mmol) was added in portions to a stirred solution of LiR (2.27 g, 13.7 mmol) in hexane (30 mL). The supension was stirred for 1 day to give a slightly cloudy solution, which was filtered and the filtrate concentrated. Cooling to −30 °C yielded colorless crystals of **1** (2.46 g) contaminated with LiOBu^t (ca. 15%). Recrystallization from hexane yielded analytically pure **1** (2.24 g, 90%). Care was taken to isolate **1** before the coproduct LiOBu^t began to crystallize. Crystals suitable for X-ray analysis were obtained from benzene; mp 130−132 °C. NMR (C$_6$D$_6$, 305 K): ^{1}H, δ 0.20 (s, 18H, SiMe$_3$), −2.04 (s, 1H, C*H*R′$_2$); ^{13}C{^{1}H}, δ 7.0 (CH*R*′$_2$), 0.4 (*C*HR′$_2$); ^{29}Si{^{1}H}, δ 12.4.

Synthesis of [K(μ-R){O(Me)Bu^t}]$_\infty$ (2). Solid, sublimed KOBu^t (3.71 g, 33.0 mmol) was added to a suspension of LiR (5.67 g, 34.2 mmol) in hexane (350 mL). The suspension was stirred for 2 days at ambient temperature and allowed to settle. After the hexane layer was filtered and the precipitate was washed with hexane (2 × 50 mL), the free-flowing, gray-white solid potassium alkyl KR (5.55 g, 85%) was isolated. Anal. Calcd for C$_7$H$_{19}$KSi$_2$: C, 42.3; H, 9.65. Found: C, 42.0; H, 9.28. Crystallization of KR from MeOBu^t/hexane gave extremely air- and moisture-sensitive, pyrophoric, colorless, single crystals of compound **2** (5.43 g, 58%), suitable for X-ray analysis.

Synthesis of [(pmdeta)K(μ-R)K(μ-R)$_2$K(μ-R)K(pmdeta)] (3). From a solution of pmdeta (0.57 g, 3.3 mmol) and KR (0.65 g, 3.3 mmol) in hexane (50 mL) at −20 °C were obtained pale yellow crystals of **3** (1.02 g, 84%), mp 58−60 °C. ^{1}H NMR (C$_6$D$_6$,

---

[22] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Zhang, S.; Clegg, W.; Izod, K.; O'Shaughnessy, P. *Organometallics* **2000**, *19*, 1190.

[23] Hoffmann, D.; Bauer, W.; Schleyer, P.v. R.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193.

[24] Tesh, K. F.; Hanusa, T. P.; Huffman, J. C. *Inorg. Chem.* **1990**, *29*, 1584.

[25] Neander, S.; Behrens, U. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1429.

[26] Eaborn, C.; Clegg, W.; Hitchcock, P. B.; Hopman, M.; Izod, K.; O'Shaughnessy, P. N.; Smith, J. D. *Organometallics* **1997**, *16*, 4728.

Table 4. Selected Average Bond Lengths (Å) and Angles (deg) in the Metal Alkyls [Li(μ-R)]$_\infty$, 1−4, and 6

	param					
compd	M−C	C−Si	M−C−M	Si−C−Si	CN[a]	ref
[Li(μ-R)]$_\infty$	2.18	1.82	153(1)	127.7(6)	2	7
[Na(μ-R)]$_\infty$ (**1**)	2.56	1.81	151	127.8(7)	2	15
[K(μ-R){O(Me)Bu^t}]$_\infty$ (**2**)	3.00	1.86	155.6(2)	126.7(5)	3	this work
[{K(μ-R)}$_4$(pmdeta)$_2$] (**3**)						this work
endocyclic	3.059(4)	1.80	71.8(1)	121.6(2)	3	this work
exocyclic	3.095(4) 3.017(4)	1.79	147.2(2)	131.4(3)	4	
[Rb(μ−R)(pmdeta)]$_2$ (**4**)	3.42	1.74	104.7(2)	125.5(5)	5	15
[Cs(μ−R)(tmeda)]$_\infty$ (**6**)	3.425(2)	1.79	151.7(3)	129.2(5)	4	this work

[a] CN = coordination number at the metal.

