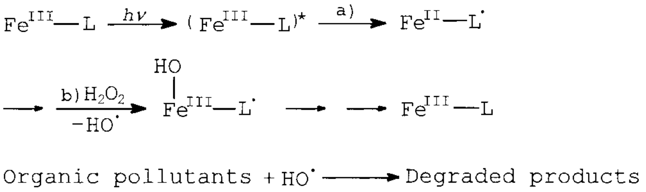
organic pollutants is minor: Almost the same degradation rate of RhB was observed as that under aerated conditions.

We propose a mechanism, based on the above results, for the photodegradation of organic pollutants in aqueous solutions of [Fe^{III}(PcS)] and H_2O_2 (Scheme 1). In this system



Scheme 1. A possible machanism for the photooxidation of organic pollutants in the aqueous [Fe(PcS)]/H_2O_2 system under irradiation with visible light. See text for details.

[Fe^{III}(PcS)] exists mainly in the form of the aqua complex.[4] Upon irradiation with visible light, the excitation of [Fe^{III}(PcS)] can cause an intramolecular electron transfer from the ligand (L) to Fe^{III}, leading to reduction of Fe^{III} to Fe^{II} (step a).[11] The reduced Fe^{II} complex immediately reacts with H_2O_2 to produce HO$^•$ (step b).[11d] According to the proposed mechanism, the degradation of organic compounds in the [Fe(PcS)]/H_2O_2 system under irradiation with visible light can be well explained without involving high-valence iron–oxo or iron–peroxo complexes.[3, 12]

Experimental Section

General procedure for the photooxidation reaction: A 500-W halogen lamp was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket (Pyrex) to cool the lamp. The jacket was wrapped with a piece of black paper containing a small window. A cutoff filter was placed on the window (diameter 3 cm) to remove wavelengths less than 470 nm and to ensure irradiation with visible light only. The center distance between the reaction vessel and the light source was 10 cm. A typical reaction mixture for irradiation contained the following initial concentrations: RhB (10 μM) or SA (0.1 mM), [Fe(PcS)] (40 μM), and H_2O_2 (1 mM). Deionized and doubly distilled water was used throughout this study. The aqueous solution was adjusted to pH 3 with diluted solutions of NaOH or $HClO_4$. At the given irradiation time intervals, a sample (3 mL) were taken out and analyzed by UV/Vis spectroscopy with a lambda Bio 20 spectrophotometer (Perkin-Elmer). The ESR spectra were measured on a Bruker EPR 300E spectrometer.

Received: January 24, 2001
Revised: April 9, 2001 [Z16495]

---

[1] a) M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96; b) T. Wu, G. Liu, J. Zhao, H. Hidaka, N. Serpone, *J. Phys. Chem.* **1999**, *103*, 4862–4867; c) T. Wu, T. Lin, J. Zhao, H. Hidaka, N. Serpone, *Environ. Sci. Technol.* **1999**, *33*, 1379–1387.

[2] a) O. Legrini, E. Oliveros, A. M. Braun, *Chem. Rev.* **1993**, *93*, 671–698; b) K. Wu, T. Zhang, J. Zhao, H. Hidaka, *Chem. Lett.* **1998**, 857.

[3] a) A. Sorokin, B. Meunier, *J. Chem. Soc. Chem. Commun.* **1994**, 1799–1800; b) A. Sorokin, J. L. Séris, B. Meunier, *Science* **1995**, *268*, 1163–1166; c) A. Sorokin, S. D. Suzzoni-Dezard, D. Póullain, J. P. Noël, B. Meunier, *J. Am. Chem. Soc.* **1996**, *118*, 7410–7411.

[4] A. Hadasch, A. Sorokin, A. Rabion, B. Meunier, *New J. Chem.* **1998**, 45–51.

[5] Total organic carbon (TOC) removal was examined by a TOC analyzer (Appllo 9000). The initial solution contained 30 μM RhB, 25 μM [Fe(PcS)], and 0.05 M H_2O_2. During the reaction process, no degradation of [Fe(PcS)] was observed as evidenced by UV/Vis spectroscopy and HPLC analysis, indicating that the TOC removal was caused by the degradation of RhB.

[6] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, *Environ. Sci. Technol.* **1998**, *32*, 2394–2400.

[7] A. Maldotti, C. Bartocci, G. Varani, A. Molinari, *Inorg. Chem.* **1996**, *35*, 1126–1131.

[8] G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513–886.

[9] C. Walling, *Acc. Chem. Res.* **1975**, *8*, 125–131.

[10] E. E. Wegner, A. W. Adamson, *J. Am. Chem. Soc.* **1966**, *5*, 394–403.

[11] a) Y. Ito, *J. Chem. Soc. Chem. Commun.* **1991**, 622–624; b) F. Adar, M. Gouterman, S. Aronowitz, *J. Phys. Chem.* **1976**, *80*, 2184–2197; c) W. A. Eaton, R. M. Hochstrasser, *J. Chem. Phys.* **1968**, *49*, 985–995; d) M. E. Balmer, B. Sulzberger, *Environ. Sci. Technol.* **1999**, *33*, 2418–2424.

