The Synthesis of the First Compound with Li-Si-Hg Bonding: $[\{Li(iPr_3Si)_2Si\}_2Hg]$—a Source for the $[Li(iPr_3Si)_2Si]^{\cdot}$ Radical**

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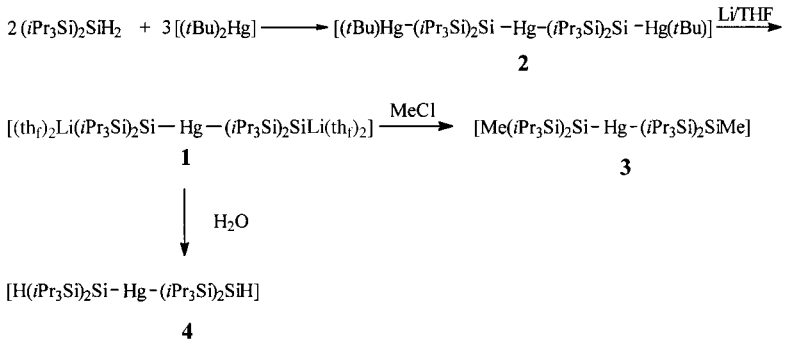

Scheme 1. The synthesis and reactions of **1**.

The chemistry of geminal organometallic reagents of the general type $[R_2CMM']$ (M, M′ = metals) is a vigorously developing field and a variety of such reagents have been recently prepared.[1] In contrast, almost nothing is known on the organosilicon $[R_2SiMM']$ analogues.[2] The first geminal dimetallic organosilicon compound, $[(iPr_3Si)_2SiLi_2]$, was first isolated in 1999 and its structure was determined.[3] The synthetic potential of compounds of the type $[R_2SiMM']$ is vast and we have therefore tried to develop new methods for the preparation of $[R_2SiMM']$ derivatives.

Herein we report the synthesis and X-ray structure of compound **1** (Scheme 1), which is a new type of a geminal dimetallic silicon compound, $[(LiSiR_2)_2Hg]$, where the geminal metals are lithium and mercury—exhibiting a novel type of connectivity unprecedented also in carbon chemistry. This connectivity provides unique possibilities as the Si–Li bond provides a nucleophilic silicon site while the Si–Hg bond can be cleaved to produce a silyl radical site.[4] Furthermore, **1** has two Si–Li sites which can be used in further transformations.

One of the best approaches to the preparation of organodilithium compounds is via the corresponding dimercury compounds.[1] We have therefore treated diorganylsilanes R_2SiH_2 with $[tBu_2Hg]$ hoping to prepare selectively the corresponding silyl dimercurial species, which could serve as a precursor to the desired $[R_2SiLi_2]$ compounds by the corresponding transmetallation reactions. The reaction of $(iPr_3Si)_2SiH_2$ with $[(tBu)_2Hg]$ leads to the trimercury compound **2** (Scheme 1). The details of the synthesis, the spectroscopic data, and the X-ray structure of **2** will be reported elsewhere.[5] Compound **1** was obtained from **2** by lithiation with lithium metal in THF (Scheme 1). The green crystals of **1** were isolated from the reaction mixture in 65% yield. The structure of **1** was first confirmed by trapping experiments. Thus, treatment of a toluene solution of **1** with MeCl or H_2O leads to the corresponding new silylmercury compounds **3** or **4**, respectively (Scheme 1), in agreement with the molecular formula of **1**.

The X-ray structure of **1**[6] (Figure 1) confirms the unusual Li-Si-Hg connectivity and shows that the Si-Hg-Si unit is linear. The two Si–Li bonds are antiperiplanar to each other and each lithium atom is coordinated to two THF molecules.

