

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/244458641>

# Dimerization of the Silole Anion [C<sub>4</sub>Ph<sub>4</sub>SiMe] – to a Tricyclic Diallylic Dianion

ARTICLE *in* ORGANOMETALLICS · JUNE 1997

Impact Factor: 4.13 · DOI: 10.1021/om970177a

---

CITATIONS

20

---

READS

17

5 AUTHORS, INCLUDING:



Honglae Sohn

Chosun University

136 PUBLICATIONS 1,658 CITATIONS

SEE PROFILE



Robert West

University of Wisconsin–Madison

339 PUBLICATIONS 9,317 CITATIONS

SEE PROFILE

# Dimerization of the Silole Anion $[\text{C}_4\text{Ph}_4\text{SiMe}]^-$ to a Tricyclic Diallylic Dianion

Honglae Sohn, Douglas R. Powell, Robert West,\* Jang-Hwan Hong,<sup>†</sup> and Wan-Chul Joo<sup>‡</sup>

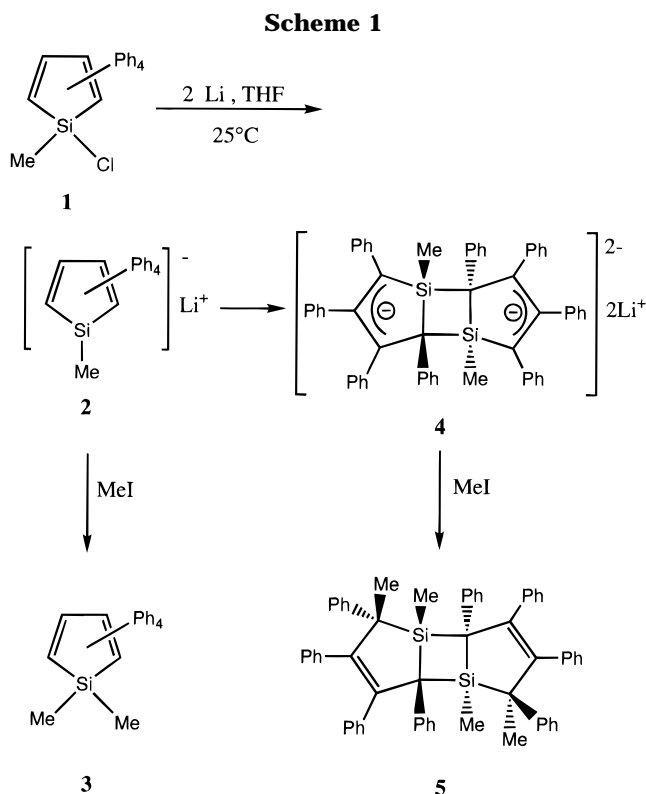
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received March 3, 1997<sup>§</sup>

**Summary:** The head-to-tail dimerization product **4**, whose structure was determined by X-ray crystallography, has been obtained from **2**, the lithium salt of a silole anion. The negative charges in **4** are located in allylic anion moieties having nearly equal C–C distances. Derivatization of **4** with iodomethane takes place stereospecifically to give just 1 of the 14 possible stereoisomers.

A great deal of interest has recently focused on the structures and bonding in anions of siloles and germoles and their possible aromaticity.<sup>1–6</sup> Several X-ray crystal structures of silole and germole dianions have been published, showing that these species are highly delocalized.<sup>4,5b,c</sup> In contrast, localized structures were found for the silole and germole monoanions recently reported by Tilley and co-workers.<sup>7,8</sup> However, a delocalized structure has been proposed for the silole anion,  $[\text{C}_4\text{Ph}_4\text{Si}t\text{-Bu}]^-$ , on the basis of its <sup>13</sup>C and <sup>29</sup>Si NMR spectra.<sup>9</sup>