[12] M. F. Sisemore, J. N. Burstyn, J. S. Valentine, *Angew. Chem.* **1996**, *108*, 195–196; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 206–208.

Branched Star-Type Polysilyllithium Compounds: The Effects of β-Silyl Substitution and of Complexation on Their Molecular Structure[**]

Yitzhak Apeloig,* Michael Yuzefovich,
Michael Bendikov, Dmitry Bravo-Zhivotovskii,*
Dieter Bläser, and Roland Boese

*Dedicated to Professor Hideki Sakurai
on the occasion of his 70th birthday*

In contrast to the wealth of information on organolithium reagents,[1] relatively little is known about the analogous silyllithium compounds, despite their important role in silicon chemistry.[2] Furthermore, only a limited number of silyl metal reagents have been characterized by X-ray crystallography.[2, 3] Of special interest are branched "hypersilyl" anions such as $[(Me_3Si)_3Si]^-$, which were often used for the synthesis of novel compounds,[2] for example, by us for the synthesis of stable silenes.[4] The $[(Me_3Si)_3Si]^-$ ion was first prepared in

---

[*] Prof. Y. Apeloig, Dr. D. Bravo-Zhivotovskii, M. Yuzefovich,
M. Bendikov
Department of Chemistry and the Lise Meitner–Minerva Center for Computational Quantum Chemistry
Technion–Israel Institute of Technology
32000 Haifa (Israel)
Fax: (+972) 48233735
E-mail: chrapel@tx.technion.ac.il, chrbrzh@tx.technion.ac.il

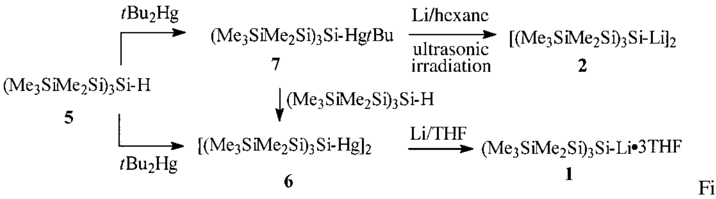
Dipl.-Ing. D. Bläser, Prof. Dr. R. Boese
Institut für Anorganische Chemie der Universität-GH Essen
Universitätstrasse 3–5, 45117 Essen (Germany)

[**] This work was supported by the Israel Science Foundation, the Minerva Foundation in München, and by the Fund for the Promotion of Research at the Technion–Israel Institute of Technology. D.B.-Z. is grateful to the Ministry of Immigrant Absorption, State of Israel, for a Kamea scholarship. We thank Dr. I. Kalikhman for her help with the NMR measurements and the referees for helpful comments.

situ by Gilman and Smith[5] and later its lithium salt was isolated and characterized as a stable complex with tetrahydrofuran (THF),[6] with 1,2-dimethoxyethane (DME),[7a] and with η^5-2,4,5-tri-*tert*-butyl-1λ^3,3λ^3-diphospholide-η^6-toluene-lithium,[7b] as well as the noncomplexed dimer.[8] Except $(Me_3Si)_3Si{-}Li$ the structures of only two additional branched silyllithium compounds were determined.[3, 9]

Herein we report on the preparation and X-ray structure determination of the first branched star-type polysilyllithium compound, $(Me_3SiMe_2Si)_3Si{-}Li$, in which three silicon atoms are contained in each side chain. Furthermore, it was isolated and characterized by X-ray crystallography both as the THF-complexed monomer $(Me_3SiMe_2Si)_3Si{-}Li \cdot 3THF$ (**1**) and as the noncomplexed dimer $[(Me_3SiMe_2Si)_3Si{-}Li]_2$ (**2**). Having precise molecular structure information of *both* complexed and noncomplexed forms of the same lithium reagent is quite unique. Except for $(Me_3Si)_3Si{-}Li \cdot 3THF$ (**3**)[6b,c] and $[(Me_3Si)_3Si{-}Li]_2$ (**4**)[8] we were unable to find other examples either of silyl- or alkyllithium compounds whose noncomplexed *and* complexed form have been structurally characterized. Comparison of the structures of the silanides **1**–**4** provides a unique opportunity to evaluate the effects of β-Me_3Si substitution and of complexation by THF on the molecular structure and the electronic nature of silyllithium derivatives.

The novel compounds **1** and **2** were synthesized (Scheme 1) by the reaction of $(Me_3SiMe_2Si)_3Si{-}H$ (**5**) with $t Bu_2Hg$ which yields either $[(Me_3SiMe_2Si)_3Si{-}Hg]_2$ (**6**) or $(Me_3SiMe_2Si)_3Si{-}Hg t Bu$ (**7**), depending on the ratio of the reagents.[10]



Scheme 1. Synthesis of the silyllithium compounds **1** and **2**.