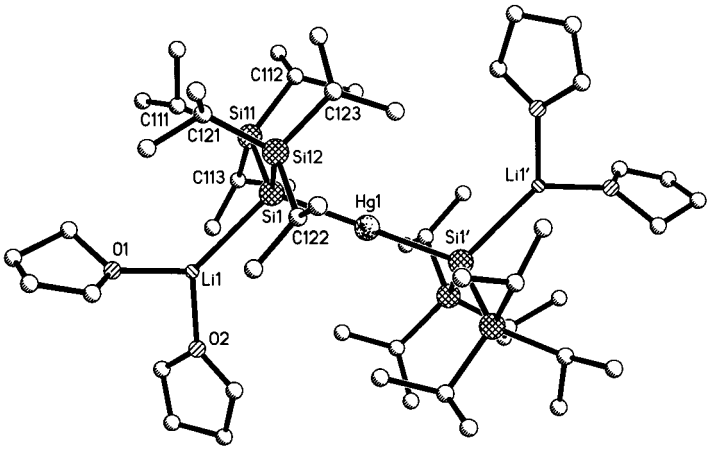

Figure 1. ORTEP drawing of **1**. Hydrogens have been omitted for clarity. Selected bond lengths [Å] and angles [°] are: Si1-Li1 2.558(11), Hg1-Si1 2.4795(13), Si1-Si12 2.324019, Si1-Si11 2.3318(18), Si11-C113 1.903(6), Si11-C112 1.907(5), Si11-C111 1.908(5), Si12-C123 1.867(8), Si12-C121 1.896(6), Si12-C122 1.949(8), Li1-O1 1.929(14), Li1-O2 1.901(13); Si1-Hg1-Si1′ 180.0, Hg1-Si1-Li1 116.3(3), Si12-Si1-Si11 117.57(7), Si12-Si1-Hg1 108.05(7), Si11-Si1-Hg1 101.39(6), Si12-Si1-Li1 104.1(3), Si11-Si1-Li1 110.0(3), C113-Si11-C112 105.3(2), C113-Si11-C111 103.5(3), C112-Si11-C111 111.9(2), Li1Si1Si1′Li1′ 180.0.

The $[(iPr_3Si)_2SiHg]$ fragments have regular bond lengths, that is, Hg–Si 2.479(1) Å is similar to the Hg–Si bond in $[(Me_3Si)_2Hg]$ (2.4913(18) Å).[7] This comparison indicates the absence of significant steric repulsion between the large substituents around the Hg center (i.e. the four iPr_3Si groups

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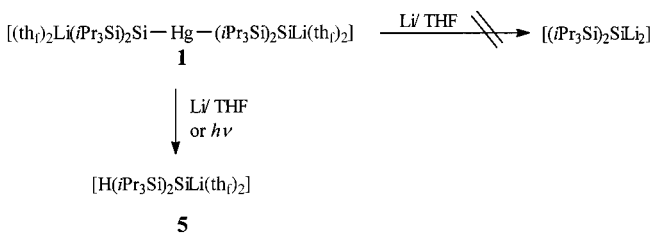
and the two $Li(thf)_2$ groups), as well as the absence of strong electronic effects of the Si–Li bonds on the Si–Hg bonds. The Si–Li bond length (2.558(1) Å) is similar to the Si–Li bond length in $[(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}\{\mathrm{Li}(\mathrm{thf})_2\}]$ (2.550 Å),[3] but significantly shorter than the usual Si–Li bond length in solvated silyllithium reagents (2.64–2.77 Å).[2, 8] This difference may be because each lithium atom is solvated by only two THF molecules, while in other $[R_3SiLi]$ compounds three molecules of THF are coordinated to Li atom.[8c]

The NMR spectroscopic data of **1** provides information about its electronic structure. The ^{199}Hg chemical shift in **1** is $\delta = 1271$, the most deshielded value known. The previously most deshielded value of $\delta = 1142$ was reported by us for $[\{(Me_3SiMe_2Si)_3Si\}_2Hg_2]$.[9] The ^{29}Si chemical shift of Si1 atom bonded to both Hg and Li, is -120.7 ppm, strongly shielded compared to $[\{(Me_3Si)_3Si\}_2Hg]$ (-54.5 ppm),[10] but it is less shielded than in $[(Me_3Si)_3SiLi(thf)_3]$ ($\delta = -189.4$)[11] and in $[(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}\{\mathrm{Li}(\mathrm{thf})_2\}_2]$ ($\delta = -292.0$).[3]

