

active surfaces, processes not accounted for in the mechanism, are responsible for the additional depletion of  $\text{Si}_2\text{H}_6$ .

Considering the complexity of the reaction and the approximations used in the kinetic treatment we consider (VIII)–(X) to be satisfactory representations of the experimental results. Since they were derived from the mechanism proposed, the extent of the agreement with the experiment provides a measure of the validity of the mechanism in describing the photochemical decomposition of  $\text{Si}_2\text{H}_6$ . It is admittedly only a partial mechanism because it does not in any way account for the formation of the solid deposit of amorphous Si:H.

**3. Formation of Solid.** The solid deposit must be formed by reaction of silicon-containing intermediates at the walls and window of the photolysis cell. The rate constant of (14) is known to be so large (i.e.,  $6.15 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$ )<sup>29</sup> that under our conditions  $\text{SiH}_2$  molecules will not reach the walls in significant amounts before they react in the gas phase. By analogy we assume that this is also true for the other silylene species  $\text{SiH}_3\text{SiH}$  and  $\text{SiH}_3\text{SiH}_2\text{SiH}$ . This leaves the monoradicals  $\text{SiH}_3$  and  $\text{Si}_2\text{H}_5$  as the only silicon-containing transients that can be responsible for the buildup of solid. This conclusion is consistent with those reached in earlier studies of the H-atom-induced decomposition of silanes<sup>30</sup> and of the 147-nm photolysis of  $\text{SiH}_4$ .<sup>15</sup> It is also in accord with the fact that the presence of NO inhibits significantly the formation of the solid deposits.

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## Metal–Silicon Bonded Compounds. 12. Crystal and Molecular Structure of Hexameric Trimethylsilyllithium, $[\text{LiSiMe}_3]_6$

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**Abstract:** The crystal and molecular structure of hexameric trimethylsilyllithium is reported. The structure has been determined from single-crystal X-ray data collected by counter methods and solved by application of the Sayre relationship. Crystals of trimethylsilyllithium are monoclinic with space group  $P2_1/a$  with  $Z = 4$  and cell dimensions of  $a = 13.933$  (3) Å,  $b = 14.078$  (3) Å,  $c = 18.902$  (4) Å, and  $\beta = 89.60$  (2)°. Full-matrix least-squares refinement gave final discrepancy factors of  $R_1 = 0.042$  and  $R_2 = 0.047$  for 1563 data having  $I > 3\sigma(I)$ . The molecular structure consists of discrete centrosymmetric hexameric units with a core of lithium atoms surrounded by trimethylsilyl groups. The geometry of the lithium core can be described in terms of a six-membered ring in a highly folded chair conformation with an acute seat-to-back angle or, alternatively, as a distorted octahedron severely compressed along a threefold axis so as to form a shortened trigonal antiprism. The six side triangular faces of the antiprism each have one long (3.25 (4) Å) and two short (2.72 (2) Å) Li–Li distances. The trimethylsilyl groups lie above these sides and are somewhat more closely associated with the two lithium atoms related by the longest lithium–lithium distance. The two average lithium–silicon distances are 2.65 and 2.77 Å. The bonding is described in terms of four-centered electron-deficient Si–Li bonds with minimal Li–Li or Li–H interactions.

### Introduction

The structures of electron-deficient organometallic compounds are of continuing interest because of their unusual bonding and reactivity. The most complex of these species (excluding those of boron) are represented by the oligomeric derivatives of alkyl lithium compounds. Much of the early work with regard to both the structure of and bonding in these

molecules has been discussed by Brown<sup>1</sup> and recent structural studies have been reviewed by Oliver.<sup>2</sup> Only a limited number of studies have appeared which deal quantitatively with the structures of the simple organolithium species and of the related metalates. These studies include the determination of the crystal structures of methyl lithium,<sup>3,4</sup> ethyllithium,<sup>5</sup> cyclohexyllithium,<sup>6</sup> and bicyclo[1.1.0]butan-1-yl lithium–TMEDA.<sup>7</sup>

Table I. Atomic Coordinates and Anisotropic Thermal Parameters for (LiSiMe<sub>3</sub>)<sub>6</sub><sup>a,b</sup>

atom	x	y	z	atom	x	y	z
Si(1)	-0.0037(2)	0.3591(1)	0.1416(1)	Si(4)	0.6552(2)	0.5227(2)	-0.3690(1)
Si(2)	0.0158(2)	0.3375(1)	-0.1261(1)	Si(5)	0.3471(2)	0.5200(2)	-0.3642(1)
Si(3)	0.2359(2)	0.4479(2)	0.0114(1)	Si(6)	0.4401(2)	0.2706(1)	-0.4781(1)
Li(1)	0.1034(9)	0.5046(9)	-0.0814(6)	Li(4)	0.4921(9)	0.6090(9)	-0.4239(6)
Li(2)	0.0929(9)	0.5164(9)	0.0881(6)	Li(5)	0.5072(9)	0.4173(8)	-0.4072(6)
Li(3)	0.0602(10)	0.3599(8)	0.0090(6)	Li(6)	0.3576(8)	0.4465(9)	-0.4936(5)
C(1)	-0.1353(6)	0.3592(5)	0.1709(4)	C(10)	0.7811(6)	0.5402(5)	-0.4038(4)
C(2)	0.0621(7)	0.3877(6)	0.2256(4)	C(11)	0.6399(6)	0.6250(6)	-0.3039(4)
C(3)	0.0226(6)	0.2280(5)	0.1267(4)	C(12)	0.6652(7)	0.4155(6)	-0.3101(4)
C(4)	0.1116(7)	0.3478(6)	-0.1967(4)	C(13)	0.2159(6)	0.4963(6)	-0.3825(4)
C(5)	0.0358(7)	0.2139(6)	-0.0899(5)	C(14)	0.3483(6)	0.6493(6)	-0.3358(4)
C(6)	-0.1005(7)	0.3251(6)	-0.1762(4)	C(15)	0.3696(6)	0.4548(6)	-0.2788(4)
C(7)	0.2868(7)	0.4907(6)	0.0986(4)	C(16)	0.3087(6)	0.2417(5)	-0.4725(4)
C(8)	0.3231(6)	0.4983(6)	-0.0562(4)	C(17)	0.4898(7)	0.2222(6)	-0.3931(4)
C(9)	0.2657(6)	0.3163(6)	0.0118(4)	C(18)	0.4866(7)	0.1845(7)	-0.5465(5)

atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Si(1)	0.0094(2)	0.0088(2)	0.0033(1)	-0.0002(2)	-0.0003(1)	0.0015(1)
Si(2)	0.0106(2)	0.0082(2)	0.0038(1)	-0.0002(2)	0.0006(1)	-0.0012(1)
Si(3)	0.0067(2)	0.0093(2)	0.0049(1)	0.0008(1)	0.0000(1)	0.0009(1)
Li(1)	0.0098(10)	0.0091(10)	0.0044(5)	-0.0010(9)	-0.0010(6)	0.0018(6)
Li(2)	0.0083(9)	0.0096(10)	0.0047(5)	-0.0004(9)	0.0000(6)	-0.0011(6)
Li(3)	0.0119(11)	0.0075(9)	0.0038(4)	-0.0011(9)	0.0003(6)	0.0009(5)
C(1)	0.0119(8)	0.0114(7)	0.0067(4)	0.0003(6)	0.0027(4)	0.0007(4)
C(2)	0.0180(9)	0.0132(7)	0.0051(3)	-0.0012(7)	-0.0039(4)	0.0021(4)
C(3)	0.0136(8)	0.0096(7)	0.0074(4)	0.0026(6)	0.0007(5)	-0.0001(4)
C(4)	0.0166(9)	0.0144(8)	0.0058(4)	-0.0009(7)	0.0038(5)	-0.0012(4)
C(5)	0.0149(9)	0.0105(7)	0.0096(5)	-0.0007(7)	0.0010(5)	0.0017(5)
C(6)	0.0146(9)	0.0165(9)	0.0075(4)	-0.0017(7)	-0.0029(5)	-0.0004(5)
C(7)	0.0166(9)	0.0177(9)	0.0068(4)	-0.0028(8)	-0.0023(5)	-0.0005(5)
C(8)	0.0140(8)	0.0140(8)	0.0081(4)	0.0002(7)	0.0032(5)	0.0026(5)
C(9)	0.0112(8)	0.0101(6)	0.0103(5)	0.0025(6)	-0.0001(5)	0.0024(4)
Si(4)	0.0091(2)	0.0087(2)	0.0036(1)	-0.0009(1)	-0.0012(1)	-0.0004(1)
Si(5)	0.0091(2)	0.0089(2)	0.0032(1)	0.0001(2)	0.0016(1)	0.0002(1)
Si(6)	0.0090(2)	0.0062(2)	0.0048(1)	-0.0011(1)	0.0005(1)	0.0002(1)
Li(4)	0.0094(11)	0.0081(9)	0.0056(5)	-0.0018(8)	0.0014(6)	0.0002(6)
Li(5)	0.0097(11)	0.0087(10)	0.0046(5)	-0.0008(8)	-0.0024(6)	0.0003(6)
Li(6)	0.0073(9)	0.0111(10)	0.0032(4)	0.0013(8)	-0.0005(5)	-0.0006(5)
C(10)	0.0119(8)	0.0118(7)	0.0076(4)	-0.0013(6)	0.0011(5)	-0.0012(4)
C(11)	0.0129(8)	0.0153(8)	0.0059(4)	0.0009(7)	-0.0016(4)	-0.0038(4)
C(12)	0.0190(10)	0.0127(8)	0.0062(4)	0.0017(7)	0.0015(5)	0.0025(4)
C(13)	0.0119(8)	0.0140(8)	0.0073(4)	-0.0016(7)	-0.0010(4)	0.0002(5)
C(14)	0.0142(8)	0.0112(7)	0.0074(4)	0.0013(6)	0.0004(5)	-0.0020(4)
C(15)	0.0127(8)	0.0184(9)	0.0053(3)	0.0018(7)	0.0017(4)	0.0034(5)
C(16)	0.0112(7)	0.0099(7)	0.0087(4)	-0.0017(6)	0.0008(4)	0.0007(4)
C(17)	0.0180(10)	0.0168(10)	0.0081(5)	0.0013(8)	-0.0024(6)	0.0034(5)
C(18)	0.0136(9)	0.0165(9)	0.0114(6)	0.0013(8)	0.0007(6)	-0.0049(6)

<sup>a</sup> Standard deviations from the variance-covariance matrix are given in parentheses for the least significant digit(s). <sup>b</sup> The form of the anisotropic temperature factor reported here is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