Compound **6** reacts with lithium in THF to yield **1**, while **7** reacts with lithium in hexane to give **2** (Scheme 1).[11] The molecular structures of **1** and **2** were determined by X-ray crystallography[12] and they are presented in Figures 1 and 2, respectively.

Both **1** and **2** adopt an unusual "back-folded" conformation (Figure 3) in which the β-Si–Si bonds point "inwards", that is, towards the Si–Li bond (Figures 1 and 2). Thus, the dihedral angle θ ($\theta = \sphericalangle$ X-Si1-Si2-Si3; Figure 3) is 46.0° in **1** and 36.0° in **2**. To the best of our knowledge, this is the first report of a "back-folded" conformation of a polysilane—a conformation typical to dendrimers.[13] Quantum-mechanical density functional calculations at the B3LYP/6-31 + G* level of theory[14] for $(H_3SiH_2Si)_3Si{-}Li \cdot 3H_2O$, a model of **1** in which all the methyl groups of **1** are substituted by hydrogen atoms and the THF ligands are modeled by water molecules, also adopts a "back-folded" conformation with $\theta = 43.1°$.[15] Similar "back-folded" conformations are adopted also by $(H_3SiH_2Si)_3SiH$ and other model systems. Thus, the calculations indicate that the "back-folded" conformation is an inherent property of **1** and **2** and not a result of other factors, for example, crystal packing effects.

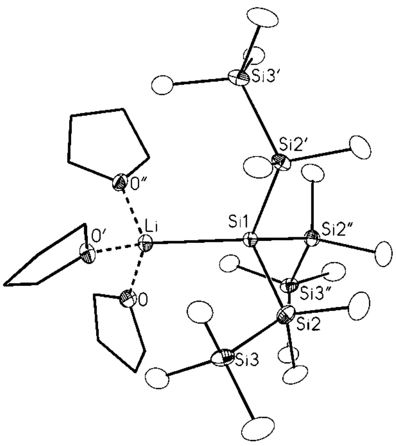


Figure 1. Molecular structure of **1** in the crystal (thermal ellipsoids for carbon (25 %); hydrogen atoms are omitted for clarity, THF carbon atoms are indicated as connective lines). The atoms labeled with ′ and ″ are symmetry equivalent with the operations z, x, y and y, z, x, respectively. Selected bond lengths [Å] and angles [°]: Si1-Li 2.760(11), Si1-Si2 2.363(2), Si2-Si3 2.352(2), Li-O 1.972(6); Li-Si1-Si2 117.74(5), Si2-Si1-Si2′ 100.08(6), Si1-Si2-Si3 115.88(7), Si1-Li-O 116.7(3), O-Li-O′ 101.3(4).

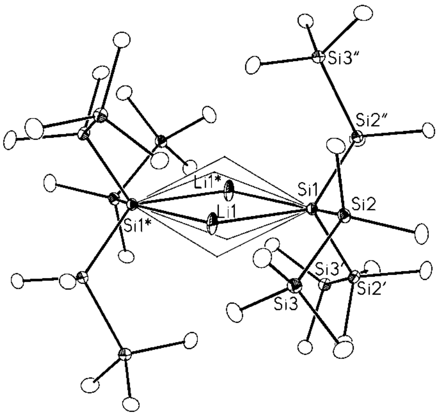


Figure 2. Molecular structure of **2** in the crystal (thermal ellipsoids for carbon (25 %); hydrogen atoms are omitted for clarity, THF carbon atoms are indicated as connective lines). The atoms labeled with ′ and ″ are symmetry equivalent with the operations $-x, x-y, z$ and $y-x, x, -z$, respectively, Si* and Li* are symmetry equivalent by the inversion center at $-x, -y, 1-z$. Only two positions of the six disordered equivalent lithium atoms (in the positions $-x, -y, 1-z$; $-y, x-y, z$; $y, y-x, -z$; $y-x, -x, z$; $x-y, x, -z$) are drawn as shaded ellipsoids, the other four as open circles. Selected bond lengths [Å] and angles [°]: Li1-Si1 2.711(8), Li1-Si* 2.737(7), Li1···Li1* 2.641(16), Si1-Si2 2.3659(6), Si2-Si3 2.3608(6); Si1-Li1-Si* 122.0(3), Li1-Si1-Li1* 58.0(3), Li1-Si1-Si2 87.4(2), Li1-Si1-Si2′ 133.6(2), Li1-Si1-Si2″ 119.4(2), Li1*-Si1-Si2 143.1(3), Li1*-Si1-Si2′ 94.1(2), Si2-Si1-Si2′ 102.62(2), Si1-Si2-Si3 112.06(2).

