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Tetraalkylammonium pentaorganosilicates: the first highly stable silicates with five hydrocarbon ligands

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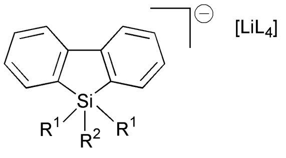
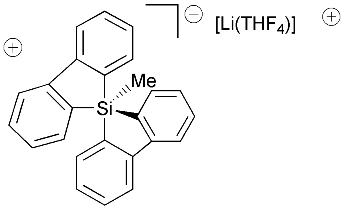
Several tetraalkylammonium pentaorganosilicates, derived from 9,9-spirobi(9*H*,9-silafluorene) were prepared from the corresponding lithium silicates and isolated and characterized as storable high melting solids.

Hypercoordinate organosilicon compounds have been studied extensively from structural, mechanistic and synthetic viewpoints.[1,2] Already many pentacoordinate anionic organosilicates containing two or more electronegative ligands such as F, Cl, OR and NR$_2$, have been synthesized and characterized by X-ray crystallography and/or NMR spectroscopy. However, whereas silicates with five carbon ligands have been proposed frequently as intermediates in the intra- and inter-molecular transfer of organosilyl groups from neutral to anionic centers,[3] they have eluded characterization and isolation until recently.

In 1996 several lithium 2,2′-biphenyldiyltriorganylsilicates **1** were identified in solution by NMR spectroscopy in our laboratory.[4] Of these spiro compound **2** was found to be stable in THF up to *ca.* 50 °C.[5] In 1999 Kolomeitsev *et al.*[6] reported an X-ray crystal structure for **3**, which is the first isolated silicate with five Si–C bonds. However, despite its two axial electron-withdrawing trifluoromethyl groups **3** decomposes already at 0–5 °C. Evidently, the biphenyldiyl ligand has a significant stabilizing influence in the bulkier **2**. We anticipated that lowering the electrophilicity of the counter ion by replacing the lithium cation in **2** for a quaternary ammonium ion would further enhance its stability[7] and possibly facilitate its isolation. Indeed we thus obtained the first pentaorganosilicates, which are storable at room temperature as white, high melting solids.



1 R^1 = Me, Ph;
R^2 = Me, n-Bu, Ph
L = THF, HMPA



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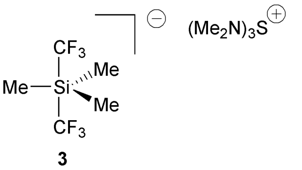

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Freshly prepared silicate **2** in THF[5] was added to a solution of tetrabutylammonium bromide in dichloromethane at −78 °C (Scheme 1).[8] A white precipitate formed instantly and quantitatively as evidenced from the absence of ^{29}Si NMR signals in the remaining solution. The very stable solid (mp 177–182 °C!) is insoluble in THF, acetone, CH$_2$Cl$_2$ and CDCl$_3$, but does dissolve in DMF in which it was characterized as **6** by ^{1}H, ^{13}C and ^{29}Si (δ −105.22) NMR spectroscopy.‡ After recrystallization from DMF the structure was confirmed by single-crystal X-ray diffraction (Fig. 1).§ Using the procedure of Scheme 1 we also obtained **7**‡ and **8**‡ as high melting stable solids.

The X-ray crystal structure of **6** shows a slightly distorted trigonal bipyramidal structure with the methyl substituent in an equatorial position and the biphenyl moieties in apical–equatorial positions. The apical Si–C bonds (2.011(2) and 2.018(2) Å) are slightly, but distinctly longer than the equatorial ones (1.924(2), 1.941(2) and 1.948(2) Å) of which the methyl Si–C2 is the shortest. The difference between these bond lengths is smaller than was found for **3**.[6] The Si–C bond distances in this five-coordinated anion are significantly longer than the standard Si–C distances (~1.88 Å) in neutral four coordinated silanes. For example, in 9,9-diphenyl-9,9-dihydro-9-silafluorene[12] Si–C distances of 1.859–1.867 Å to the biphenyl moiety are found.