In addition the structures of a number of alkali metal metalates have been reported and are discussed elsewhere.<sup>8</sup>

The bonding in the organolithium derivatives has generally been treated in terms of an interaction between several metal orbitals and an orbital from the bridging carbon atom,<sup>1</sup> following the early model suggested by Rundle<sup>9</sup> for electron-deficient bridge bonds. An alternative suggestion by Craubner<sup>10</sup> makes use of Li-H-C bridge bonds, with a significant role played by the metal-hydrogen interaction. This view has been supported by Stucky,<sup>6,11</sup> who suggests that, in addition to the lithium-carbon multicenter bonding, lithium-hydrogen interactions can make a significant contribution to the bonding and to the stereochemistry in alkyllithium derivatives. Finally, various suggestions have been made with regard to the contribution of Li...Li interactions to the stability of the (LiR)<sub>n</sub> aggregates. The earlier contributions dealing with this form of interaction have been discussed elsewhere<sup>12</sup> but have not clearly resolved this issue.

Compounds containing direct silicon-main group metal bonds have been studied less extensively than have the carbon analogues. The structure of potassium silyl, KSiH<sub>3</sub>, is a sodium chloride-like arrangement with apparently discrete K<sup>+</sup> and SiH<sub>3</sub><sup>-</sup> ions.<sup>13</sup> More recently Gaines and Iorns<sup>14</sup> have reported the insertion of a silicon atom into a carborane cage; this represents the first instance of the formation of an electron-deficient silicon-containing system. Although the inclusion of silicon in the carborane system yields an electron-deficient bond, the ability of many carborane derivatives to incorporate one or more other atoms into the cage suggests that this is not a restrictive test for the ability of an atom or group to enter into electron-deficient bonding.<sup>15</sup>

Our preliminary report<sup>16</sup> of the trimethylsilyllithium hexamer represents the only example in which silicon has been shown to form discrete electron-deficient bonds. We now wish to provide a detailed report on the structure of this compound and discuss the implications of this structure with respect to

Table II. Interatomic Distances and Angles for the Trimethylsilyllithium Hexamers

