

Dilithium Derivative of Tetraphenylsilole: An $\eta^1-\eta^5$ Dilithium Structure

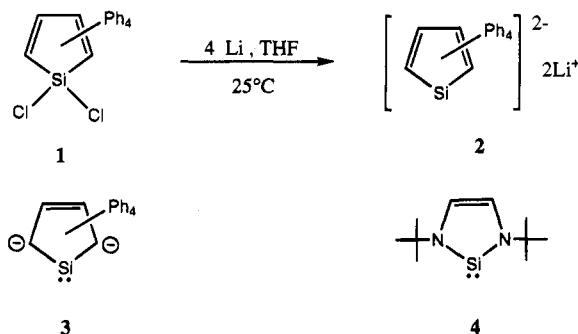
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Recent years have seen renewed interest in the problems of chemical bonding in siloles and silole anions.^{1–6} In 1990 Joo and co-workers reported the conversion of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) to the disodium salt by reaction with sodium metal.⁵ The corresponding dilithium derivative (**2**) was recently reported by Boudjouk et al.^{2b} The ¹³C and ²⁹Si NMR spectra of **2** (in solution) were interpreted in terms of a silole dianion with considerable aromatic delocalization and strong participation of a resonance form with silylene character, **3**. The latter is isolobal with the stable 6 π electron ring silylene **4**.⁷



Here we report the X-ray crystal structure of **2**, crystallized from THF. The structure, shown as a thermal ellipsoid diagram in Figure 1, contains two different lithium atoms. One Li is η^5 -bonded to the silole ring⁸ and also coordinated to two THF molecules; the other is η^1 -bonded to the silicon atom and coordinated to three THF molecules. The silole ring is almost planar, with the Si atom just 11 ppm out of the plane of the four carbon atoms. The C–C distances within the ring are nearly equal, ranging from 142.6 to 144.8 ppm (Figure 1).

This unprecedented structure of **2** is related to that recently proposed for lithium silolide, [(HC)₄SiH]Li, on the basis of MO calculations.³ This predicted structure also has η^5 -lithium bonding and nearly equal C–C distances, as observed for **2**.

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(8) The η^5 -coordination of the lithium is not entirely symmetrical; the lithium is displaced toward the C₁–C₂ bond. See data in Figure 1.

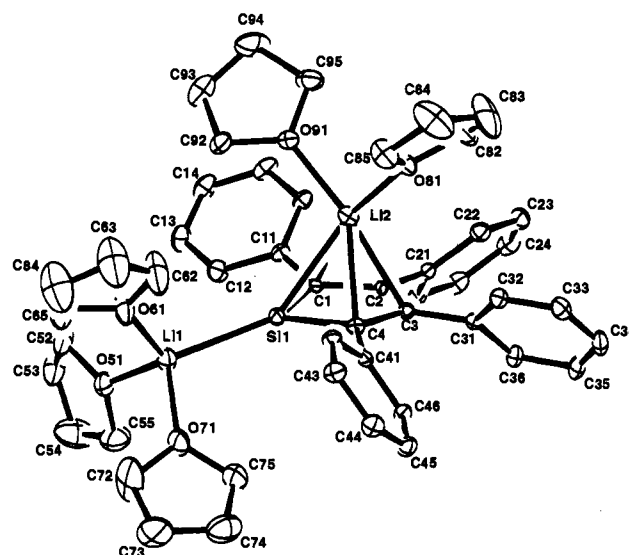


Figure 1. Thermal ellipsoid diagram of structure of **2**. Selected bond lengths, pm: Si–C1, 185.0(3); Si–C2, 184.0(3); Si–Li1, 266.8(6); Si–Li2, 259.7(5); C1–C2, 144.8(4); C2–C3, 143.0(4); C3–C4, 142.6(4); C1–Li2, 231.7(6); C2–Li2, 230.0(7); C3–Li2, 234.9(7); C4–Li2 238.3(7). Intramolecular angles, deg: C1–Si–C4, 88.6(1); C1–Si–Li1, 143.7(2); C1–Si–Li2, 60.0(2); C4–Si–Li1, 126.8(2); C4–Si–Li2, 62.2.

Another example of η^5 bonding of a silole ring to a transition metal has also been reported recently, the complex {Cp*₂Ru(H)[η^5 -Me₄C₄SiSi(SiMe₃)₃]}[BPh₄][–] (**5**).⁹

To aid in understanding the structure of **2**, we carried out calculations on the dilithium salt of the unsubstituted silole **6**, at the Hartree–Fock and the correlated MP2 levels using the 6-31+G* basis set.¹⁰ (Geometrical parameters were optimized at the MP2(fc)/6-31+G* level). Two different dilithio complexes were found to be minima (Figure 2). One of these, **6a**, corresponds closely to the X-ray structure, with one lithium atom bonded to silicon and the other above the plane of the molecule, in close contact to all five ring atoms. The other structure, **6b**, is of C_{2v} symmetry with both lithiums η^5 -coordinated, one above and one below the ring, forming an inverse double-decker sandwich structure. **6a** and **6b** can be described as resulting from the coordination of two lithium cations to a silole dianion **7**. In **6b** the two Li⁺ ions coordinate to the aromatic ring electrons while the second Li⁺ is attached to the in-plane lone pair on silicon. **6b** was calculated to be more stable than **6a** by 21 kcal mol^{–1} (MP2(fc)/6-31+G*/(MP2(fc)/6-31+G*), but of course solvation by THF¹¹ as well as crystal packing forces could reverse this order.

