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Crystal Structures of (Tris(trimethylsilyl)methyl)- and (Tris(dimethylphenylsilyl)methyl)potassium

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Summary: Crystals of $(RMe_2Si)_3CK$ *(R = Me,* **1***; R = Ph,* **2***), obtained from MeK and* $(RMe_2Si)_3CH$*, contain linear chains of alternate potassium cations and planar* $[(RMe_2Si)_3C]^-$ *anions, with weak interactions between chains; in* **1** *the central carbon atoms of the anions are midway between the potassium cations, but in* **2** *cation–anion pairs are linked by* η^6 *coordination of phenyl groups.*

Methylpotassium has been carefully studied by X-ray powder methods and neutron diffraction,[1,2] but as far as we are aware there has hitherto been no single-crystal X-ray investigation of a donor-free organopotassium compound. We report the preparation and structures of compounds **1** and **2**, which contain bulky organosilyl groups.

$$\underset{\mathbf{1}}{(Me_3Si)_3CK} \qquad \underset{\mathbf{2}}{(PhMe_2Si)_3CK}$$

The colorless, exceedingly air- and moisture-sensitive compound **1** can be obtained by either of the routes[1,3]

$$(Me_3Si)_3CH \xrightarrow[-MeH]{+MeLi} (Me_3Si)_3CLi \xrightarrow[-LiOBu^t]{+KOBu^t} \mathbf{1} \qquad (a)$$

$$KOBu^t \xrightarrow[-LiOBu^t]{+MeLi} MeK \xrightarrow[-MeH]{+(Me_3Si)_3CH} \mathbf{1} \qquad (b)$$

It is easier to remove the byproduct $LiOBu^t$ from the sparingly soluble MeK in the first step of route b than from the more soluble **1** in the second step of route a; therefore, route b is preferred.[9] Compound **1** reacts with toluene (to give benzylpotassium) and with tetrahydrofuran (THF) at room temperature, but it may be recrystallized from hot benzene. The yellow compound **2**, which is also very reactive toward air and moisture, is made similarly by route b,[10] but it is much less soluble in benzene than **1** and some THF must be added to bring it into solution for recrystallization. It is remarkable that both **1** and **2** crystallize without coordinated solvent from cold solutions containing Et_2O or THF.

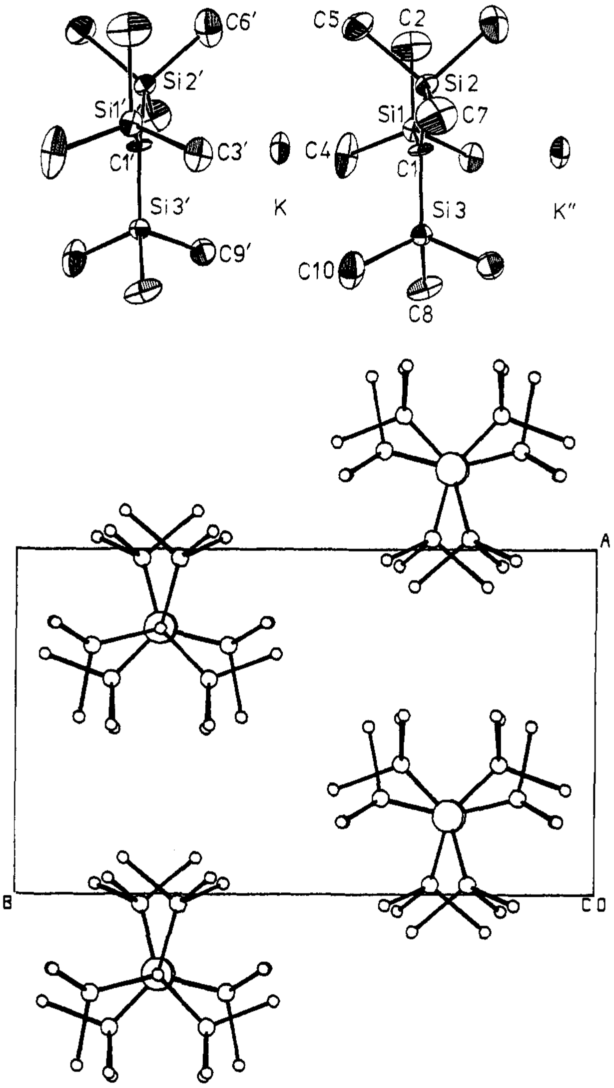

Figure 1. Structure of $(Me_3Si)_3CK$ (**1**), showing views across chains (above) and along chains (below). Selected bond distances and angles: K–C(1) = 3.090(11), K–C(1)' = 3.104(11), K···C(3)' = 3.226(11), K···C(4) = 3.187(13), K···C(5) = 3.191(12), K···C(6)' = 3.29(2), K···C(9)' = 3.311(11), K···C(10) = 3.16(2) Å; C(1)–K–C(1)' = 178.5(3), K–C(1)–K'' = 179.2(3), Si(1)–C(1)–Si(2) = 120.9(5), Si(1)–C(1)–Si(3) = 119.3(5), Si(2)–C(1)–Si(3) = 119.8(6)°.