molecule 1		molecule 2		molecule 1		molecule 2	
atoms	distance, Å	atoms	distance, Å	angle	deg	angle	deg
Li(1)–Li(2)	3.21(2)	Li(6)–Li(5')	3.27(2)	C(1')–Si(1')–Li(1)	67.5(4)	C(13)–Si(5)–Li(6)	79.0(4)
Li(1)–Li(3)	2.72(2)	Li(6)–Li(4')	2.72(2)	C(2')–Si(1')–Li(2')	84.2(3)	C(15)–Si(5)–Li(5)	81.9(3)
Li(1)–Li(2')	2.76(2)	Li(6)–Li(5)	2.69(2)	C(3')–Si(1')–Li(3')	78.6(3)	C(14)–Si(5)–Li(4)	69.9(4)
Li(1)–Li(3')	3.26(2)	Li(6)–Li(4)	3.24(2)	C(2')–Si(1')–C(1')	103.1(4)	C(15)–Si(5)–C(13)	103.7(4)
Li(2)–Li(3)	2.70(2)	Li(5')–Li(4')	2.72(2)	C(2')–Si(1')–C(3')	103.7(4)	C(15)–Si(5)–C(14)	102.9(4)
Li(2)–Li(3')	3.32(2)	Li(5')–Li(4)	3.21(2)	C(1')–Si(1')–C(3')	103.1(4)	C(13)–Si(5)–C(14)	103.4(4)
Li(3')–Si(3')	2.74(1)	Li(4)–Si(4)	2.78(1)	Li(1)–Si(1')–Li(2')	61.1(4)	Li(6)–Si(5)–Li(5)	59.2(3)
Li(3')–Si(1')	2.65(1)	Li(4)–Si(5)	2.62(1)	Li(1)–Si(1')–Li(3')	76.3(4)	Li(6)–Si(5)–Li(4)	75.7(4)
Li(3')–Si(2')	2.65(1)	Li(4)–Si(6')	2.68(1)	Li(2')–Si(1')–Li(3')	59.6(4)	Li(5)–Si(5)–Li(4)	60.6(4)
Li(2')–Si(1')	2.78(1)	Li(5)–Si(5)	2.78(1)	C(4)–Si(2)–Li(1)	80.8(4)	C(16)–Si(6)–Li(6)	78.0(4)
Li(2')–Si(3')	2.64(1)	Li(5)–Si(4)	2.64(1)	C(5)–Si(2)–Li(3)	74.0(4)	C(18)–Si(6)–Li(4')	79.3(4)
Li(2')–Si(2')	2.65(1)	Li(5)–Si(6)	2.64(1)	C(6)–Si(2)–Li(3')	73.6(4)	C(17)–Si(6)–Li(5)	73.4(4)
Li(1)–Si(1')	2.63(1)	Li(6)–Si(4')	2.64(1)	C(4)–Si(2)–C(5)	102.8(4)	C(16)–Si(6)–C(18)	103.3(4)
Li(1)–Si(3)	2.68(1)	Li(6)–Si(5)	2.66(1)	C(4)–Si(2)–C(6)	104.9(4)	C(16)–Si(6)–C(17)	103.7(4)
Li(1)–Si(2)	2.78(1)	Li(6)–Si(6)	2.75(1)	C(5)–Si(2)–C(6)	103.0(4)	C(18)–Si(6)–C(17)	103.1(4)
Li(3')–C(3')	2.94(1)	Li(4)–C(11)	3.08(1)	Li(1)–Si(2)–Li(3)	60.0(3)	Li(6)–Si(6)–Li(4)	60.1(4)
Li(3')–C(5')	2.80(1)	Li(4)–C(14)	2.66(2)	Li(1)–Si(2)–Li(2')	60.8(4)	Li(6)–Si(6)–Li(5)	59.9(3)
Li(3')–C(9')	2.93(2)	Li(4)–C(18')	2.97(2)	C(1')–Si(1')–Li(1)	67.5(4)	C(13)–Si(5)–Li(6)	79.0(4)
Li(2')–C(2)	3.20(1)	Li(5)–C(12)	2.88(1)	C(2')–Si(1')–Li(2')	84.2(3)	C(15)–Si(5)–Li(5)	81.9(3)
Li(2')–C(6)	2.79(1)	Li(5)–C(15)	3.13(2)	C(3')–Si(1')–Li(3')	78.6(3)	C(14)–Si(5)–Li(4)	69.9(4)
Li(2')–C(7')	2.73(2)	Li(5)–C(17)	2.77(1)	C(2')–Si(1')–C(1')	103.1(4)	C(15)–Si(5)–C(13)	103.7(4)
Li(1)–C(1')	2.59(1)	Li(6)–C(10')	2.75(1)	C(2')–Si(1')–C(3')	103.7(4)	C(15)–Si(5)–C(14)	102.9(4)
Li(1)–C(4)	3.10(1)	Li(6)–C(16)	2.99(1)	C(1')–Si(1')–C(3')	103.1(4)	C(13)–Si(5)–C(14)	103.4(4)
Li(1)–C(8)	3.10(1)	Li(6)–C(13)	2.96(1)	Li(1)–Si(1')–Li(2')	61.1(4)	Li(6)–Si(5)–Li(5)	59.2(3)
Si(1')–C(1')	1.912(8)	Si(5)–C(13)	1.893(8)	Li(1)–Si(1')–Li(3')	76.3(4)	Li(6)–Si(5)–Li(4)	75.7(4)
Si(1')–C(2')	1.883(7)	Si(5)–C(15)	1.884(7)	Li(2')–Si(1')–Li(3')	59.6(4)	Li(5)–Si(5)–Li(4)	60.6(4)
Si(1')–C(3')	1.903(7)	Si(5)–C(14)	1.897(8)	C(4)–Si(2)–Li(1)	80.8(4)	C(16)–Si(6)–Li(6)	78.0(4)
Si(2)–C(4)	1.887(8)	Si(6)–C(16)	1.878(8)	C(5)–Si(2)–Li(3)	74.0(4)	C(18)–Si(6)–Li(4')	79.3(4)
Si(2)–C(5)	1.890(8)	Si(6)–C(18)	1.883(9)	C(6)–Si(2)–Li(3')	73.6(4)	C(17)–Si(6)–Li(5)	73.4(4)
Si(2)–C(6)	1.891(8)	Si(6)–C(17)	1.882(8)	C(4)–Si(2)–C(5)	102.8(4)	C(16)–Si(6)–C(18)	103.3(4)
Si(3')–C(7')	1.897(8)	Si(4)–C(12)	1.881(8)	C(4)–Si(2)–C(6)	104.9(4)	C(16)–Si(6)–C(17)	103.7(4)
Si(3')–C(8')	1.895(8)	Si(4)–C(10)	1.885(8)	C(5)–Si(2)–C(6)	103.0(4)	C(18)–Si(6)–C(17)	103.1(4)
Si(3')–C(9')	1.898(8)	Si(4)–C(11)	1.906(7)	Li(1)–Si(2)–Li(3)	60.0(3)	Li(6)–Si(6)–Li(4')	60.1(4)
Li(1)–H(31')	2.39(1)	Li(6)–H(69)	2.76	Li(1)–Si(2)–Li(2')	60.8(4)	Li(6)–Si(6)–Li(5)	59.9(3)
Li(1)–H(33')	2.52	Li(6)–H(67)	2.97				
Li(1)–H(42)	2.92	Li(6)–H(76)	2.92				
Li(1)–H(41)	3.08	Li(6)–H(78)	2.83				