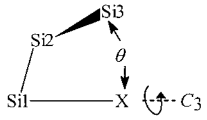
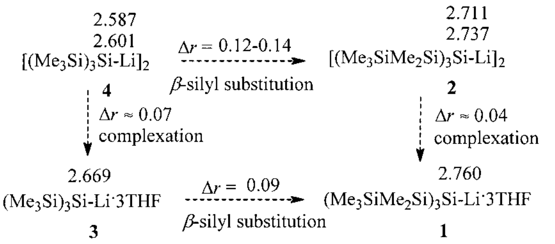


Figure 3. Definition of dihedral angle θ in lithium silanides **1** and **2**; $\theta = \sphericalangle$(X-Si1-Si2-Si3), where the point X is placed along the C_3 axis of the Si_3Si unit.

Comparison of the structures of **1** and **2** with those of the analogous silanides **3**[6b,c] and **4**,[8] which have one Me_2Si group less in each branch, reveals the following (Scheme 2): 1) The Si–Li bond lengths in **1** (2.760 Å) and **2** are 0.09–0.14 Å longer than those in **3** (2.669 Å[6c, 16]) and **4**, respectively. This elongation can be attributed to the



Scheme 2. Changes in the Si–Li bond length [Å] in compounds **1**–**4**.

effect of β-Me_3Si substitution.[17] 2) Comparison of the structures of the dimers **2** and **4** with those of the corresponding THF-complexed **1** and **3**, respectively, shows that complexation by THF elongates the Si–Li bond by 0.02–0.08 Å. This elongation is significantly less than the elongation due to β-Me_3Si substitution.[18]

Calculations (at B3LYP/6-31+G*+ZPE level of theory) for the model anion $[(H_3Si)_3Si]^-$ show that α-H_3Si substituents strongly stabilize silyl anions, that is, by 43.1 kcal mol^{-1} for three α-H_3Si groups relative to three methyl groups [Eq. (1a)]. In $(H_3Si)_3Si$–Li the α-silyl effect is smaller, 19.7 kcal mol^{-1} [Eq. (1b)]. β-H_3Si substituents are also stabilizing, but the effect is about three–five times smaller than for α-H_3Si substitution; that is, three β-H_3Si groups stabilize the silyl anion by 12.1 kcal mol^{-1} [Eq. (2a)] and the silyllithium compound by only 3.9 kcal mol^{-1} [Eq. (2b)]. Thus, stabilization by β-H_3Si groups is about three times larger for silyl anions than for the corresponding silyllithium compounds.[19] The β-H_3Si stabilization of $(H_3SiH_2Si)_3Si$–Li·3H_2O is 9.0 kcal mol^{-1} [Eq. (2c)], a value intermediate between those for the corresponding silyl anion and the noncomplexed silyllithium compound. The contribution of hyperconjugation (between the anionic silicon center and the adjacent β-Si–Si bonds) to the β-silyl stabilization is small. Thus, the Si2–Si3 bond in $[(H_3Si3H_2Si2)_3Si]^-$ (2.364 Å) is only slightly longer than that in $(H_3SiH_2Si)_3SiH$ (2.356 Å). Similarly, in **1** the Si2–Si3 bond (2.352 Å) is even shorter than the Si1–Si2 bond (2.363 Å). We conclude that the stabilization of silyl anions by β-H_3Si groups results mainly from charge polarization and not from hyperconjugation.

$$(H_3Si)_3Si^- + Me_3Si\text{-}H \longrightarrow Me_3Si^- + (H_3Si)_3Si\text{-}H \tag{1a}$$

$$(H_3Si)_3Si\text{-}Li + Me_3Si\text{-}H \longrightarrow Me_3Si\text{-}Li + (H_3Si)_3Si\text{-}H \tag{1b}$$

$$(H_3SiH_2Si)_3Si^- + (MeH_2Si)_3Si\text{-}H \longrightarrow (MeH_2Si)_3Si^- + (H_3SiH_2Si)_3Si\text{-}H \tag{2a}$$

$$(H_3SiH_2Si)_3Si\text{-}Li + (MeH_2Si)_3Si\text{-}H \longrightarrow (MeH_2Si)_3Si\text{-}Li + (H_3SiH_2Si)_3Si\text{-}H \tag{2b}$$

$$(H_3SiH_2Si)_3Si\text{-}Li\cdot 3\,H_2O + (MeH_2Si)_3Si\text{-}H \longrightarrow (MeH_2Si)_3Si\text{-}Li\cdot 3\,H_2O + (H_3SiH_2Si)_3Si\text{-}H \tag{2c}$$