This work demonstrates the accessibility of very stable pentaorganosilicates with only carbon ligands. The synthetic procedure allows for variation in carbon ligands of the silicate and for variation of its counter cation. Developments to explore the potential of the 'all carbon silicates' are currently underway.

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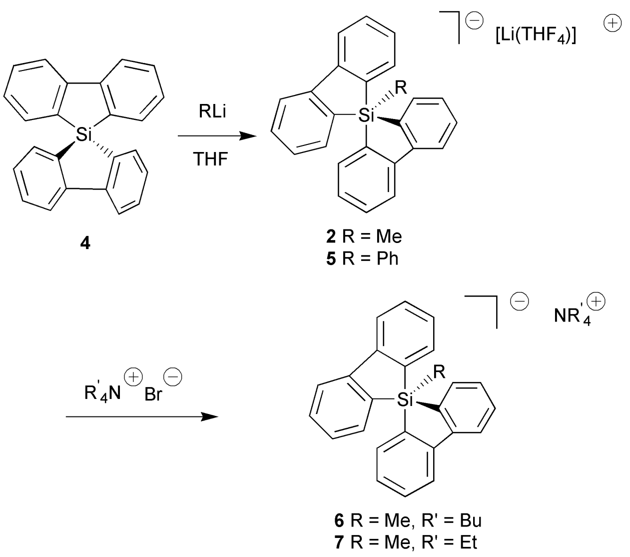

Scheme 1

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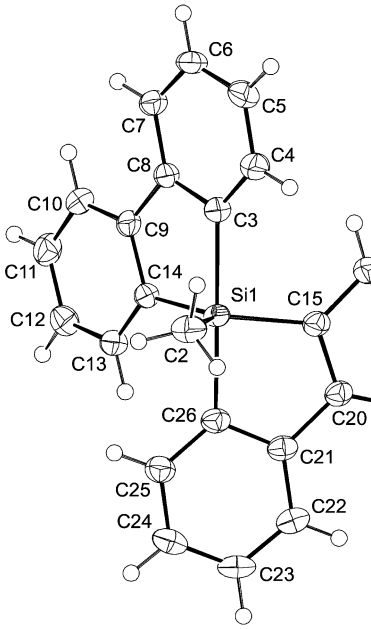

Fig. 1 Displacement ellipsoid plot of the anion of **6** drawn at the 50% probability level. The disordered tetrabutylammonium cation is omitted for clarity.

referees for making us aware of a related study on the Li$^+$ salt of the silicate.[13]