Treatment of **1** with excess of Li in THF did not lead to the expected complex $[(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{SiLi}_2]$. Instead a new silyllithium reagent, $[\mathrm{H}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{SiLi}(\mathrm{thf})_2]$(**5**), was obtained as the major product (Scheme 2). The mechanism of this intriguing reaction is under current study.



Scheme 2. Lithiation or irradiation of **1**.

Irradiation of **1** in hexane also yields **5** as the major product (Scheme 2). The EPR spectrum observed during the irradiation of **1** (Figure 2) can be interpreted as a superposition of the signals of three radicals: the first silyl radical with an α-Si–Li bond $[(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{LiSi}]^{\bullet}$ (**6**), silyl radical $(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{HSi}^{\bullet}$ (**7**), and the Hg-substituted radicals $[\mathrm{RLi}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{SiHg}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}]^{\bullet}$ (**8**, R = H or Li).[12] The structure of **6** is confirmed by the presence of a quartet centered at $g = 2.0073$ resulting from interaction of the unpaired electron with a ^{7}Li nuclei (I = 3/2) and two quartets of satellites resulting from interaction of the unpaired electron with the α- and β-^{29}Si nuclei and a further splitting by interaction with the ^{7}Li nuclei $a\{^7\mathrm{Li}\} = 1.25$ G (Figure 2c). The hyperfine coupling constant (hfc) value $a\{^{29}\mathrm{Si}(\alpha)\} = 32.0$ G is intermediate between the α constants measured for branched $(R_3Si)_3Si^{\bullet}$ radicals (55.6–63.8 G)[4, 13] and for cyclic polysilyl anion radicals, $[\mathrm{c}\text{-}(R_2Si)_{4-6}]^{\bullet-}$ (5.0–7.0 G).[14, 15] Quantum-mechanical calculations[16] are consistent with the observed hfc in **6**. Thus, for the model radical $[(Me_3Si)_2LiSi]^{\bullet}$, which has a planar geometry around the central Si atom, the calculations predict $a\{^{29}\mathrm{Si}(\alpha)\} = 30.2$ G and $a\{^7\mathrm{Li}\} = 1.0$ G, in good agreement with the experimental values of **6**. It is of note that the calculated $a\{^{29}\mathrm{Si}(\alpha)\} = 8.7$ G for $(Me_3Si)_2Si^{-\bullet}$ is much lower than for