It is tempting to assign the significant elongation of the Si–Li bond in **1** versus that in **3** and that in **2** versus that in **4**, respectively, to electronic interactions between the Si–Li bond and the β-Si–Si bonds. However, quantum-mechanical calculations show that this is not the case. Thus, the calculated Si–Li bond lengths (at B3LYP/6-31+G*) in several relevant model compounds, either complexed or noncomplexed, do not change significantly upon β-H_3Si substitution: r(Si–Li) = 2.460 ($(H_3Si)_3Si$–Li (**8a**)), 2.459 ($(MeH_2Si)_3Si$–Li), 2.468 ($(H_3SiH_2Si)_3Si$–Li (**9a**)), 2.458 ($(Me_3Si)_3Si$–Li), 2.677 ($(H_3Si)_3$-Si–Li·3H_2O (**8b**)), 2.676 ($(MeH_2Si)_3Si$–Li·3H_2O), 2.655 Å ($(H_3SiH_2Si)_3Si$–Li·3H_2O (**9b**)).[20] These calculations show that the β-H_3Si groups play a minor role in controlling the Si–Li bond length (e.g., compare **9a** with **8a** or **9b** with **8b**). Supporting this conclusion is the fact that $(Me_3Si)_3SiMe_2Si$-$Me_2Si(Me_3Si)_2Si$–Li·3THF (**10**), with only one β-Me_3Si substituent, has practically the same Si–Li distance (2.657 Å)[3] as in **3**. We therefore propose that *steric factors*, present in **1** and **2**, but not in the calculated model systems (where methyl is substituted by hydrogen), are responsible for the significant elongation of the Si–Li bond upon β-Me_3Si substitution (Scheme 2). Furthermore, calculations for **9b** show that elongation of the Si–Li bond from 2.655 to 2.760 Å requires only 0.2 kcal mol^{-1}, indicating that even small steric effects or crystal packing forces may cause significant bond elongation.[21a] Steric repulsions are evident in the X-ray structures of **1** and **2**, for example, in **2** between the back-folded β-Me_3Si groups (the methyl ··· methyl distances (C···C 3.861 Å) are somewhat shorter[22] than the sum of their van der Waals radii (4.00 Å)[23]) and in **1** between the OCH_2 groups of the THF ligands and the β-Me_3Si groups (C···C 3.926 Å).

Complexation of the model **8a** and **9a** by three water molecules (producing **8b** and **9b**, respectively) elongates significantly the Si–Li bond length of the monomers, that is, by about 0.2 Å,[20] in contrast to β-H_3Si substitution which has no effect on the Si–Li bond.

What are the effects of β-silyl substitution and complexation by THF on the ionic/covalent character of lithium silanides? The ^{29}Si chemical shift (in toluene) of the formally anionic Si1 atom in **1** is observed at $\delta = -177$, shifted by 12 ppm downfield relative to that of **3** ($\delta = -189$). A similar downfield shift upon β-Me_3Si substitution was observed for $Me_3Si(Me_2Si)_2$–Li ($\delta = -62.7$) relative to Me_3SiMe_2Si–Li ($\delta = -74.9$)[11a] and in **10** ($\delta = -182$)[3] relative to **1**. A downfield shift is usually interpreted as indicating a reduced negative charge. However, as the changes in the chemical shift are relatively small, their interpretation in terms of ionicity is questionable. We have therefore turned to theoretical criteria. In agreement with Klinkhammer[8] we find that all lithium silanides (e. g., **8** and **9**) have strongly ionic silicon–lithium bonds.

However, according to the calculated natural bond order (NBO) charges[24a,b] (MP2/6-31+G*//B3LYP/6-31+G*) there is very little change in the charge on the lithium atom as a result of β-H_3Si substitution (i.e., 0.80–0.83 electrons in both **8a** and **9a**) or on the Li·3H_2O fragment in **8b** or **9b** (0.89–0.90 electrons). However, β-H_3Si substitution does affect the charge distribution within the silanide anion; that is, the charge on the central silicon atom is reduced by about 0.1 electrons in **9a** and **9b** compared to that in **8a** and **8b**, respectively, due to charge polarization to the β-H_3Si groups. Complexation increases the charge on the Li·3H_2O fragment relative to the charge on lithium in the uncomplexed monomers (0.90 electrons versus 0.80–0.83 electrons, respectively). Natural resonance theory (NRT) analysis[24a,c] indicates that the degree of ionicity of the Si–Li bond in **8a** remains essentially unchanged, at 76–81% ionic character, upon elongation of the Si–Li bond from 2.5 to 2.8 Å, suggesting that the observed elongations of the Si–Li distance in **1** versus those in **3** and in **2** versus those in **4** (Scheme 2) do *not* indicate a higher ionic character of the Si–Li bonds in **1** and **2** relative to that in **3** and **4**. Our conclusion is that the ionicity of the Si–Li bond does not change significantly by β-H_3Si substitution but that complexation by THF slightly increases its ionicity.

Preliminary experiments show that the dimers **2** and **4** differ in reactivity from THF-complexed lithium silanides **1** and **3**. Further studies aimed at probing the differences in the chemistry of the four closely related silanides **1**–**4**, as well as attempts to synthesize more complex silanides are in progress.

Experimental Section

All operations were carried out under vacuum using Schlenk techniques.