Notes and references

‡ *Selected analytical and spectroscopic data*: **6**: mp 177–182 °C; ^{1}H NMR (400 MHz, DMF-d^7): δ 7.73 (d, *J* 7.6 Hz, 4H, CH aryl), 7.52 (d, *J* 7.0 Hz, 4H, CH aryl), 7.06 (t, *J* 7.2 Hz, 4H, CH aryl), 6.91 (m, 4H, CH aryl), 3.33 (m, 8H, NCH$_2$), 1.72 (m, 8H, NCH$_2$C*H*$_2$), 1.36 (m, 8H, NCH$_2$CH$_2$C*H*$_2$), 0.94 (t, *J* 7.3 Hz, 12H, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.33 (s, 3H, CH$_3$); ^{13}C NMR (100.6 MHz, DMF-d^7): δ 133.78, 129.57, 128.05, 127.46, 126.15, 125.03, 119.28 (CH aryl), 58.86 (CH$_2$), 24.15 (CH$_2$), 20.12 (CH$_2$), 13.70 (CH$_3$), signals of quaternary carbons were not detected; ^{29}Si NMR (79.5 MHz, DMF-d^7): δ −105.22; MS HR–EI [Found: 348.1346; C$_{25}$H$_{20}$Si (MH − NBu$_4$)$^{+\cdot}$, calc. 348.1334]. **7**: mp 127–130 °C; ^{1}H NMR (400 MHz, DMF-d^7): δ 7.78 (d, *J* 7.6 Hz, 1H, CH aryl), 7.73 (d, *J* 7.6 Hz, 4H, CH aryl), 7.56–7.49 (m, 5H, CH aryl), 7.43–7.39 (m, 2H, CH aryl), 7.10 (t, *J* 7.1 Hz, 2H, CH aryl), 6.96 (m, 2H, CH aryl), 3.46 (m, 8H, NCH$_2$), 1.33 (m, 12H, NCH$_2$C*H*$_3$), 0.36 (s, 1H, CH$_3$); ^{13}C NMR (100.6 MHz, DMF-d^7): δ 141.37 (C$_q$), 129.57, 128.05, 127.46, 124.92, 119.42 (CH aryl), 52.59 (CH$_2$), 7.58 (2 × CH$_3$), signals of other quaternary carbons were not detected; ^{29}Si NMR (79.5 MHz, DMF-d^7): δ −105.12; MS HR–EI [Found: 348.1341; C$_{25}$H$_{20}$Si (MH − NEt$_4$)$^{+\cdot}$, calc. 348.1334]. **8**: mp 132–135 °C; ^{1}H NMR (400 MHz, DMF-d^7): δ 7.82 (d, *J* 7.5 Hz, 3H, CH aryl), 7.34 (d, *J* 6.6 Hz, 4H, CH aryl), 7.11 (t, *J* 6.9 Hz, 4H, CH aryl), 7.06 (m, 3H, CH aryl), 6.89 (t, *J* 6.9 Hz, 4H, CH aryl), 6.79 (m, 3H, CH aryl), 3.43 (m, 8H, NCH$_2$), 1.34 (m, 12H, NCH$_2$C*H*$_3$); ^{13}C NMR (100.6 MHz, DMF-d^7): δ 154.15 (C$_q$), 136.88, 133.62, 129.40, 127.88, 127.30, 126.49, 125.99, 119.13 (CH aryl), 52.38 (CH$_2$), 7.33 (CH$_3$), signals of other quaternary carbons were not detected; ^{29}Si NMR (79.5 MHz, DMF-d^7): δ −99.59; MS HR–EI [Found 410.1481; C$_{30}$H$_{22}$Si (MH − NEt$_4$)$^{+\cdot}$, calc. 410.1491].

§ *Crystal structure determination of* **6**: [C$_{16}$H$_{36}$N]$^+$[C$_{25}$H$_{19}$Si]$^-$, M_w = 589.95, colourless plate, 0.30 × 0.30 × 0.12 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 10.9938(2), b = 19.2264(3), c = 19.4424(3) Å, β = 121.5485(8)°, V = 3502.16(10) Å^3, Z = 4, D_c = 1.119 g cm^{-3}. X-Ray intensities were measured on a Nonius KappaCCD diffractometer with a rotating anode (λ = 0.71073 Å) at a temperature of 150(2) K. 56276 reflections were measured of which 5828 were unique (R_{int} = 0.094); 4809 reflections were observed [$I > 2\sigma(I)$]. The theta range was 1.62–24.50° with indices *hkl* −12/12, −22/22, −22/22. An absorption correction was not considered necessary (μ = 0.10 mm^{-1}). The structure was solved with direct methods (SHELXS86[9]) and refined with SHELXL97[10] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The *n*-butyl groups were refined with a disorder model. 426 refined parameters, 88 restraints. *R*-values [obs. refl.]: $R1$ = 0.0515, $wR2$ = 0.1258. *R*-values [all refl.]: $R1$ = 0.0646, $wR2$ = 0.1340. GoF = 1.022. Residual electron density between −0.44 and 0.43 e Å^{-3}. Molecular illustration, structure checking and calculations were performed with the PLATON[11] package.CCDC reference number 173731.See http://www.rsc.org/suppdata/cc/b1/b109816k/ for crystallographic data in CIF or other electronic format.

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