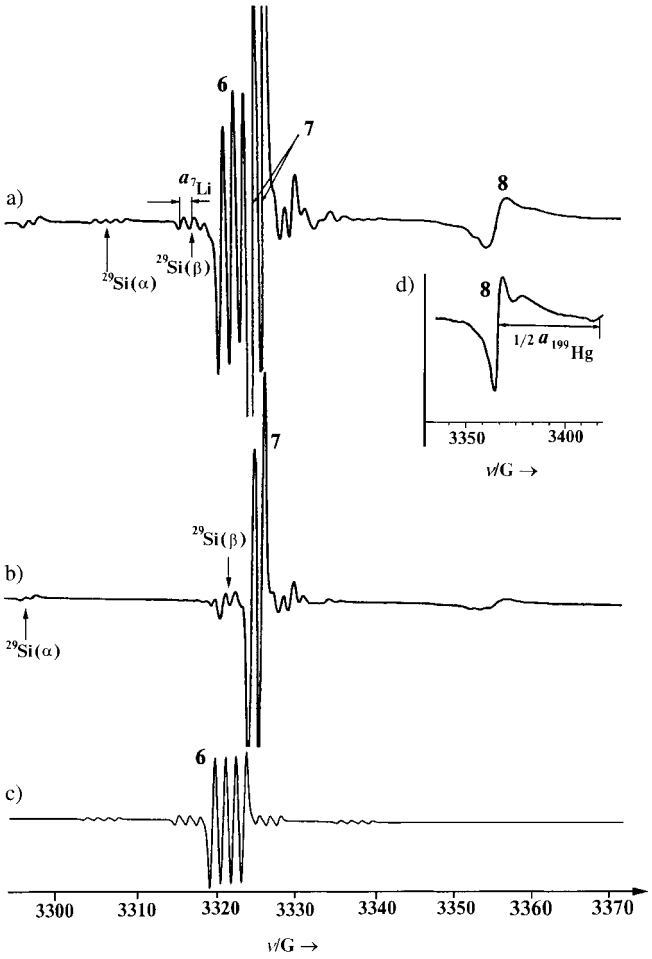


Figure 2. Experimental EPR spectra in hexane at 300 K and simulated EPR spectra: a) The spectrum observed during UV irradiation of **1**. b) The spectrum of silyl radical $\mathrm{H}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}^{\bullet}$ (**7**) after the UV irradiation was stopped. c) Computer simulation of the EPR spectrum of the silyl radical $[\mathrm{Li}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}]^{\bullet}$ (**6**) using the $a\{^7\mathrm{Li}\} = 1.25$ G, $a\{^{29}\mathrm{Si}(\alpha)\} = 32.0$ G, and $a\{^{29}\mathrm{Si}(\beta)\} = 10.0$ G as parameters (see discussion). d) (Inset) Upfield components of possible radicals $[\mathrm{R}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{SiHg}(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}]^{\bullet}$ (**8**, R = Li or H).

$(Me_3Si)_2LiSi^{\bullet}$. The observed hyperfine interaction of the unpaired electron with ^{7}Li nucleus indicates that the Si–Li bond in **6** does not dissociate in solution. This proposal is also supported by the high $a\{^{29}\mathrm{Si}(\alpha)\}$ value of 32.0 G in **6**, because if **6** did dissociate to $(Me_3Si)_2Si^{-\bullet}$ and Li^+ ions a much lower $a\{^{29}\mathrm{Si}(\alpha)\}$ of around 9 G would be expected.

Experimental Section

Standard Schlenk techniques were used for all syntheses and all sample manipulations.

1: $[t\mathrm{Bu}_2\mathrm{Hg}]$ (13.5 g 43.0 mmol) were added under argon to $(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{SiH}_2$[19] (10.0 g, 29.0 mmol) in three equal portions while heating the mixture to 120 °C. A new portion of $[t\mathrm{Bu}_2\mathrm{Hg}]$ was added after complete evolution *iso*-butane from the reaction mixture (approximately every 4 h). After evaporation of the volatile compounds, THF (50 mL) and Li powder 7.0 g, 1.0 mol) were added and the mixture was stirred at RT for 1 h. The mixture was decanted from the lithium powder and the solvent was evaporated. Crystallization from hexane gave (11.2 g, 9.4 mmol) of green crystals of **1** in 65 % yield.

^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.51$ (br m, 100 H), 3.54 (t, 16 H; CH_2O); ^{13}C NMR (200 MHz, C_6D_6): $\delta = 17.6$ (Me_2CH), 22.0 ($MeCH$), 25.3 (CH_2-CH_2O), 68.5 (CH_2-CH_2O); ^{29}Si NMR (400 MHz, C_6D_6): $\delta = -120.9$