$(Me_3SiMe_2Si)_3Si{-}Li \cdot 3\,THF$ (**1**): Compound **6** (7.1 g, 5.7 mmol), which was prepared by reaction of **5** (prepared from $HSiCl_3$ and $Me_3SiMe_2Si{-}Li$ in hexane) with tBu_2Hg,[10] was stirred for 48 h with an excess of lithium (7.0 g, 1.0 mol) in THF (in 50 mL). After mercury precipitation was complete the solution was decantated from the metallic residue and evaporated, yielding 4.9 g (7.9 mmol, 69% yield) of crude **1**. Compound **1** was recrystallized from pentane to give white crystals suitable for an X-ray structure determination.

^1H NMR (C_6D_6): $\delta = 0.30$ (s, 27H; $SiMe_3$), 0.55 (s, 18H; $SiMe_2$), 1.33 (m, 12H; CH_2), 3.45 (t, 12H; CH_2O); ^{13}C NMR (C_6D_6): $\delta = 0.02$ ($SiMe_3$), 3.33 ($SiMe_2$), 25.5 (CH_2), 68.5 (CH_2O); ^{29}Si NMR (C_6D_6): $\delta = -176.8$ (Si–Li), -33.8 ($SiMe_2$), -15.8 ($SiMe_3$).

$[(Me_3SiMe_2Si)_3Si{-}Li]_2$ (**2**): Compound **7** (6.4 g (9.4 mmol), which was prepared from **5** (see above)[10] and tBu_2Hg, was stirred in an ultrasonic bath for 48 h with an excess of Li (7.0 g, 1.0 mol) in hexane (50 mL). After mercury precipitation was complete the solution was decantated from the metallic residue and evaporated yielding 2.4 g (2.8 mmol, 60% yield) of crude **2**. Compound **2** was recrystallized from pentane to give white crystals suitable for an X-ray structure determination.

^1H NMR (C_6D_6): $\delta = 0.39$ (s, 27H; $SiMe_3$), 0.55 (s, 18H; $SiMe_2$); ^{13}C NMR (C_6D_6): $\delta = 0.08$ ($SiMe_3$), 2.95 ($SiMe_2$); ^{29}Si NMR (C_6D_6): $\delta = -176.8$ (Si–Li), -33.8 ($SiMe_2$), -15.8 ($SiMe_3$).

Received: February 6, 2001 [Z16569]

---

[1] *Lithium Chemistry* (Eds.: A.-M. Sapse, P. von R. Schleyer), Wiley, New York, **1995**, and references therein.

[2] a) J. Belzner, U. Dehnert in *The Chemistry of Organosilicon Compounds, Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, chap. 14; b) K. Tamao, A. Kawachi, *Adv. Organomet. Chem.* **1995**, *38*, 1; c) P. D. Lickiss, C. M. Smith, *Coord. Chem. Rev.* **1995**, *145*, 75; d) A. Sekiguchi, V. Y. Lee, M. Nanjo, *Coord. Chem. Rev.* **2000**, *210*, 11.

[3] Y. Apeloig, G. Korogodsky, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *Eur. J. Inorg. Chem.* **2000**, 1091.

[4] Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *J. Am. Chem. Soc.* **1996**, *118*, 12228.

[5] H. Gilman, C. L. Smith, *J. Organomet. Chem.* **1967**, *8*, 245.

[6] a) G. Gutekunst, A. G. Brook, *J. Organomet. Chem.* **1982**, *225*, 1; b) A. Heine, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *Inorg. Chem.* **1993**, *32*, 2694; c) H. V. R. Dias, M. M. Olmstead, K. Ruhlandt-Senge, P. P. Power, *J. Organomet. Chem.* **1993**, *462*, 1.

[7] a) G. Becker, H.-M. Hartmann, A. Münch, H. Riffel, *Z. Anorg. Allg. Chem.* **1985**, *530*, 29; b) R. Ficker, W. Hiller, M. Boehringer, G. Becker, *Z. Kristallogr.* **1996**, *211*, 341.

[8] K. W. Klinkhammer, *Chem. Eur. J.* **1997**, *3*, 1418.

[9] Y. Apeloig, M. Yuzefovich, M. Bendikov, D. Bravo-Zhivotovskii, K. Klinkhammer, *Organometallics* **1997**, *16*, 1265.

[10] For full details see: D. Bravo-Zhivotovskii, M. Yuzefovich, M. Bendikov, K. Klinkhammer, Y. Apeloig, *Angew. Chem.* **1999**, *111*, 1169; *Angew. Chem. Int. Ed.* **1999**, *38*, 1100.

[11] For the preparation of simple silyllithium compounds by mercury–lithium exchange, see: a) A. Sekiguchi, M. Nanjo, C. Kabuto, H. Sakurai, *Organometallics* **1995**, *14*, 2630; b) A. Sekiguchi, M. Nanjo, C. Kabuto, H. Sakurai, *Angew. Chem.* **1997**, *109*, 74; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 113.

