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Structural Characterization of Two Modifications of Tris(tetrahydrofuran)(tris(trimethylsilyl)silyl)lithium: A Compound with a ^{29}Si–^{7}Li NMR Coupling

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The crystal structures of $(Me_3Si)_4Si{\cdot}THF$ ($a = b = 12.310(1)$ Å, $c = 17.308(2)$ Å, tetragonal, space group $P4/ncc$ (No. 130), $Z = 4$), $[(Me_3Si)_4Si][(Me_3Si)_3SiLi(THF)_3]_2$ ($a = b = 15.146(8)$ Å, $c = 21.338(10)$ Å, trigonal, space group $P\bar{3}c1$ (No. 165), $Z = 2$), $(Me_3Si)_3SiLi(THF)_3$ ($a = b = 31.342(4)$ Å, $c = 22.000(6)$ Å, rhombohedral, space group $R3c$ (No. 161), $Z = 24$), and $(Me_3Si)_3SiSi(SiMe_3)_3{\cdot}THF$ ($a = 11.360(3)$ Å, $b = 17.131(6)$ Å, $c = 18.952(6)$ Å, $\beta = 91.21(3)°$, monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$), have been determined by low-temperature X-ray analysis. Whereas the small Si–Si–Si angle in (tris(trimethylsilyl)silyl)lithium of 102.1° supports the ionic character of the Si–Li bond, there must be at least some covalent contribution leading to a $^1J[^{29}Si,^{7}Li]$ coupling constant of 38.6 Hz. A modified preparation for $(Me_3Si)_3SiLi(THF)_3$ is reported giving the pure product rather than the cocrystallization product $[(Me_3Si)_4Si][(Me_3Si)_3SiLi(THF)_3]_2$, where the starting material is still present in the ratio 1:2. The pure product is far more reactive than the cocrystallized material and is as pyrophoric as ^{t}BuLi powder.

Introduction

(Tris(trimethylsilyl)silyl)lithium is a versatile reagent for the synthesis of a great variety of polysilyl derivatives. This precursor is stable and dissolves well even in nonpolar hydrocarbons when coordinated with THF (tetrahydrofuran) first. Since the development of this ligand by Gilman and Smith,[1,2] it has been used widely in both transition metal chemistry[3–5] and main group chemistry.[5–8] The high steric requirements, along with the good solubility of the products in hydrocarbons and the electron-releasing properties of $-Si(SiMe_3)_3$, make it a very useful ligand. The original 1968 recipe for $(Me_3Si)_3SiLi(THF)_3$ of Gilman and Smith[2] has been modified and optimized by Gutekunst and Brook[9] in 1982, resulting in a cleaner reaction and higher yield. From the integrated NMR signals it was shown that the compound contains three molecules of THF per Li, but no crystal structure data were available. We report in this paper the crystal structures of $(Me_3Si)_4Si$ (**1**), $[(Me_3Si)_4Si][(Me_3Si)_3SiLi(THF)_3]_2$ (**2**), $(Me_3Si)_3SiLi(THF)_3$ (**3**), and $(Me_3Si)_3SiSi(SiMe_3)_3$ (**4**). The ^1J[Si,Li] coupling (observed in both the ^{29}Si and ^{7}Li NMR spectra) shows that the Si–Li bond in **3** is retained in solution.

Results and Discussion

Preparation of 1–4. Compound **1** was prepared in good yield (69%) by the literature method.[1] **2** and **3** were prepared according to eqs 1 and 2, respectively. For the preparation, we employed the published procedure[9] with the minor modification of using the pure methyllithium rather than the methyllithium–lithium bromide complex. It can be seen clearly from eq 1 that the lithiation has not come to completion after 24 h, as 1 equiv of the tetrakis(trimethylsilyl)silane starting material cocrystallizes with 2 equiv of the (tris(trimethylsilyl)silyl)lithium product. After the reaction mixture is stirred for 4 d at room temperature, the metalation reaction is completed and pure product is obtained according to eq 2.[10] **3** is oxidatively coupled by lead dichloride, leading to **4** rather than the expected $Pb[Si(SiMe_3)_3]_2$

$$3Si(SiMe_3)_4 + 2MeLi \xrightarrow[\text{1-d stirring}]{\text{THF}} \underset{\mathbf{2}}{[Si(SiMe_3)_4][(Me_3Si)_3SiLi(THF)_3]_2} + 2Me_4Si \quad (1)$$

$$Si(SiMe_3)_4 + MeLi \xrightarrow[\text{4-d stirring}]{\text{THF}} \underset{\mathbf{3}}{(Me_3Si)_3SiLi(THF)_3} + Me_4Si \quad (2)$$

$$PbCl_2 + 2(Me_3Si)_3SiLi(THF)_3 \xrightarrow[\text{toluene}]{-78\ °C} \underset{\mathbf{4}}{(Me_3Si)_3SiSi(SiMe_3)_3} + 2LiCl + Pb \quad (3)$$

During the preparation of this publication, we learned of a recent report by Geanangel et al.[11] which describes a similar synthesis of **4**.