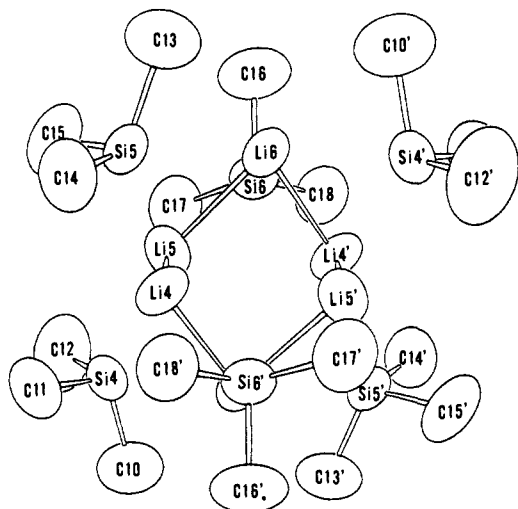
molecule 1		molecule 2		molecule 1		molecule 2	
atoms bonded	distance, Å	atoms bonded	distance, Å	atoms bonded	distance, Å	atoms bonded	distance, Å
Li(1)–H(53)	3.25	Li(6)–H(60')	2.66	Li(1)–H(53)	3.25	Li(6)–H(60')	2.66
Li(1)–H(54)	2.83	Li(6)–H(59')	2.60	Li(1)–H(54)	2.83	Li(6)–H(59')	2.60
Li(2')–H(49')	2.80	Li(5)–H(65)	2.95	Li(2')–H(49')	2.80	Li(5)–H(65)	2.95
Li(2')–H(56')	2.44	Li(5)–H(66)	2.61	Li(2')–H(56')	2.44	Li(5)–H(66)	2.61
Li(2')–H(35')	3.16	Li(5)–H(73)	3.13	Li(2')–H(35')	3.16	Li(5)–H(73)	3.13
Li(2')–H(36')	3.06	Li(5)–H(75)	2.93	Li(2')–H(36')	3.06	Li(5)–H(75)	2.93
Li(2')–H(47)	2.66	Li(5)–H(80)	2.61	Li(2')–H(47)	2.66	Li(5)–H(80)	2.61
Li(2')–H(48)	2.67	Li(5)–H(81)	2.69	Li(2')–H(48)	2.67	Li(5)–H(81)	2.69
Li(3')–H(57')	2.83	Li(4)–H(61)	3.02	Li(3')–H(57')	2.83	Li(4)–H(61)	3.02
Li(3')–H(55')	2.78	Li(4)–H(63)	2.93	Li(3')–H(55')	2.78	Li(4)–H(63)	2.93
Li(3')–H(39')	2.79	Li(4)–H(71)	2.76	Li(3')–H(39')	2.79	Li(4)–H(71)	2.76
Li(3')–H(37')	2.91	Li(4)–H(72)	2.31	Li(3')–H(37')	2.91	Li(4)–H(72)	2.31
Li(3')–H(43)	2.66	Li(4)–H(82')	2.87	Li(3')–H(43)	2.66	Li(4)–H(82')	2.87
Li(3')–H(45)	2.71	Li(4)–H(84')	2.88	Li(3')–H(45)	2.71	Li(4)–H(84')	2.88

the proposed models for bonding in the lithium aggregates and with respect to the participation of silicon and other atoms in electron-deficient bond formation. We shall also consider the effect of hydrogen atoms on the stability and stereochemistry of these electron-deficient structures.

### Experimental Section

Trimethylsilyllithium was prepared by cleavage of bis(trimethylsilyl)mercury as previously described.<sup>17</sup> The crystal for the X-ray structure determination was grown from hot cyclohexane solution and loaded into a thin-walled capillary under argon with the data taken as previously described.<sup>18</sup> Rotation and oscillation photographs and counter data were used to determine the monoclinic space group  $P2_1/a$ .

Lattice constants were obtained by least-squares refinement based on 15 reflections with  $2\theta$  between 15 and 20° centered with Mo  $K\alpha$  radiation (0.710 69 Å) using a programmed centering routine. The unit cell parameters are  $a = 13.933(3)$  Å,  $b = 14.078(3)$  Å,  $c = 18.902(4)$  Å,  $\beta = 89.60(2)^\circ$ ,  $V = 3707.5$  Å<sup>3</sup>,  $\rho(\text{calcd}) = 0.861$  g cm<sup>-3</sup>,  $Z = 4$ ,  $\mu = 2.23$  cm<sup>-1</sup>. The  $\theta$ - $2\theta$  scan technique was used with a scan rate of 2°/min and a scan range from  $2\theta(\text{Mo } K\alpha_1) - 1.0$  to  $2\theta(\text{Mo } K\alpha_2) + 1.0$ . Background counts were taken for one-half the scan time. A total of 3147 reflections were collected to  $\sin \theta/\lambda < 0.45$ . During data collection the intensities of five standard reflections decreased approximately 25%; a stepwise correction was used. Of the 3147 reflections examined, there were 1682 reflections with  $I > 3.0\sigma(I)$ ; 15 weak reflections were symmetry forbidden for the space group  $P2_1/a$  and were removed as were 104 reflections which were related by Laue symmetry, yielding 1563 reflections which were used



**Figure 1.** A perspective view of the  $(\text{LiSiMe}_3)_6$  molecule with the labeling scheme. The atoms are represented by 50% probability thermal ellipsoids. Hydrogen atoms are omitted for sake of clarity.

throughout the solution and refinement of the structure.

**Solution and Refinement of the Structure.** The structure was solved by application of Sayre's method<sup>19</sup> to the 246 reflections for which  $E_H$  was greater than 1.3. The normalized structure factors,  $E_H = (F^2 / \langle F^2 \rangle)^{1/2}$ , where the denominator is a local average in intervals of 0.01 for  $\sin^2 \theta / \lambda^2$ , were calculated with the program NEWES<sup>20</sup> and used as input for a local version of the program REL.<sup>21</sup> The  $E_H$  terms were ordered in decreasing magnitude of the function  $|E_H| \sum_K |E_{H-K}| |E_{H-K}|$  and the first three linearly independent  $E$ 's were fixed in sign in order to determine the origin. The next four reflections were then assigned arbitrary signs and each of the 16 resulting sets of signs was used in an iterative application of Sayre's relationship. The set with the highest consistency index,  $C = 0.888$ , required four cycles of iteration and phased all 246 reflections. The resulting  $E$  map gave the positions of four silicon atoms. Subsequent Fourier syntheses established the remaining nonhydrogen positions.<sup>22</sup> Full-matrix least-squares refinement on  $F$  yielded discrepancy factors:

$$R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\| = 0.080$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.103$$