Here we report the synthesis of the methyltetraphenylsilole anion  $[\text{C}_4\text{Ph}_4\text{SiMe}]^-$  (anion of **2**), its dimerization product, the dianion **4**, and the product of derivatization of the latter with iodomethane, **5** (Scheme 1). The reduction of  $\text{C}_4\text{Ph}_4\text{SiMeCl}$  (**1**)<sup>10</sup> with 2 equiv of lithium in THF gave a dark red solution of the silole **2**. The structure of **2** was shown by immediate quenching with  $\text{CH}_3\text{I}$ , which produced  $\text{C}_4\text{Ph}_4\text{SiMe}_2$  (**3**) in 60% yield.<sup>11</sup> If **2** was allowed to stand in solution at room temperature for 24 h, it slowly dimerized to the diallylic



species **4** (attempts to obtain crystals of **2** for X-ray analysis led invariably to **4**).<sup>13</sup> The sodium salt of the  $[\text{C}_4\text{Ph}_4\text{SiMe}]^-$  anion also dimerizes to the disodium salt of the dianion of **4**.<sup>14</sup>

The X-ray crystal structure of **4** is shown in Figure 1.<sup>15</sup> The dianion sits on a crystallographic center of symmetry. The moderately high *R* factors are due to the displacement disorder of one of four tetrahedrally

\* To whom correspondence should be addressed. Fax: (+608) 262–6143. E-mail: west@chem.wisc.edu.

<sup>†</sup> R&D Center, Samsung Fine Chemicals Co. Ltd., Taejeon 305-380, Korea.

<sup>‡</sup> Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746, Korea.

<sup>§</sup> Abstract published in *Advance ACS Abstracts*, June 1, 1997.

(1) (a) Gordon, M. S.; Boudjouk, P.; Anwar, T. *J. Am. Chem. Soc.* **1983**, *105*, 4972. (b) Damewood, J. R., Jr. *J. Org. Chem.* **1986**, *51*, 5078.

(2) (a) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337. (b) Goldfuss, B.; Schleyer, P. v. R. *Organometallics* **1995**, *14*, 1553. (c) Goldfuss, B.; Schleyer, P. v. R.; Hampel, F. *Organometallics* **1996**, *15*, 1755.

(3) (a) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387. (b) Hong, J.-H.; Boudjouk, P. *Bull. Soc. Chim. Fr.* **1995**, *132*, 495. (c) Hong, J.-H.; Pan, Y.; Boudjouk, P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 186. (d) Hong, J.-H.; Boudjouk, P.; Stoicescu, I. *Organometallics* **1996**, *15*, 2179.

(4) Freeman, W. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882.

(5) (a) Bankwitz, U.; Sohn, H.; Powell, D. R.; West, R. *J. Organomet. Chem.* **1995**, *499*, C7. (b) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Mueller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608. (c) West, R.; Sohn, H.; Bankwitz, U.; Powell, D. R.; Mueller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002.

(6) Dufour, P.; Dubac, J.; Dartiguenave, M.; Dartiguenave, Y. *Organometallics* **1990**, *9*, 3001.

(7) Freeman, W. P.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L.; Gantzel, P. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1887.

(8) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.

(9) Hong, J.-H.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 5883.

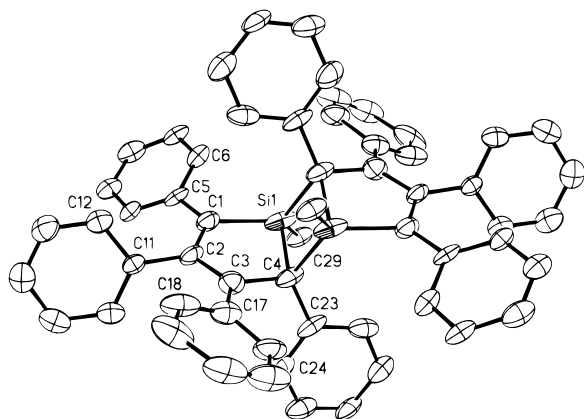
(10) Curtis, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 6011.

