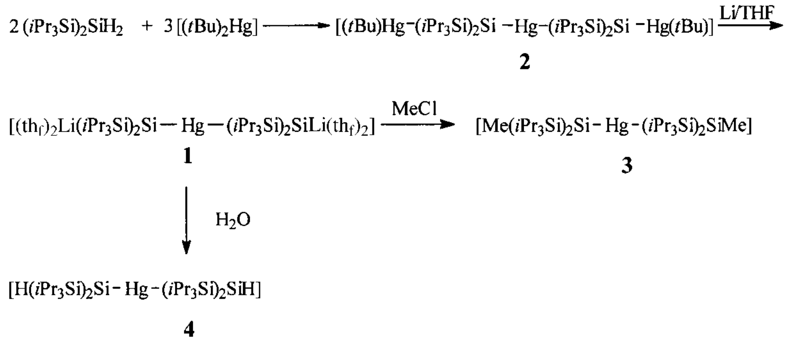
The Synthesis of the First Compound with Li-Si-Hg Bonding: [{Li(iPr$_3$Si)$_2$Si}$_2$Hg]—a Source for the [Li(iPr$_3$Si)$_2$Si]$^\cdot$ Radical[**]

Dmitry Bravo-Zhivotovskii,*
Michael Yuzefovich, Nadejda Sigal,
Gady Korogodsky, Karl Klinkhammer,
Boris Tumanskii, Alex Shames, and
Yitzhak Apeloig*

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$_3$Si)$_2$SiLi$_2$], 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, [($LiSiR_2$)$_2$Hg], 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.



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

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$_2$Hg] 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$_3$Si)$_2$SiH$_2$ with [(tBu)$_2$Hg] 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.

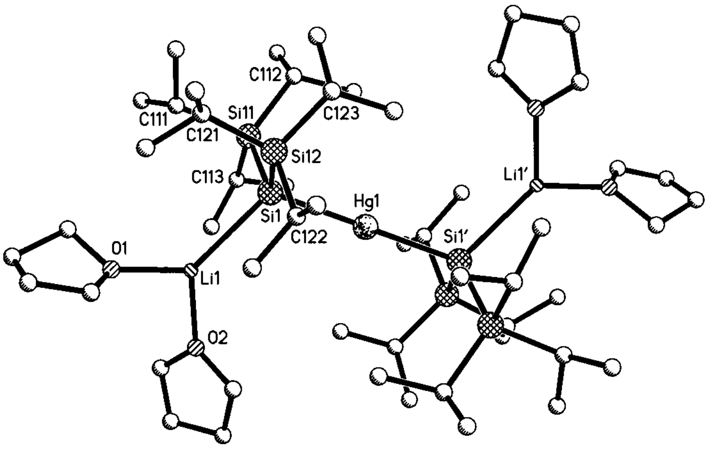


Figure 1. ORTEP drawing of **1**. Hydrogens have been omitted for clarity. Selected bond lengths [Å] and angles [°] are: Si1-Li1 2.558(11), Hg1-Si1 2.4795(13), Si1-Si12 2.324019, Si1-Si11 2.3318(18), Si11-C113 1.903(6), Si11-C112 1.907(5), Si11-C111 1.908(5), Si12-C123 1.867(8), Si12-C121 1.896(6), Si12-C122 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$_3$Si)$_2$SiHg] fragments have regular bond lengths, that is, Hg–Si 2.479(1) Å is similar to the Hg–Si bond in [(Me_3Si)$_2$Hg] (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$_3$Si groups

---

[*] Dr. D. Bravo-Zhivotovskii, Prof. Dr. Y. Apeloig, M. Yuzefovich, N. Sigal, G. Korogodsky
Department of Chemistry and the Lise Meitner-Minerva Center for Computational Quantum Chemistry
Technion-Israel Institute of Technology
Haifa 32000 (Israel)
Fax: (+972) 4823-3735
E-mail: chrbrzh@tx.technion.ac.il, chrapel@tx.technion.ac.il

Priv.-Doz. Dr. K. Klinkhammer
Institut für Anorganische Chemie der Universität
Pfaffenwaldring 55, 70550 Stuttgart (Germany)

Prof. Dr. B. Tumanskii
Institute of Organoelement Compounds
Russian Academy of Sciences (INEOS) Moscow B-334, 117813 (Russia)