We will concentrate discussion on structure **6a**, which corresponds to the crystal structure of **2**. The calculated C_α–C_β and C_β–C_{β1} distances of 142.0 and 142.6 pm for **6a** are in good agreement with the measured values of **2** (Figure 1). Likewise the Si–C distance and C–Si–C angle correspond closely in the calculated and measured structures. As predicted from the calculations for **6a**, in **2** the η^1 -bound lithium is shifted “up” toward the side of the molecule on which the other, η^5 -lithium is located. The Si–Li vector forms an angle of 9.3° with the mean SiC₄ plane.

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(10) The Gaussian 92 series of programs was used. Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, J.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, Baker, J.; Stewart, J. J. P.; Pople, J. A.; *Gaussian 92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.

(11) This point is under current computational investigation.

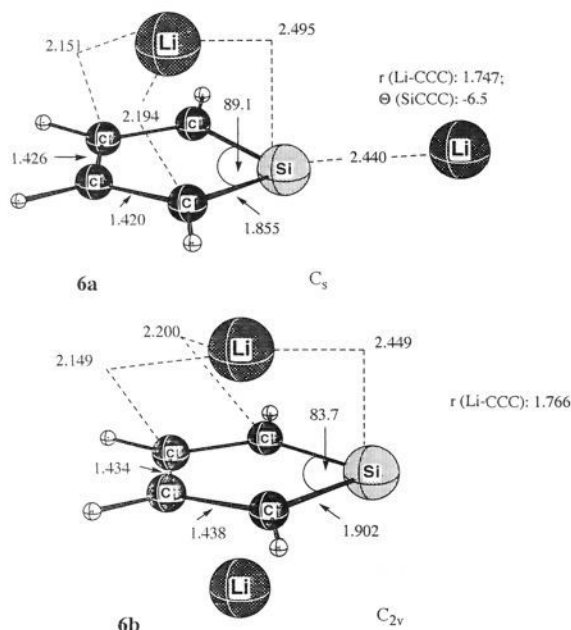


Figure 2. Calculated structures for $\text{Li}_2(\text{CH}_4)\text{Si}$: above, $\eta^1-\eta^5$ structure, **6a**; below, $\eta^5-\eta^5$ structure, **6b**.

The distances involving the lithium atoms are much longer in **2** than in **6a**, as expected because of the THF solvation of the lithium cations in **2**. To learn how these longer distances might affect the structure, **6a** was recalculated with the lithium atoms fixed at the distances corresponding to **2**. The overall structure was unchanged, and the energy was increased by only $2.6 \text{ kcal mol}^{-1}$.

The long Si– Li_1 distance in **2** suggests that the in-plane Si–Li interaction is predominantly ionic. The structure can be interpreted as being composed of an isolated, solvated lithium cation (Li_1) and an anionic complex in which the other lithium is η^5 -coordinated to the silole dianion.

The ^{13}C and ^{29}Si NMR spectra for solid **2** were also investigated. In the ^{13}C NMR spectrum two signals were observed at 68.1 and 69.6 ppm, in a relative ratio of 2:3, assigned

to the α -carbon atoms of the THF molecules. This is consistent with the X-ray structure for **2** and indicates that the crystal chosen for X-ray study was representative of the bulk sample. Two resonances assigned to the β -carbons of the THF molecules were also seen at 25.9 and 26.4 ppm (the peak at 25.9 ppm was the stronger, but an accurate intensity ratio could not be determined).

With the structure for **2** in the solid state established, the possible structure of this compound in solution can be considered. Might it revert to a structure of type **6b**, predicted to be thermodynamically more stable? The isotropic ^{29}Si NMR chemical shift for solid **2**, 87.3 ppm, is distinctly downfield of the solution value, 68.54 ppm. For the α - and β -carbons of silole dianion **2** in solution, Boudjouk et al. report $\delta = 129.71$ and 151.22 .⁶ We find peaks at similar positions in the ^{13}C NMR spectrum of solid **2**, but definite assignments could not be made because many aromatic ring resonances appear in this same region. To provide some further evidence the ^7Li NMR spectrum of **2** was determined in THF solution. A single resonance was observed at $+0.23$ ppm, even at -100 °C. This would be compatible with a single environment for the two lithium atoms in solution, i.e., with a structure like **6b**, but could also result from rapid inter- or intramolecular exchange of the lithium cations between nonequivalent sites as in **6a**. Thus the structure of **2** in solution is still uncertain.¹²

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Supporting Information Available: Details of the crystallographic analysis of **2** (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) Recently we have found that the dilithio derivative of tetraphenylgermole, $(\text{PhC})_4\text{GeLi}_2 \cdot 4\text{dioxane}$, has an $\eta^5-\eta^5$ structure, similar to **6b**. West, R.; Denk, M.; Sohn, H.; Bankwitz, U. *Abstracts of papers*, VIIIth International Conference on the Organometallic Chemistry of Germanium, Tin and Lead, Sendai, Japan, Sept 17–21, 1995, p 24.