Crystal Structure of 1. The molecule of tetrakis(trimethylsilyl)silane adopts approximate T_d symmetry (Figure 1), and the basic structural dimensions in the solid state are in good agreement with the electron diffraction study of the molecule[13] (Table I). The $SiMe_3$ groups are staggered as in a molecular gear-wheel, and the whole molecule appears as an almost ideal sphere with an outer shell of hydrogen atoms, followed by a layer of carbon

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Table I. Selected Bond Lengths (Å) and Angles (deg) for **1**–**4**

compound	av Si–C	av Si–Si	av Si–Li	av Si–Si–Si	av Si–Si–Li
$(Me_3Si)_4Si$ (**1**)[a]	1.879(4)	2.346(1)		109.5(1)	
$(Me_3Si)_4Si$ in **2**	1.878(10)	2.334(4)		109.5(2)	
$(Me_3Si)_3SiLi(THF)_3$ in **2**[b]	1.888(5)	2.334(3)	2.674(13)	101.8(1)	116.4(1)
$(Me_3Si)_3SiLi(THF)_3$ (**3**)[c]	1.888(7)	2.330(2)	2.644(12)	102.4(1)	115.8(2)
$(Me_3Si)_3SiSi(SiMe_3)_3$ (**4**)	1.875(3)	2.373(2)[d]		104.8(1)[e]	
		2.390(2)		113.8(1)[f]	

[a] Crystallographic D_2 symmetry. [b] Crystallographic C_3 symmetry. [c] Two independent molecules, one of which has crystallographic C_3 symmetry. [d] Only the Si–Si distances of the trimethylsilyl groups at the periphery of the molecule have been averaged; the second value is the length of the central Si(1)–Si(5) bond. [e] Average $Me_3Si–Si–SiMe_3$. [f] Average $Me_3Si–Si–Si(SiMe_3)_3$.

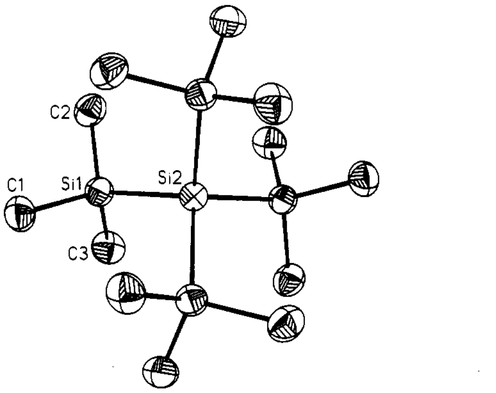

Figure 1. Structure of $(Me_3Si)_4Si$ (**1**) in the solid state. The uncoordinated THF molecule is omitted.

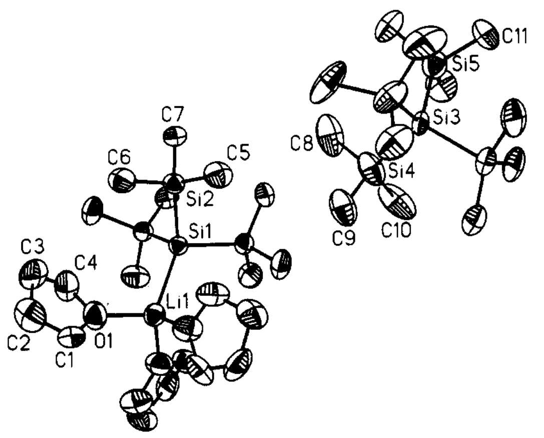

Figure 2. Structure of $[(Me_3Si)_4Si][(Me_3Si)_3SiLi(THF)_3]_2$ (**2**) in the solid state.

atoms and a core of silicon atoms. The Si–Si bond of 2.346(1) Å and the average Si–C bond of 1.879(4) Å are slightly shorter than those in the gas phase (2.361(3) and 1.889(3) Å).[13] A librational correction increased the Si–Si distances by 0.004 Å and Si–C by about 0.003 Å.

Crystal Structures of 2 and 3. In **2**, 1 equiv of tetrakis(trimethylsilyl)silane cocrystallizes with 2 equiv of (tris(trimethylsilyl)silyl)lithium (Figure 2). The structures of the two components of **2** are almost identical to those of the same compounds crystallized independently as **1** and **3**. The lithiation has almost no influence on the Si–C and the Si–Si bond lengths (Table I). The average Si–Li bond length of 2.66 Å is consistent with the three other Si–Li bonds reported for molecular structures (2.63 Å in $(Me_3Si)_3SiLi·1.5DME$,[14] DME = $MeOCH_2CH_2OMe$; 2.70 Å in $Me_3SiLi·1.5 TMEDA$,[15] TMEDA = $Me_2NCH_2CH_2NMe_2$; 2.65 Å in $[Me_3SiLi]_6$).[16] The parameter most affected by replacing a $SiMe_3$ group with $Li(THF)_3$ is the Si–Si–Si angle. It is reduced from the ideal tetrahedral value of 109.5° in **1** to a mean value of 102.1° in **2** and **3**. The bulk of the $Li(THF)_3$ group alone is not sufficient to account for this reduction, because in the even more sterically crowded $(Me_3Si)_3SiSi(SiMe_3)_3$ (**4**) the average $Me_3Si–Si–SiMe_3$ angle is reduced only to 104.8° (Table I).