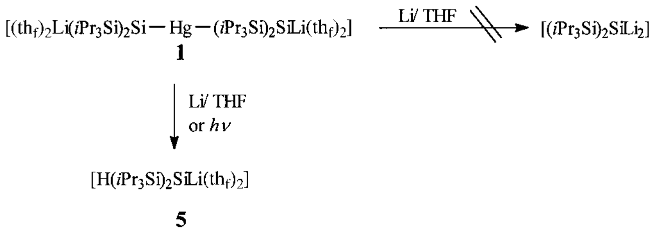
Dr. A. Shames
Ben-Gurion University of the Negev
Beer-Sheva 84105 (Israel)

[**] This research was supported by the Israel Science Foundation administrated by the Israel Academy of Sciences and Humanities, the Fund for the Promotion of Research at the Technion, and the Minerva Foundation in Munich. D.B.-Z. is grateful to the Ministry of Immigrant Absorption, State of Israel, for a Kamea scholarship.

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 $[(iPr_3Si)_2Si\{Li(thf)_2\}]$ (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 $[(iPr_3Si)_2Si\{Li(thf)_2\}_2]$ ($\delta = -292.0$).[3]

Treatment of **1** with excess of Li in THF did not lead to the expected complex $[(iPr_3Si)_2SiLi_2]$. Instead a new silyllithium reagent, $[H(iPr_3Si)_2SiLi(thf)_2]$(**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 $[(iPr_3Si)_2LiSi]^{\bullet}$ (**6**), silyl radical $(iPr_3Si)_2HSi^{\bullet}$ (**7**), and the Hg-substituted radicals $[RLi(iPr_3Si)_2SiHg(iPr_3Si)_2Si]^{\bullet}$ (**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 $a\{^{7}Li\} = 1.25$ G (Figure 2c). The hyperfine coupling constant (hfc) value $a\{^{29}Si(\alpha)\} = 32.0$ 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, $[c\text{-}(R_2Si)_{4-6}]^{\bullet -}$ (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 $a\{^{29}Si(\alpha)\} = 30.2$ G and $a\{^{7}Li\} = 1.0$ G, in good agreement with the experimental values of **6**. It is of note that the calculated $a\{^{29}Si(\alpha)\} = 8.7$ G for $(Me_3Si)_2Si^{-\bullet}$ is much lower than for $(Me_3Si)_2LiSi^{\bullet}$. 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 $a\{^{29}Si(\alpha)\}$ value of 32.0 G in **6**, because if **6** did dissociate to $(Me_3Si)_2Si^{-\bullet}$ and Li^{+} ions a much lower $a\{^{29}Si(\alpha)\}$ of around 9 G would be expected.