Hydrogen atoms were assigned ideal positions 0.97 Å from the carbon atoms in expected geometry<sup>23</sup> with the methyl groups staggered with respect to each other. For each assigned hydrogen position a peak was found among the highest peaks on the difference map within 0.2 Å. Full-matrix anisotropic least-squares refinement of nonhydrogen atom parameters, with fixed contributions from the hydrogen atoms with isotropic thermal parameters assigned values 10% higher than that of the heavy atom to which they were attached, yielded final values of  $R_1 = 0.042$ ,  $R_2 = 0.047$ , an error of fit of 1.44, and a residual electron density in the final difference synthesis of 0.14 e/Å<sup>3</sup>. The asymmetric unit was found to contain two independent halves of adjacent  $(\text{LiSiMe}_3)_6$  hexamers located about crystallographic inversion centers. Each molecule possesses  $C_i$ -T crystallographic symmetry and  $D_{3d}-\bar{3}2m$  idealized molecular symmetry.

Atomic coordinates and anisotropic thermal parameters are given in Table I. The bond distances and bond angles for the two molecules present are listed in Table II. A listing of observed and calculated structure factors is available.<sup>24</sup>

**Description of the Structure.** Trimethylsilyllithium hexamer crystallizes as discrete molecular units consisting of six-membered lithium rings in a "folded-chair" conformation with a seat-to-back angle of 70.5°. The molecules have approximately  $D_{3d}$  symmetry with the six smaller faces around the edge of the ring occupied by trimethylsilyl groups while the large faces on the top and bottom of the ring remain open. As initially pointed out,<sup>16</sup> an alternative description of the structure may be given in terms of a distorted octahedron with two opposite faces open.<sup>6</sup> The 12 shortest Li-Li distances fall into two classes of six distances each. The shorter of these two classes has an average value of 2.72 Å and occurs between the lithium atoms adjacent to one another on the edge of the ring. The second class comprises the

lithium atoms meta to each other and has an average value for the distances of 3.25 Å. Each trimethylsilyl group is located 2.06 Å above a plane described by three lithium atoms and displaced from the center of the triangular face so that it lies nearly over the longest edge of the triangle. The lithium-silicon distances average 2.65 and 2.77 Å to the base and apical lithium atoms of the triangular face, respectively. These features are clearly shown in Figures 1-4, which give the labeling scheme, a stereoscopic view of the discrete molecule, a stereoscopic view of the molecular packing, and a partial view showing the location of the trimethylsilyl groups above the triangular face of the lithium atoms. A projection showing the location of the silicon on a triangular face of the lithium atoms is given in the supplementary material.<sup>24</sup>

## Discussion

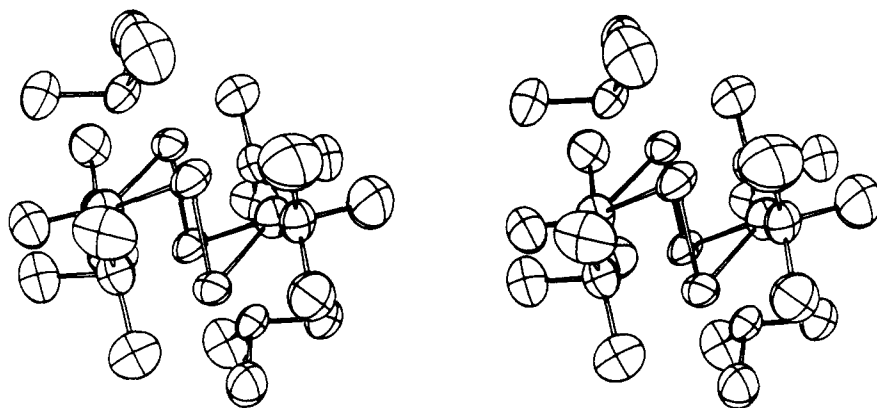
Table III<sup>24</sup> provides a comparison of the Li-Li, Li-C, and Li-Si bond distances and of selected Li-C-Li bond angles for all known structures of alkyl- and silyllithium compounds. Cyclohexyllithium and trimethylsilyllithium have similar hexameric structures; in both cases the 12 shortest Li-Li distances fall into two groups. In the first group the distances for the carbon derivative average 2.40 Å, whereas in the silicon derivative the corresponding average is 2.72 Å ( $\Delta = +0.32$  Å); in the second group the average distances are respectively 2.97 and 3.25 Å ( $\Delta = +0.28$  Å). Thus the substitution of silicon for a carbon leads to an expansion of the lithium core by approximately 0.3 Å. The bridging group 4 atoms in both compounds are located as described above. The two short and one long Li-C or Li-Si bond distances on each face average 2.18 and 2.30 and 2.65 and 2.77 Å for the two compounds, respectively. This is depicted clearly in Figure 5, which shows the projection of the bridging groups onto the triangular lithium faces for the two compounds.