(11) (a) Preparation of **2**: A solution of  $\text{Ph}_4\text{C}_4\text{SiMeCl}$  (8.70 g, 20 mmol) in THF (130 mL) was stirred with 2 equiv of Li (0.278 g, 40 mmol) for 12 h at  $-78^\circ\text{C}$  under an argon atmosphere. The color of the solution slowly changed to red-violet. (b) Preparation of **3**: An excess of MeI was slowly added to a solution of **2** (20 mmol) in THF (130 mL) at  $-78^\circ\text{C}$ . The solution was warmed to room temperature and stirred for 2 h. The volatiles were then removed under reduced pressure. The residue was extracted with hexane (200 mL) and filtered. Yellow crystals of **3** were obtained in 60% yield (5.0 g) after the solution was concentrated and cooled to  $-10^\circ\text{C}$ . Mp:  $176\text{--}178^\circ\text{C}$  (lit.<sup>12</sup>  $176\text{--}178^\circ\text{C}$ ). The NMR spectra of **3** agreed with those reported earlier.<sup>12</sup>

(12) Henry, G. K.; Shinimoto, R.; Zhou, Q.; Weber, W. P. *J. Organomet. Chem.* **1988**, *350*, 3.

(13) Characterization of **4**: black crystals, yield 85%, 12.6 g; <sup>1</sup>H NMR (300.133 MHz, THF-*d*<sub>8</sub>)  $\delta$  6.25–7.50 (br m, 40H, Ph), 0.085 (s, 6H,  $-\text{CH}_3$ ). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.36 MHz) in THF-*d*<sub>8</sub>  $\delta$  24.85, solid state  $\delta$  19.3.

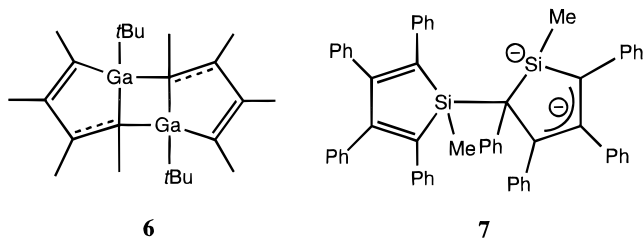
(14) (a) Joo, W. C.; Hong, J. H.; Son, H. E.; Kim, C. H. *Abstracts of IXth International Symposium on Organosilicon Chemistry*; Edinburgh, U.K., July 16–20, 1990; B8. (b) Hong, J.-H. Ph.D. Thesis, Sung Kyun Kwan University, Seoul, Korea, 1989.



**Figure 1.** Thermal ellipsoid diagram of the structure of **4**. Selected bond lengths (pm): Si1–C1, 189.4(12); Si1–C4, 191.8(12); C1–C2, 144(2); C2–C3, 139.5(14); C3–C4, 158(2); Si1–C29, 179.4(10); Si1–C4#, 188.3(11); Si1–Si1#, 259.7(6). Intramolecular angles (deg): C1–Si1–C4, 93.1(5); Si1–C1–C2, 108.4(7); Si1–C4–C3, 102.8(7); C1–C2–C3, 117.9(10); C2–C3–C4, 115.9(10); C4–Si1–C4#, 93.8(5); Si1–C4–Si1#, 86.2(5); C1–Si1–C4#, 119.3(5); C3–C4–Si1#, 107.9(7); C1–Si1–C29, 110.6(5); C4–Si1–C29, 113.7(5); C29–Si1–C4#, 120.8(6).

arranged THF molecules around Li. The dianion adopts a chair conformation, in which the  $C_2Si_2$  and  $C_4Si$  rings are nearly planar, having sums of internal angles 360.0 and 538.1°, respectively. The anionic charges are delocalized over the three ring carbons; the allylic C1–C2 and C2–C3 distances are nearly equal (139.6 and 143 pm). The folding angle between the plane of the four-membered ring and the vector of the C2 bisecting atoms Si1 and C4 of the five-membered ring is 114.8°.

The formation of **4** from **2** is superficially similar to the dimerization of the gallole  $C_4Me_4Ga-t-Bu$ , to give **6**, recently reported by Cowley et al.<sup>16</sup> In **6**, however, there seems to be no allylic delocalization, and this dimer is much less stable than **4**, undergoing dissociation to the monomeric gallole in solution.