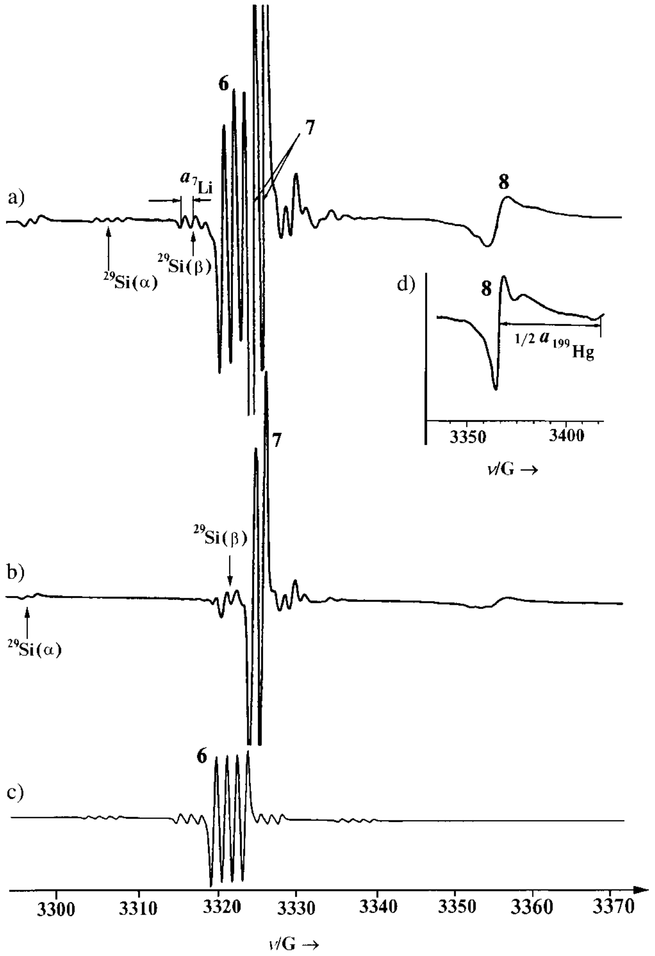


Figure 2. Experimental EPR spectra in hexane at 300 K and simulated EPR spectra: a) The spectrum observed during UV irradiation of **1**. b) The spectrum of silyl radical $H(iPr_3Si)_2Si^{\bullet}$ (**7**) after the UV irradiation was stopped. c) Computer simulation of the EPR spectrum of the silyl radical $[Li(iPr_3Si)_2Si]^{\bullet}$ (**6**) using the $a\{^{7}Li\} = 1.25$ G, $a\{^{29}Si(\alpha)\} = 32.0$ G, and $a\{^{29}Si(\beta)\} = 10.0$ G as parameters (see discussion). d) (Inset) Upfield components of possible radicals $[R(iPr_3Si)_2SiHg(iPr_3Si)_2Si]^{\bullet}$ (**8**, R = Li or H).

Experimental Section

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

1: $[tBu_2Hg]$ (13.5 g 43.0 mmol) were added under argon to $(iPr_3Si)_2SiH_2$[19] (10.0 g, 29.0 mmol) in three equal portions while heating the mixture to 120 °C. A new portion of $[tBu_2Hg]$ 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 (Me_2CH), 25.3 (CH_2-CH_2O), 68.5 (CH_2-CH_2O); ^{29}Si NMR (400 MHz, C_6D_6): $\delta = -120.9$

((*i*Pr$_3$Si)$_2$*Si*), 30.23 ((*i*Pr$_3$*Si*)$_2$Si); ^{199}Hg NMR (400 MHz, C$_6$D$_6$): $\delta = 1271.6$. Methylation of **1** with MeCl gave **3** (90 %). **3**: ^{1}H NMR (C$_6$D$_6$): $\delta = 0.69$ (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$_6$D$_6$): $\delta = -1.7$ (Si-Me), 15.3 (Me$_2$*C*H), 20.8 (*Me*$_2$CH), 21.0 (*Me*$_2$CH); ^{29}Si NMR (C$_6$D$_6$): $\delta = -25.1$ ((*i*Pr$_3$Si)$_2$*Si*), 18.1 ((*i*Pr$_3$*Si*)$_2$Si); ^{199}Hg NMR (C$_6$D$_6$): $\delta = 501.0$; MS(CI) *m*/*z* 916 (M^+); m.p. 186 °C (decomp., evacuated capillary). Hydrolysis of **1** gave **4** (95 %). **4**: ^{1}H NMR (C$_6$D$_6$): $\delta = 1.24$ (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$_6$D$_6$): $\delta = 15.2$ (Me$_2$*C*H), 20.4 (*Me*$_2$CH), 20.5 (*Me*$_2$CH); ^{29}Si NMR (C$_6$D$_6$): $\delta = -81.5$ ((*i*Pr$_3$Si)$_2$*Si*), 24.0 ((*i*Pr$_3$*Si*)$_2$Si); ^{199}Hg NMR (C$_6$D$_6$): $\delta = 691.0$; 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$_6$D$_6$): $\delta = 1.41$ (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$_6$D$_6$): $\delta = 15.8$ (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$_6$D$_6$): $\delta = -205.4$ ((*i*Pr$_3$Si)$_2$Si), 20.8 ((*i*Pr$_3$Si)$_2$Si).

Received: October 29, 2001 [Z18129]

---

[1] I. Marek, J.-F. Normant, *Chem. Rev.* **1996**, *96*, 3241.

[2] a) J. Belzner, U. Dehnert in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, p. 779; b) P.Lickiss, C. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75; c) K. Tomao, A. Kawachi, *Adv. Organometallic. Chem.* **1995**, *38*, 1; d) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.* **2000**, *210*, 11.

[3] [(*i*Pr$_3$Si)$_2$SiLi$_2$] was prepared by the reaction of the corresponding silacyclopropene in THF with Li metal; A. Sekiguchi, M. Ichinohe, S. Yamaguchi, *J. Am. Chem. Soc.* **1999**, *121*, 10231.

[4] Y. Apeloig, D. Bravo-Zhivotovskii, M. Yuzefovich, M. Bendikov, A. I. Shames, *Appl. Magn. Reson.* **2000**, *18*, 425.