[12] Crystal structure determinations: **1** ($C_{15}H_{45}LiSi_7 \cdot 3\,C_4H_8O$): crystal dimensions 0.28 × 0.19 × 0.16 mm, Nicolet R3 diffractometer, $Mo_{K\alpha}$ radiation, $T = 180$ K. Cell dimensions $a = b = c = 20.372(3)$ Å, $V = 8455(5)$ Å^3, cubic crystal system, $Z = 8$, $\rho_{calcd} = 1.014\ g\,cm^{-3}$, $\mu = 0.248\ mm^{-1}$, space group $Pa\bar{3}$ (no. 205), data collection of 5615 intensities ($2\Theta_{max} = 45.0°$), 1574 independent ($R_{merg} = 0.066$), 1146 observed ($F_o \geq 4\sigma(F)$), structure solution with statistical methods (Siemens-SHELXS) and refinement on F^2 (Siemens-SHELXTL 5.03) (117 parameters). The hydrogen positions were calculated and refined using the riding model and isotropic displacement parameters (ADPs) for all methyl substituents and the methylene groups of the THF ligands. $R1 = 0.0461$, $wR2$ (all data) $= 0.1379$, $w^{-1} = \sigma^2(F_o^2) + (0.1\,P)^2$, where $P = [(\max F_o^2) + (2F_c^2)]/3$, GOF ($F^2$) $= 0.94$, maximum residual electron density 0.245 e Å^{-3}. Both anion and coordinated lithium cation possess crystallographic C_3 symmetry. **2** ($C_{30}H_{90}Li_2Si_{14}$): crystal dimensions 0.65 × 0.53 × 0.48 mm, Nicolet R3 diffractometer, $Mo_{K\alpha}$ radiation, $T = 125$ K. Cell dimensions $a = b = 18.338(4)$, $c = 14.173(3)$ Å, $V = 4127(1)$ Å^3, hexagonal crystal system, $Z = 3$, $\rho_{calcd} = 1.036\ g\,cm^{-3}$, $\mu = 0.345\ mm^{-1}$, space group $R\bar{3}$ (no. 148), data collection of 6629 intensities ($2\Theta_{max} = 60.0°$), 2659 independent ($R_{merg} = 0.0463$), 2337 observed ($F_o \geq 4\sigma(F)$), structure solution with statistical methods (Siemens-SHELXS) and refinement on F^2 (Siemens-SHELXTL 5.03) (76 parameters). Hydrogen positions were calculated and refined using the riding model and equal isotropic ADPs. $R1 = 0.0348$, $wR2$ (all data) $= 0.0983$, $w^{-1} = \sigma^2(F_o^2) + (0.05P)^2 + 3.9P$, where $P = [(\max F_o^2) + (2F_c^2)]/3$, GOF ($F^2$) $= 1.041$, maximum residual electron density 1.2 e Å^{-3}. The anions show crystallographic C_3 symmetry and are bridged pairwise by two lithium cations, thus forming dimers. The two cations between the anions occupy six major positions which are equally distributed around the C_3 axis. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-408588 (**1**) and CCDC-408587 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1999**, *99*, 1665.

[14] a) All calculations were performed by using the Gaussian 94 program. Gaussian 94 (Revision B.1-E.1), 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, A. G. Baboul, 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, **1995**; b) R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, **1989**; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; d) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; e) W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, Wiley-VCH, Weinheim, **2000**.

[15] Other conformations exist, but they are higher in energy.

[16] An even shorter Si–Li bond of 2.644 Å (average of 2.614 Å and 2.673 Å for two crystallographically independent molecules) was reported for **3**.[6b]

[17] The Li–O bond length in **1** (1.976 Å)is slightly longer than in **3** (av. 1.945 Å[6c]).

[18] In both dimers **2** and **4** the two central silicon and the two lithium atoms form a planar four-membered ring. In **2** the Li ··· Li distance of 2.641 Å is 0.12 Å shorter than that in **4**. The formally negatively charged Si1 atom is more strongly pyramidalized in **2** than in **4**; that is the Si2-Si1-Si2′ bond angles are 102.6° in **2** and 107.5° in **4**. Agostic Li ··· CH interactions are probably responsible for the relatively short Li ··· C4″ distance of 2.70 Å in **2**. These Li ··· C agostic interactions are stronger in **4** (r(Li ··· C) = 2.49 Å).[8]

[19] This factor is 1.4 for alkyllithium compounds. P. von R. Schleyer, J. Chandrasekhar, A. J. Kos, T. Clark, G. W. Spitznagel, *J. Chem. Soc. Chem. Commun.* **1981**, 882.

[20] For $[(H_3SiH_2Si)_3Si{-}Li]_2$ and $[(H_3Si)_3Si{-}Li]_2$ only constrained geometries could be studied as full-geometry optimizations lead to rearrangements (e.g., hydrogen atoms migrate to silicon). Therefore, a comparison of the structures of these model dimers with the corresponding complexed lithium silanides **8b** and **9b**, as shown for **1**–**4** in Scheme 2, was not possible.