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((iPr$_3$Si)$_2$*Si*), 30.23 ((iPr$_3$*Si*)$_2$Si); ^{199}Hg NMR (400 MHz, C_6D_6): $\delta = 1271.6$. Methylation of **1** with MeCl gave **3** (90%). **3**: ^{1}H NMR (C_6D_6): $\delta = 0.69$ (s, 6H; Si-Me), 1.25 (d, ^3J(H,H) = 5.8 Hz, 72H; *Me*$_2$CH), 1.54 (m, ^3J(H,H) = 5.8 Hz, 12H; Me$_2$C*H*); ^{13}C NMR (C_6D_6): $\delta = -1.7$ (Si-Me), 15.3 (Me$_2$*C*H), 20.8 (*Me*$_2$CH), 21.0 (*Me*$_2$CH); ^{29}Si NMR (C_6D_6): $\delta = -25.1$ ((iPr$_3$Si)$_2$*Si*), 18.1 ((iPr$_3$*Si*)$_2$Si); ^{199}Hg NMR (C_6D_6): $\delta = 501.0$; MS(CI) m/z 916 (M^+); m.p. 186 °C (decomp., evacuated capillary). Hydrolysis of **1** gave **4** (95%). **4**: ^{1}H NMR (C_6D_6): $\delta = 1.24$ (d, ^3J(H,H) = 2.3 Hz, 72H; *Me*$_2$CH), 1.41 (m, ^3J(H,H) = 5.8 Hz, 12H; Me$_2$C*H*) 3.73 (s, 2H; SiH); ^{13}C NMR (C_6D_6): $\delta =$ 15.2 (Me$_2$*C*H), 20.4 (*Me*$_2$CH), 20.5 (*Me*$_2$CH); ^{29}Si NMR (C_6D_6): $\delta = -81.5$ ((iPr$_3$Si)$_2$*Si*), 24.0 ((iPr$_3$*Si*)$_2$Si); ^{199}Hg NMR (C_6D_6): $\delta = 691.0$; MS(CI) m/z 888 (M^+); m.p. 204 °C (decomp., evacuated capillary). Lithiation of **1** with Li powder in THF for 1 h at RT gave **5** (75%) after crystallization from pentane. **5**: ^{1}H NMR (C_6D_6): $\delta = 1.41$ (br m, 50H; (C*H*$_3$)$_2$C*H*$_2$C*H*$_2$-C*H*$_2$O), 3.50 (t, m, 9H; CH$_2$-O, SiH); ^{13}C NMR (C_6D_6): $\delta = 15.8$ (Me$_2$*C*H), 21.3 (*Me*$_2$CH), 25.4 (*C*H$_2$-CH$_2$O), 68.4 (CH$_2$-*C*H$_2$O); ^{29}Si NMR (C_6D_6): $\delta =$ -205.4 ((iPr$_3$Si)$_2$Si), 20.8 ((iPr$_3$Si)$_2$Si).

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[6] Crystal structure analysis of **1**: $C_{52}H_{116}HgLi_2O_4Si_6$, $M_r = 1188.46$, triclinic, $P\bar{1}$, $a = 11.1351(18)$, $b = 11.6866(19)$, $c = 14.379(2)$ Å, $\alpha = 109.931(10)$, $\beta = 91.515(10)$, $\gamma = 112.774(9)°$, $V = 1594.6(4)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.238$ Mg m^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 25.63$ cm^{-1}, $F(000) =$ 630, $T = 173$ K. A green crystal of approximate dimensions $0.4 \times 0.4 \times 0.3$ mm^3 was coated with nujol, fixed on a glass fiber, and mounted on a Siemens P4 four-circle diffractometer. The cell parameters had been determined by the position of 32 selected reflections ($22° < 2\theta < 25°$). The structure was solved and refined on the base of 8152 unique out of 9124 measured reflections ($R_{int} =$ 0.079). The structure solution was accomplished by direct methods. The refinement on F^2 was carried out by full-matrix least-squares techniques (Bruker-SHELXTL NT 5.1). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included on calculated positions and refined with fixed isotropic thermal parameters equal to 1.5 times of the U_{eq} value of the bonded carbon employing appropriate riding models. Final R indices for 8152 data and 307 parameters: R_1 ($I > 2\sigma(I)$) = 0.054, $wR_2 = 0.133$ (all data), GOF = 1.026. Min./max. residual electron density: -2.266/ 2.193 e Å^{-3} (near Hg). CCDC-171794 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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