This displacement may be a consequence of minimization of the repulsive interactions at the expense of carbon or silicon bonding to the third lithium atom. An alternative explanation of the bonding focuses on three-centered Li-C-Li bonds with only minimal interaction to the third lithium atom. This might be viewed as the coordination of two trimers, as depicted in Figure 6, with essentially  $sp^2$ -hybridized lithium atoms, leaving a p orbital available which is properly oriented to interact with the carbon or silicon atoms on the second trimeric unit to provide the necessary bonding to lead to the hexameric structure observed. In this description, the  $\text{Me}_3\text{Si}$  units are tipped away from the second trimeric unit to afford better silicon (or carbon) to lithium interaction and to release the strain from repulsion.

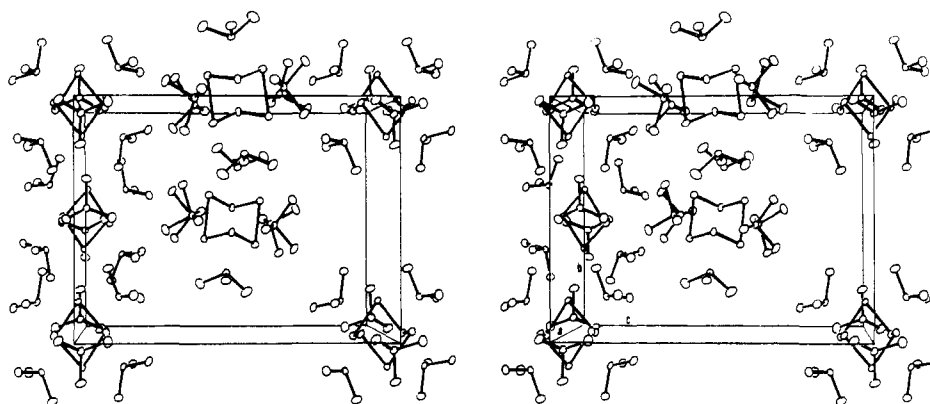
Each of these bonding proposals, the model suggested initially by Brown<sup>25</sup> and the related model suggested by Stucky,<sup>6</sup> have some advantages. In fact each of these suggestions differ primarily in the emphasis placed on different aspects of the same description. Unfortunately none of these provides the answer to the question regarding Li-Li bonding.

The data thus far accumulated suggest that Li-Li interactions are not important in the stability of the lithium aggregates. These data are the Raman studies of Scoval et al.,<sup>26</sup> which suggested minimal contribution to the stability of the compound through Li-Li interactions, the EPR study of Kochi et al.,<sup>27</sup> which shows only coupling to the three adjacent lithium atoms on formation of a radical on the bridging atom, and finally the current studies, along with those of Stucky et al.,<sup>6</sup> which show that the lithium core can be greatly expanded with the structure remaining very similar in nature. This latter feature provides definitive evidence that Li-Li interaction is not essential for aggregate formation, but does not rule out possible Li-Li interaction in selected cases, especially those where the Li-Li distances are substantially less than the observed distance in the  $\text{Li}_2$  molecule.<sup>12</sup>

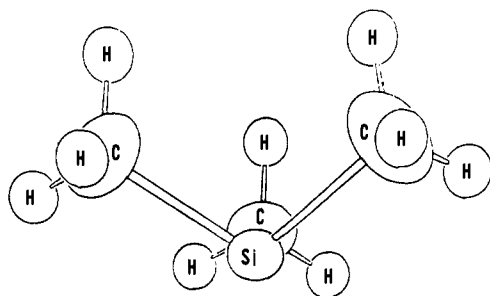
Further we must consider the recurring proposal, first suggested by Craubner,<sup>10</sup> that lithium-hydrogen interactions of



**Figure 2.** A stereoscopic view of the  $(\text{LiSiMe}_3)_6$  molecule with hydrogen atoms omitted. The atoms are represented by 50% probability thermal ellipsoids.

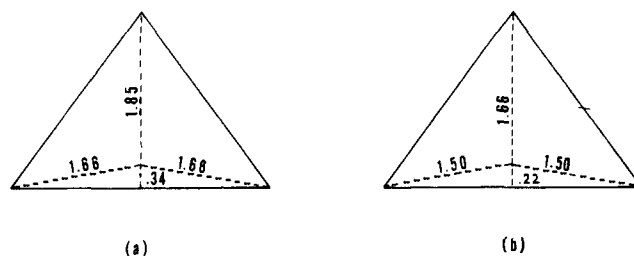


**Figure 3.** A stereoscopic packing diagram for the  $(\text{LiSiMe}_3)_6$  with the atoms represented by 50% probability thermal ellipsoids. Hydrogen atoms are omitted for sake of clarity.



**Figure 4.** A partial view showing the location of the trimethylsilyl groups above the triangular face of the lithium atoms with calculated hydrogen positions included.

the type  $\text{M}-\text{C}-\text{H}-\text{M}$  play a major role in the bonding present within these molecules. Stucky et al.<sup>6,11</sup> have supported this, suggesting that the lithium-hydrogen interactions influence both the structure and stereochemistry of the cyclohexyllithium hexamer and of  $\text{LiBMe}_4$ , while Hooz et al. have suggested a similar interaction in lithium dimesitylborohydride bis(dimethoxyethane).<sup>28</sup> This proposal is based on the short  $\text{Li}-\text{H}$  distances of  $\sim 1.9$ – $2.2$  Å observed in these and in other organolithium derivatives when compared to the  $\text{Li}-\text{H}$  distance



**Figure 5.** Projections showing the relative positions of the bridging silicon (a) and carbon (b) atoms to the three closest lithium atoms in  $(\text{LiSiMe}_3)_6$  and  $(\text{Li}-c\text{-C}_6\text{H}_{11})_6 \cdot 2\text{C}_6\text{H}_6$ . In (a) the  $\text{Li}-\text{Si}$  distances used were 2.65 and 2.77 Å and the  $\text{Li}-\text{Li}$  distances used were 2.72 and 3.25 Å. In (b) the corresponding  $\text{Li}-\text{C}$  and  $\text{Li}-\text{Li}$  distances used were 2.31, 2.18, 2.40, and 2.97 Å.

in  $\text{Li}-\text{H}$  ( $2.043(1)$  Å)<sup>29</sup> and on the shift in the  $\text{C}-\text{H}$  infrared stretching frequencies as well as other physical properties.