**Figure 2.** Thermal ellipsoid diagram of the structure of **5**. Selected bond lengths (pm): Si1–C1, 194.00(14); Si1–C4, 192.40(14); C1–C2, 153.6(2); C2–C3, 134.5(2); C3–C4, 155.3(2); Si1–C29, 186.7(2); C1–C30, 154.4(2); Si1–C4#, 192.22(14); Si1–Si1#, 265.84(7). Intramolecular angles (deg): C1–Si1–C4, 96.72(6); Si1–C1–C2, 101.27(9); Si1–C4–C3, 101.63(9); C1–C2–C3, 120.33(12); C2–C3–C4, 118.96(12); C4–Si1–C4#, 92.55(6); Si1–C4–Si1#, 87.45(6); C1–Si1–C4#, 120.53(6); C3–C4–Si1#, 116.94(10); C1–Si1–C29, 111.72(6); C4–Si1–C29, 119.48(7); C29–Si1–C4#, 113.73(6); Si1–C1–C30, 109.10(10); C2–C1–C30, 109.80(11); C5–C1–C2, 107.94(11).

The dimerization of **2** could take place *via* nucleophilic attack of the negatively charged silicon of one monoanion on the  $\alpha$ -carbon of another, to give **7**, in which one negative charge is stabilized by allylic resonance. Rapid ring closure might then take place to give the doubly stabilized anion of **4**. An alternative mechanism would involve anions of **2** in the planar transition state for inversion; these would have some Si=C double-bond character and so might dimerize by head-to-tail, 2 + 2 cycloaddition, known for silenes.<sup>17</sup> In either case, dimerization does not take place for silole anions in which the silicon substituent is  $SiMe_3$ <sup>8</sup> or *t*-Bu,<sup>9</sup> presumably because these substituents hinder the reaction. Deactivation by dimerization may, however, be anticipated for other silole anions with small groups attached to silicon.

Derivatization of **4** with iodomethane gives, remarkably, a single stereospecific addition product, **5**,<sup>18</sup> among the 14 possible isomers which could result from the combination of two chiral silicon atoms and four different reactive sites in **4**.

The X-ray crystal structure of **5** (Figure 2)<sup>19</sup> shows that both of the added methyl groups are located on the carbon next to the silicon and on the same side of the molecule as the silicon methyl group. **5** also has an inversion center of symmetry. The nonbonded Si–Si distance of **5** is longer than that of **4** by 6.3 pm. The Si–C bond distances, Si–C1 (194.0 pm) and Si–C4

(15) X-ray structure analysis of  $4 \cdot 0.65 C_4H_8O$ :  $(C_{28}H_{23}Si)_2[Li(C_4H_8O)_4] \cdot 0.65 C_4H_8O$ ,  $M_r = 1486.73$ , monoclinic,  $C2/c$ ,  $a = 25.866(10)$  Å,  $b = 16.092(4)$  Å,  $c = 20.303(5)$  Å,  $\beta = 90.85(2)^\circ$ ,  $V = 8450(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcld}} = 1.169$  Mg m<sup>-3</sup>,  $F(000) = 3207$ ,  $\lambda = 1.54178$  Å,  $\Theta = 113(2)$  K. A black single crystal (crystal size  $0.50 \times 0.30 \times 0.30$  mm) was mounted under a coating of Paratone-N. Data were collected by the  $\omega$ -scan method in the range  $3.23^\circ \leq \theta \leq 57.10^\circ$  on a Siemens P4 diffractometer. Of a total of 5858 reflections, 5711 ( $R_{\text{int}} = 0.0644$ ) were independent. The structure was solved by direct methods with the SHELXS-86 program and refined by the full-matrix least-squares method with use of the SHELXL-93 program.  $R(F) = 0.1585$ ;  $R_w(F^2 - \text{all}) = 0.4214$ . The thermal ellipsoids were drawn at the 50% probability level. The Li atom is surrounded by four tetrahedrally arranged THF molecules. One of the Li-bound THF molecules is disordered. The disordered group is modeled with three orientations having occupancies of 0.14(2), 0.46(2), and 0.40(2). Also, there is an unbound THF solvent molecule which only partially occupies a site in the lattice. The occupancy for the unbound THF was refined to 0.646(13).