The structure of **1** (Figure 1)[11] consists of linear chains of alternating potassium cations and $(Me_3Si)_3C^-$ anions, the latter having a planar CSi_3 skeleton perpendicular to the chain. Within each anion three methyl groups corresponding to C(2), C(7), and C(8) lie close to the CSi_3 plane and the others, three on one side and three on the other, surround the adjacent potassium ions, so that the cations are effectively 8-coordinate. (The crystallographic data are not sufficiently precise to allow identification of specific K···H interactions.) The K–C distances in **1** are similar to those in MeK, in which each K^+ ion is surrounded by six Me groups at the corners of a distorted octahedron, and in a range of alkylpotassium compounds containing coordinated amines or ethers.[4] The planarity of the anion

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[1] Weiss, E.; Sauermann, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 133–134; *Chem. Ber.* **1970**, *103*, 265–271.

[2] Weiss, E.; Lambertsen, T.; Schubert, B.; Cockcroft, J. K. *J. Organomet. Chem.* **1988**, *358*, 1–14. Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501–1523.

[3] Eaborn, C.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 827–828.

[4] Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169–278.

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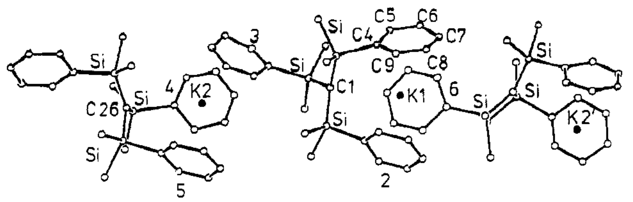

Figure 2. Structure of $(PhMe_2Si)_3CK$ (**2**). Selected bond distances and angles: K(1)–C(1) = 3.26(2), K(2)–C(26) = 3.46(3), K(1)–C(4) = 2.97(2), K(1)–C(5) = 3.03(2), K(1)–C(6) = 3.28(2), K(1)–C(7) = 3.49(2), K(1)–C(8) = 3.46(3), K(1)–C(9) = 3.23(2) Å (similar K–C distances are found to atoms of the rings labeled 2–6); mean Si–C = 1.84(2), Si–Me 1.89(2), Si–Ph 1.92(2) Å; mean Si–C–Si = 118(2), C–Si–C = 103(1)°.

is of special interest. High-level calculations indicate that the gas-phase ion CH_3^- is planar but that in solid compounds, e.g. MeK, the adjacent cations polarize the loosely bound electron density to give a pyramidal structure.[4] The planar coordination in **1** is associated with the presence of cations disposed symmetrically on either side of the anion. A planar anion is found in solvent-free $MCH(SiMe_3)_2$ (M = Na)[5] and in the solvent-separated ion pair $[Li(12\text{-crown-}4)_2][CPh_3]THF$.[6]

In **2** also (Figure 2)[12] the CSi_3 skeleton is almost planar (sum of angles at C(1) 352° and at C(26) 358°). Each potassium is associated with the central carbon of only one anion (K(1)–C(1) = 3.26(2) Å, K(2)–C(26) = 3.46(3) Å), and the pseudotetrahedral coordination is completed by η^6 interactions with two phenyl groups from the same anion and one from the next anion in the chain. We are aware of only one other compound, *viz.* $[(\eta^6\text{-}C_6H_5Me)_3K\{Sn(CH_2Bu^t)_3\}]$, in which potassium is coordinated by three phenyl groups,[7] though coordination by one or two phenyl groups is found in organoaluminates and some transition-metal complexes. The mean distance from potassium to the centroid of the η^6-Ph rings in **2** (2.96 Å) is shorter than those from potassium to the centroids of η^6-coordinated arene solvent molecules in a range of compounds, but it is longer than that to the centroid of the single η^6-Ph group in $Ph_3CK\{MeN(CH_2CH_2NMe_2)_2\}$ (2.87 Å), in which there is no close interaction between potassium and the central carbon of the anion.[8]

The chemistry of **1** and **2** is being explored.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, least-squares planes, and thermal parameters for **1** and **2** and a figure giving the residual electron density along K–C–K for **1** (22 pages). Ordering information is given on any current masthead page.