Table 5. Molecular Parameters for Compounds 2, 3, and 6

	$C_{12}H_{31}KOSi_2$ (**2**)	$C_{46}H_{122}K_4N_6Si_8$ (**3**)	$C_{13}H_{35}CsN_2Si_2$ (**6**)
M_r	286.6	1140.6	408.5
T (K)	173(2)	293	173(2)
cryst syst	orthorhombic	triclinic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)	$P2/c$ (No. 7)
a (Å)	10.909(5)	11.848(2)	6.6427(4)
b (Å)	11.783(2)	12.044(3)	9.8160(9)
c (Å)	14.447(6)	13.593(7)	16.5419(11)
α (deg)		76.29(3)	
β (deg)		87.74(3)	100.166(4)
γ (deg)		84.52(2)	
V (Å^3)	1857(1)	1875.4	1061.7(1)
Z	4	1	2
abs coeff (mm^{-1})	0.40	0.39	1.85
θ_{max} for data collcn (deg)	22	25	25.10
no. of indep rflns	2274 (R_{int} = 0.093)	6560	1865 (R_{int} = 0.051)
no. of rflns with $I > 2\sigma(I)$	1578	3507	1681
no. of data/restraints/params	2274/36/174	3507/0/321	1865/0/84
R1($I > 2\sigma(I)$)	0.067	0.059	0.039
wR2(all data)	0.181	R_w = 0.056[a]	0.137
largest diff peak and hole (e Å^{-3})	0.33 and −0.28	0.31 and −0.10	0.57 and −1.32

[a] $R_w = \{(\sum w\Delta^2)/\sum w|F_o|^2\}^{1/2}$ for $I > 2\sigma(I)$.

305 K): δ 2.36 (m, 8H, CH_2), 2.21 (s, 15H, NMe), −0.10 (s, 36H, $SiMe_3$), −2.11 (s, 2H, CH).

Synthesis of [Rb(μ-R)(pmdeta)]$_2$ (4) (by W.-P. Leung).[15] Solid LiR (0.71 g, 4.28 mmol) was added to a suspension of RbOAr (Ar = $C_6H_2Bu^t{}_2$-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 to −30 °C; colorless, crystalline LiOAr(thf) (mp 256−258 °C)[27] was filtered off. pmdeta (0.74 g, 4.27 mmol) was added to the filtrate, and the mixture was filtered and concentrated; cooling the solution gave pale yellow crystals of **4** (1.20 g, 67%), mp 62−64 °C.

Synthesis of [Cs(μ-R){O(Me)Bu^t}$_2$]$_\infty$ (5). Solid LiR (3.68 g, 22.2 mmol) was added to a solution of $CsOCH_2CH(Et)Bu^n$, freshly prepared from 2-ethylhexanol (3.25 g, 25 mmol) and cesium metal, in hexane (100 mL). The suspension was stirred for 2 days. The mixture was then filtered. The precipitate was washed with hexane (40 mL), leaving the residual very sensitive, colorless solid CsR (3.64 g, 56%), which was insoluble in hydrocarbons and became slightly pink after 2 days at ambient temperature. Crystallization at −20 °C from an $MeOBu^t$/hexane mixture yielded very thin, colorless needles of **5**. The cesium ether adduct **5** was soluble in benzene and was characterized by NMR spectroscopy but decomposed within a few hours at room temperature. ^{1}H NMR (C_6D_6, 294 K): δ 3.02 (s, 6H, Bu^tOCH_3), 1.06 [s, 18H, $MeOCC(CH_3)_3$], 0.27 (s, 18H, $SiMe_3$), −2.18 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6/$MeOBu^t$): δ 72.2 [$OC(CH_3)_3$], 49.1 (OMe), 27.1 [$OC(CH_3)_3$], 7.3 (CHR'_2) (CHR'_2 had too low intensity to be identified). ^{133}Cs NMR: δ 97.5 ($\Delta w_{1/2}$ = 1.5 kHz).