(16) Cowley, A. H.; Brown, D. S.; Decken, A.; Kamepalli, S. *J. Chem. Soc., Chem. Commun.* **1996**, 2425.

(17) Brook, A. G.; Brook, M. A. *Adv. Organomet. Chem.* **1996**, 39, 71.

(18) Characterization of **5**: colorless transparent crystals, quantitative yield; mp 336–339 °C; <sup>1</sup>H NMR (300.133 MHz, CDCl<sub>3</sub>)  $\delta$  6.70–7.03 (br m, 40H, Ph), 1.65 (s, 6H, –CH<sub>3</sub>), 0.52 (s, 6H, SiCH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75.403 MHz, CDCl<sub>3</sub>)  $\delta$  150.39, 144.25, 143.62, 142.26, 140.61, 140.44, 131.97, 130.99, 130.34, 129.00, 127.34, 127.23, 127.15, 126.24, 125.81, 125.30, 123.26, 47.44, 45.63, 29.25, –2.36; <sup>29</sup>Si{<sup>1</sup>H} NMR (99.36 MHz, CDCl<sub>3</sub>)  $\delta$  21.99; MS (EI)  $m/z$  (%) 828 (21) [M<sup>+</sup>], 798 (6) [M<sup>+</sup> – 2 Me], 414 (35) [M<sup>+</sup>/2]; high-resolution MS calcd for C<sub>60</sub>H<sub>52</sub>Si<sub>2</sub> 828.3607, found 828.3595. Anal. Calcd for C<sub>60</sub>H<sub>52</sub>Si<sub>2</sub>: C, 86.91; H, 6.32. Found: C, 87.00; H, 6.20.

(192.4), of the five-membered ring in **5** are 4.5 and 0.8 pm longer than those in **4**, respectively. Moreover, these distances in **5** are much longer than the corresponding

(19) X-ray structure analysis of **5**:  $\text{C}_{60}\text{H}_{52}\text{Si}_2$ ,  $M_r = 829.20$ , monoclinic,  $\text{P}2_1/n$ ,  $a = 9.5459(2) \text{ \AA}$ ,  $b = 10.0792(2) \text{ \AA}$ ,  $c = 22.7846(3) \text{ \AA}$ ,  $\beta = 93.545(2)^\circ$ ,  $V = 2188.03(7) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.259 \text{ Mg m}^{-3}$ ,  $F(000) = 880$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\Theta = 133(2) \text{ K}$ . A colorless transparent single crystal ( $0.36 \times 0.34 \times 0.18 \text{ mm}$ ) was mounted under a coating of Krytox oil. Intensity data were collected by the  $\psi$  scan method ( $3.04^\circ < \theta < 26.42^\circ$ ) on a Siemens P4 diffractometer equipped with a CCD area detector. From a total of 7212 measured data, 3945 were independent ( $R_{\text{int}} = 0.0164$ ). The structure was solved by direct methods and refined by a full-matrix least-squares method on  $F^2$  using the SHELXTL+ program.  $R(F_o) = 0.0352$ ,  $R_w(F^2\text{-all}) = 0.0889$ ,  $S = 1.046$  for 3945 data and 280 variables. The thermal ellipsoids were drawn at the 50% probability level.

Si–C ( $\alpha$ ) bond distances in  $\text{C}_4\text{Ph}_4\text{SiMe}_2$  (186.8(3) pm)<sup>20</sup> and  $\text{C}_4\text{Ph}_4\text{SiCl}_2$  (182.8(7), 183.6 (10) pm).<sup>2c</sup>

**Acknowledgment.** This research was supported by the National Science Foundation.

**Supporting Information Available:** Tables giving details of the X-ray structure determinations, atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for **4**·0.65 $\text{C}_4\text{H}_8\text{O}$  and **5** (18 pages). Ordering information is given on any current masthead page.

OM970177A

(20) Parkanyi, L. *J. Organomet. Chem.* **1981**, 216, 9.