[21] a) Another example is the observation that the Si–Li distance in **3**[6b,c,16] and in **4**[8,21b] is elongated by about 0.03–0.10 Å as a function of the crystallographic unit; b) personal communication from Dr. K. W. Klinkhammer.

[22] In **2** the Si1 ··· Si1* distance of 4.766 Å is longer than that in **4** (4.40 Å), which may also indicate steric repulsion between the $(Me_3SiMe_2Si)_3Si$ fragments.[18]

[23] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry—Principles of Structure and Reactivity, 4th ed.*, HarperCollins, New York, **1993**, p. 292.

[24] a) NBO 4.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **1996**; b) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899; c) E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593.

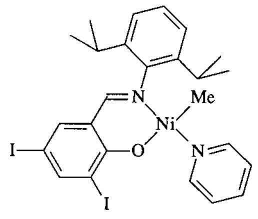
High Molecular Mass Polyethylene Aqueous Latexes by Catalytic Polymerization**

Florian M. Bauers and Stefan Mecking*

Emulsion polymerization of olefinic monomers is one of the most important and also versatile polymerization processes.[1] Polymer latexes are obtained, that is, stable aqueous dispersions of surfactant-stabilized polymer microparticles in the range of 50 to 1000 nm diameter. Numerous applications of latexes (for example, in coatings) involve the formation of films upon evaporation of the dispersing medium, and the environmental friendliness and nonflammability of water is particularly advantageous. To date, polymer latexes are produced by free-radical processes exclusively.[2] Transition metal catalyzed coordination polymerization has received comparatively little attention, as the early transition metal catalysts[3] used commercially for polyolefin production are extremely sensitive to moisture. Carrying out such reactions in water is a highly attractive goal, however, as many polymer microstructures are not available by means other than catalytic polymerization. We[4] and others[5] have recently reported the successful polymerization of ethylene in water by neutral nickel(II) complexes.[6, 7] However, dispersions consisting of low molecular mass material with a degree of polymerization of less than 100 (M_n values typically 1000 g mol^{-1}) were obtained. The formation of higher molecular mass polymers (with chain length considerably above the entanglement limit) is a crucial prerequisite to fully exploit the unique property profile of latexes. At the same time, the complex steps of microparticle formation during polymerization must afford stable dispersions of these high molecular mass polymers.

With complexes $[(\mathrm{X}^\frown\mathrm{O})\mathrm{Ni}^{\mathrm{II}}\mathrm{R}(\mathrm{L})]$, where X = P (type **1**) or X = N (type **2**, $\mathrm{N}^\frown\mathrm{O}$ = salicylaldimine), materials of relatively similar maximum weight-average molecular mass (M_w) are accessible by traditional ethylene polymerization in apolar organic media.[8, 9] By contrast, in water, the latter offer access to polymers with much higher M_w and M_n values than the low molecular weight materials obtained in water with complexes of type **1**.[4b] In regard to particle formation, a comparison with free-radical emulsion polymerization is instructive.[10] In classical emulsion polymerization, water-soluble initiators are used. Chain growth initially affords water-soluble oligomeric radicals, which nucleate particles by collapsing upon themselves after reaching a certain chain length or by entering a surfactant micelle. Similar considerations appear reasonable for the aforementioned emulsion-type catalytic polymerization by a hydrophilically modified water-soluble complex of type **1**, which affords stable latexes of low molecular mass material.[4] However, a certain water-sensitivity[4b, 9c] of salicylaldimine-substituted complexes (type **2**) can be problematic to an analogous approach.

As a different concept to enable formation of a large number of latex particles during polymerization, a very fine dispersion of the catalyst precursor was achieved in the form of a solution of a lipophilic complex (**2a**) in submicron-size compartments of a hydrocarbon solvent, dispersed in the continuous aqueous phase.[14] A mixture of water, surfactant, and a solution of the complex in a small amount of hydrocarbon (toluene and a small portion of hexadecane as a hydrophobic additive[11]) was subjected to high shear, generated either by ultrasound or by means of a modified high-pressure homogenizer. Mini-emulsions consisting of a large number of small hydrophobic droplets (diameter about 100 nm, 10^{16}–10^{17} droplets L^{-1}) containing the catalyst resulted. Exposure of the mini-emulsions to ethylene in a pressure reactor resulted in polymerization to form stable polyethylene latexes



2a

---

[*] Dr. S. Mecking, Dipl.-Chem. F. M. Bauers
Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum der Albert-Ludwigs-Universität Freiburg
Stefan-Meier-Strasse 31, 79104 Freiburg (Germany)
Fax: (+49) 761-203-6319
E-mail: mecking@uni-freiburg.de

[**] This work was supported by BASF AG. F.M.B. thanks the Deutsche Forschungsgemeinschaft for a stipend (Graduiertenkolleg Strukturbildung in makromolekularen Systemen). We thank R. Thomann for TEM analyses, and U. Westphal for skillful assistance with GPC investigations.