Synthesis of [Cs(μ-R)(tmeda)]$_\infty$ (6). tmeda (1.5 mL) was added to solid CsR (0.17 g), prepared as shown above, suspended in hexane (20 mL). The mixture was heated under reflux for 5 min and then filtered hot. Slow cooling of the filtrate to ambient temperature yielded white needles of the salt **6** (0.15 g, 63%). ^{1}H NMR (C_6D_6, 294 K): δ 2.36 (s, 4H, CH_2), 2.12 (s, 12H, NMe_2), 0.05 (s, 18H, $SiMe_3$), −0.41 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6, 294 K): δ 57.6, 45.2, 0.6, −4.77. $^{133}Cs\{^1H\}$ NMR: δ 81.7 ($w_{1/2} \approx$ 330 Hz).

Synthesis of Cs{N(R)C(Bu^t)C(H)R} (7). 2-Cyano-2-methylpropane (0.41 mL, 3.7 mmol) was added to a stirred suspension of CsR (1.10 g, 3.8 mmol) in pentane (20 mL) at −50 °C. The reaction mixture was warmed to ambient temperature, but no visible reaction was noticed; methyl *tert*-butyl ether (2 mL) was added, and stirring was continued for 12 h. The suspension was filtered, and the residue **7** (0.91 g, 64%) was dried in vacuo; crystallization of the residue from benzene, layered with pentane (toluene was too reactive), afforded very thin needles of **7**, mp 164 °C (too sensitive for elemental analysis). ^{1}H NMR: δ 3.80 (s, 1H, C*H*), 1.26 (s, 9H, Bu^t), 0.41 (s, 9H, $NSiMe_3$), 0.31 (s, 9H, $CSiMe_3$). ^{13}C NMR: δ 181 (*ipso*, *C*Bu^t), 79.3 (d, ^1J = 132.8 Hz, *C*H), 40.4 (*ipso*, *C*Me$_3$), 31.2 (q, ^1J = 124.3 Hz, C*Me*$_3$), 5.8 (q, ^1J = 115.7 Hz, NSi*Me*$_3$), 2.7 (q, ^1J = 117.4 Hz, CSi*Me*$_3$). $^{29}Si\{^1H\}$ NMR: δ −16.4 ($CSiMe_3$), −36.5 ($NSiMe_3$). ^{133}Cs NMR: δ −86.9 ($w_{1/2}$ = 13 Hz).

X-ray Structure Determinations of Compounds 2, 3, and 6. Unique data sets were collected with an Enraf-Nonius CAD4 (**2** and **3**) or KappaCCD (**6**) diffractometer, using a crystal coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 173(2) K (**2** and **6**) or sealed in a capillary at room temperature (**3**). For **2** and **6** refinement was on F^2 for all reflections using SHELXL-93,[28] and for **3** refine-

---

[27] Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

[28] Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.

ment was on F for reflections with $I > 2\sigma(I)$ using MOLEN.[29] All non-H atoms were anisotropic, and the hydrogen atoms were included in the riding mode. For **2** the absolute structure was assigned by refinement of the Flack parameter.[30] Parameters are listed in Table 5.

Acknowledgment. We thank Prof. W. -P. Leung for his contributions relating to complexes **1** and **4**,[15] Dr. A. G. Avent for the $^{29}Si\{^1H\}$ and ^{133}Cs NMR spectra, the European Community for a Human Capital and Mobility Grant (category 20) for W.M.B., the Sir Run Run Shaw Foundation for a studentship for D.-S.L. and recently (2000) the Royal Society for a visiting fellowship for D.-S.L., the Chinese Government and the British Council for a studentship for S.T. and the EPSRC for other support.

Supporting Information Available: Tables giving X-ray crystallographic data and figures giving additional views of **2**, **3**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0004287

---

(29) Fair, C. K. MOLEN Program for Crystal Structure Solution and Refinement; Enraf-Nonius, Delft, The Netherlands, 1990.

(30) (a) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876. (b) Bernadinelli, G.; Flack, H. D. *Acta Crystallogr., Sect. A* **1985**, *41*, 500.