In the trimethylsilyllithium hexamer, the shortest calculated hydrogen-lithium atom distance is 2.31 Å, with most values greater than 2.5 Å. These values lie outside of the interaction distances reported in cyclohexyllithium hexamer, indicating that the observed structure is a result of  $\text{Li}-\text{Si}$  multicentered bonding and is not influenced significantly by  $\text{Li}-\text{H}$  interactions. Support for this conclusion has been provided elsewhere<sup>8</sup> and was derived from a consideration of metal-hydrogen distances in species which are known to have bridging hydrogen atoms.

These results imply that the structure of the trimethylsilyllithium hexamer is governed by the metal-silicon bonding interactions and by the repulsive interactions between the substituent groups which are both determined by  $\text{Li}-\text{Si}$  distances and by the orientation and size of the substituent groups.

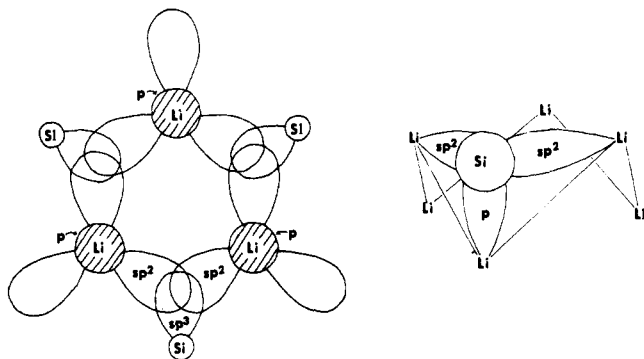


Figure 6. Two views of the trimethylsilyl hexamer depicting the bonding between the bridging silyl group and the lithium atoms.

The marked similarity between this structure and that of cyclohexyllithium hexamer<sup>6</sup> suggests that the metal-hydrogen interactions have little effect on the stereochemistry of these two derivatives, even though Li-H interactions may be present in the cyclohexyl derivative.

The average Li-C distance in a series of organolithium compounds is 2.27 Å (Table SIII<sup>24</sup>) and the corresponding average of all Li-Si distances in trimethylsilyllithium is 2.68 Å. Subtracting the covalent radius of carbon from the average Li-C distance gives an effective radius for lithium of 1.50 Å, whereas from the trimethylsilyl derivative we obtain 1.51 Å. Considering the crudeness of the approximation this suggests that the "effective bonding radius" for lithium in multicentered bonds is 1.5 Å, a value somewhat greater than the radius of lithium observed in Li<sub>2</sub> (1.34 Å); this result is in keeping with the weaker nature of the multicentered interaction.

It appears likely that other silyllithium compounds will have structures similar to that of trimethylsilyllithium in the solid state and in solution and that in the germanium analogues complex structures of a similar nature with Li-Ge distances on the order of 2.7 Å will obtain.

Further work is necessary in the area of the structures of electron-deficient organolithium, silyllithium, and germyllithium compounds to determine the validity of the suggestions proposed, but they do provide a basis from which future studies may be started.

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**Supplementary Material Available:** Listings of observed and calculated structure amplitudes ( $\times 10$ ), the calculated atomic coordinates for the hydrogen atoms, a comparison of the Li-Li, Li-C, and Li-S bond distances and of selected Li-C-Li bond angles (Table SIII), and a projection of the trimethylsilyl group on the triangular face of the lithium atoms (17 pages). Ordering information is given on any current masthead page.

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## Allylation of Quinones with Allyltin Reagents<sup>1</sup>

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**Abstract:** Lewis acid (BF<sub>3</sub>) catalyzed allylation of quinones with allyl- (**2a**), 2-methyl-2-propenyl- (**2b**), *trans*-2-butenyl- (**2c,d**), 3-methyl-2-butenyl- (**2e,f**), and *trans*-cinnamyltrialkyltin (**2g**) gives the corresponding allylhydroquinones with high regioselectivity. Vitamin K<sub>2(5)</sub> (**7**) and coenzyme Q<sub>1</sub> (**9**) were prepared in yields of 78 and 75%, respectively. These reactions appear to proceed through allylquinol intermediates which undergo rearrangement under the influence of BF<sub>3</sub>. The success of this synthesis of vitamin K<sub>2(5)</sub> and coenzyme Q<sub>1</sub> depends on the fact that the reaction of 3-methyl-2-butenyltin with quinones occurs at the  $\alpha$  carbon of the allylic system.

### Introduction

In the past decade there has been considerable interest in the reactions of allyltin compounds<sup>2</sup> because of their marked

reactivity toward electrophiles.<sup>3</sup> However, only a few synthetically useful reactions of allyltin reagents have been reported. Trialkylallyltin reagents are easily prepared without