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(5) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Diansheng, L.; Shun, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1386–1387.

(6) Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 2174–2175.

(7) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1993**, 554–555 and references therein.

(8) Hoffmann, D.; Bauer, W.; Schleyer, P. v. R.; Pieper, U.; Stalke, D. *Organometallics* **1993**, *12*, 1193–1200.

(9) MeLi (13.3 mmol) in Et_2O (9.5 cm^3) was added to a stirred slurry of $KOBu^t$ (12.4 mmol) in Et_2O (30 cm^3) at −10 °C, and after 10 min the precipitate of MeK was allowed to settle, washed with Et_2O (2 × 15 cm^3) at −10 °C, and then slurried with Et_2O (15 cm^3) at −20 °C. $(Me_3Si)_3CH$ (13 mmol) was added dropwise, and the stirred mixture was warmed to 20 °C over 14 h. Solvent was removed under vacuum, the residue was washed with petroleum ether (2 × 15 cm^3, bp 40–60 °C) and extracted into benzene at 60 °C, and the concentrated extract was cooled to give colorless needles of **1**: mp 155 °C dec; ^1H NMR (360 MHz, C_6D_6) δ 0.31; ^{13}C NMR (62.88 MHz, C_6D_6) δ 3.4 (CSi_3), 8.4 ($SiMe_3$); ^{29}Si NMR (49.68 MHz, C_6D_6) δ −12.7.

(10) The analogous reaction between MeK and $(Me_2PhSi)_3CH$ in Et_2O gave a yellow solid in suspension. Solvent was removed, and the residue was washed with petroleum ether (3 × 30 cm^3) and recrystallized from hot (60 °C) toluene/THF to give yellow hexagonal plates of **2**: mp 190 °C dec; ^1H NMR (360 MHz, THF-d_8) δ 0.00 (s, 18H, $SiMe_2$), 6.94 (m, 3H, *p*-Ph), 7.03 (m, 6H, *m*-Ph), 7.80 (m, 6H, *o*-Ph); ^{13}C NMR (125.76 MHz, THF-d_8) δ −6.2 (CSi_3), 7.0 ($SiMe_3$), 125.5, 126.4, 135.4, 155.2 (Ph); ^{29}Si NMR (99.36 MHz, THF-d_8) δ −10.2.

(11) Crystal data for **1**: $C_{10}H_{27}KSi_3$, M_r = 270.7, monoclinic, space group $P2_1/c$, a = 9.137(5) Å, b = 15.046(9) Å, c = 12.388(13) Å, β = 106.86(7)°, V = 1629.7 Å^3, Z = 4, D_c = 1.10 g cm^{-3}, $F(000)$ = 592, Mo Kα radiation, λ = 0.710 69 Å, μ = 5.1 cm^{-1}, T = 173 K, 3170 reflections (2989 unique) of which 2309 with $|F^2| > 2\sigma(F^2)$ used, no decay correction, absorption correction by DIFABS, structure analysis by SHELXS-86 direct methods, full-matrix least-squares refinement by Enraf-Nonius MOLEN programs with non-H atoms anisotropic and H atoms fixed at calculated positions with $U_{iso} = 1.3U_{eq}$ for parent atoms, final R = 0.117 and R' = 0.180. The final difference map showed the two largest maxima (*ca.* 1.6 e Å^{-3} on the line joining K and C(1) at a distance of 1.34 and 1.45 Å from C(1): we believe this to be an artifact.

(12) Crystal data for **2**: $C_{25}H_{33}KSi_3$ M_r = 456.9, trigonal, space group $P3_1$, a = 9.292(5) Å, c = 50.196(29) Å, V = 3753.3 Å^3, Z = 6, D_c = 1.21 g cm^{-3}, $F(000)$ = 1464, Mo Kα radiation, λ = 0.710 69 Å, μ = 3.6 cm^{-1}, T = 173 K, 4890 reflections (4410 unique) of which 2430 with $|F^2| > 2\sigma(F^2)$ used, no decay correction, absorption correction by DIFABS, structure solution and refinement as for **1**, final R = 0.114 (preferred hand), R' = 0.114. The quality of the data set is lowered by the presence of the long c axis, which causes some overlap of reflections.