[5] Y. Apeloig, D. Bravo-Zhivotovskii, M. Yuzefovich, unpublished results.

[6] Crystal structure analysis of **1**: C$_{52}$H$_{116}$HgLi$_2$O$_4$Si$_6$, $M_r = 1188.46$, triclinic, $P\bar{1}$, $a = 11.1351(18)$, $b = 11.6866(19)$, $c = 14.379(2)$ Å, $\alpha = 109.931(10)$, $\beta = 91.515(10)$, $\gamma = 112.774(9)^\circ$, $V = 1594.6(4)$ Å^3, $Z = 1$, $\rho_{\text{calcd}} = 1.238$ Mg m^{-3}, $\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, $\mu = 25.63$ cm^{-1}, $F(000) = 630$, $T = 173$ K. A green crystal of approximate dimensions 0.4 × 0.4 × 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 ($22^\circ < 2\theta < 25^\circ$). The structure was solved and refined on the base of 8152 unique out of 9124 measured reflections ($R_{\text{int}} = 0.079$). 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).

[7] N. L. Pickett, O. Just, D. G. VanDerveer, W. S. Rees, Jr., *Acta Crystallogr. Sect. C* **2000**, *56*, 412.

[8] a) Y. Apeloig, G. Korogodsky, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *Eur. J. Inorg. Chem.* **2000**, 1091; b) Y. Apeloig, M. Yuzefovich, M. Bendikov, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *Angew. Chem.* **2001**, *113*, 3106; *Angew. Chem. Int. Ed.* **2001**, *40*, 3016; c) the force constants for stretching the Si–Li bonds are very small and therefore the energy required to cause relatively large changes in Si–Li is small.[8b]

[9] D. Bravo-Zhivotovskii, M. Yuzefovich, M. Bendikov, K. Klinkhammer, Y. Apeloig, *Angew. Chem.* **1999**, *111*, 1169; *Angew. Chem. Int. Ed.* **1999**, *38*, 1100.

[10] J. Arnold, T. D. Tilley, A. Rheingold, S. J. Geib, *Inorg. Chem.* **1987**, *26*, 2106.

[11] A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694.

[12] The large negative *g*-factor shift of **8** ($g = 1.998$) results from the large spin-orbital coupling of the mercury. The EPR spectroscopy of Hg-substituted radicals is under current study and will be reported elsewhere.

[13] a) S. Kyushin, H. Sakurai, H. Matsumoto, *Chem. Lett.* **1998**, 107; b) S. Kyushin, H. Sakurai, T. Betsuyaki, H. Matsumoto, *Organometallics* **1997**, *16*, 5386; c) M. Kira, T. Obata, I. Kon, H. Hashimoto, M. Ichinohe, H. Sakurai, S. Kyushin, H. Matsumoto, *Chem. Lett.* **1998**, 1097.

[14] C. L. Wadsworth, R. West, Y. Nagai, H. Watanabe, T. Muraoka, *Organometallics* **1985**, *4*, 1659.

[15] a) $a\{^{29}\text{Si}(\alpha)\} = 29.9$ G for the potassium anion radical salt of dialkylsilylene, 2,2,5,5-tetrakis (trimethylsilyl) silacyclopentane-1,1-diyl;[15b] b) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **1999**, *121*, 9722.

[16] Calculations were performed using standard techniques as implemented in the Gaussian 98 series of programs (Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**). All structures were fully optimized at B3LYP/6-31G(d) level and vibrational frequencies were computed at the same level. Hfc were calculated[17] at the MP2/6-31G(d) level. The reliability of MP2/6-31G(d)//B3LYP/6-31G(d) level of theory was tested by calculating the hfc of simple silyl radicals; e.g. in Me$_3$Si$^\bullet$ the calculated $a\{^{29}\text{Si}(\alpha)\}$ is 174 G, in good agreement with the experimental value of 181 G.[18]

[17] N. Rega, M. Cossi, V. Barone, *J. Chem. Phys.* **1996**, *105*, 11060.

[18] C. Chatgilialoglu, *Chem. Rev.* **1995**, *95*, 1229.

[19] P. P. Gaspar, A. M. Beatty, T. Chen, T. Hail, D. Lei, W. R. Winchester, J. Braddock-Wilking, N. P. Rath, W. T. Klooster, T. F. Koetzle, S. A. Mason, A. Albinati, *Organometallics* **1999**, *18*, 3921.