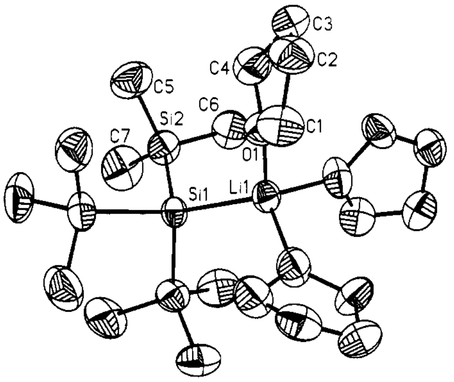

Figure 3. Structure of $(Me_3Si)_3SiLi(THF)_3$ (**3**) in the solid state.

The nature of the Si–metal bond might have an influence on the Si–Si–Si angle of the ligand. The difference in electronegativity between silicon and lithium is about 0.9, whereas it is 0.3 between (for example) silicon and aluminum and 0.0 between silicon and copper. That means that the bond between silicon and lithium is much more ionic than Si–Al or Si–Cu and is closer to the extreme description $(Me_3Si)_3Si^{-}\ {}^{+}Li(THF)_3$. The Si–Si–Si angles of 101.8° in **2**, 102.4° in **3**, and 104.0° in $(Me_3Si)_3SiLi·1.5DME$[14] indicate that the lone pair in this resonance extreme is stereochemically active. The Si–Si–Si angles of 107.5° [17] in $(Me_3Si)_3SiAlPh_2(THF)$ and 110.0° [18] in both $[Li(THF)_4][Cl_3AlSi(SiMe_3)_3]$ and $[Li(THF)_4][Cu_5Cl_4\{Si(SiMe_3)_3\}_2]$ also show a correlation between Si–Si–Si angle and M–Si electronegativity difference. This thesis is supported by the ^{29}Si NMR chemical shift of the central silicon atom. In **3** this shift is −189.4 ppm (Figure 4), in **4** it is −130.04 ppm, and in $[Li(THF)_4][Cl_3AlSi(SiMe_3)_3]$[18] it is −115.66 ppm, indicating that the electron density at silicon decreases as the Si–Si–Si angle increases.

Crystals of **2** decompose rapidly and exothermally when exposed to air,[9] but **3** is orders of magnitude more reactive. On exposure to air, it catches fire instantaneously, and it is comparable in reactivity to ${}^{t}BuLi$ powder. We are convinced that the accidental use of the cocrystallized material **2** instead of the pure material **3** is one of the reasons for the not very clean reactions which have been reported with (tris(trimethylsilyl)silyl)lithium. Both materials crystallize very well from pentane as white powders.

NMR Studies of 3. Although we pointed out earlier that the Si–Li bond is polar, there must be a significant covalent contribution, since we observe a $^{1}J[^{29}Si,^{7}Li]$ NMR coupling in both the ^{29}Si and the ^{7}Li NMR spectra (Figure 4). The

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Table II. Crystal Data for **1**–**4**

	1	**2**	**3**	**4**
formula	$C_{12}H_{36}Si_5 + C_4H_8O$	$C_{54}H_{138}Li_2O_6Si_{13}$	$C_{21}H_{51}LiO_3Si_4$	$C_{18}H_{54}Si_8 + C_4H_8O$
formula weight	392.96	1262.69	470.92	567.44
space group	*P*4/*ncc* (No. 130)	$P\bar{3}c1$ (No. 165)	*R*3*c* (No. 161)	$P2_1/c$ (No. 14)
a, Å	12.310(1)	15.146(8)	31.342(4)	11.360(3)
b, Å	12.310(1)	15.146(8)	31.342(4)	17.131(6)
c, Å	17.308(2)	21.338(10)	22.000(6)	18.952(6)
α, deg	90	90	90	90
β, deg	90	90	90	91.21(3)
γ, deg	90	120	120	90
V, Å^3	2623	4239	18716	3687
Z	4	2	24	4
ρ_{calc}, Mg m^{-3}	0.995	0.989	1.003	1.022
μ, mm^{-1}	0.274	0.233	0.207	0.299
2θ range, deg	8–55	8–49	8–50	8–45
no. of reflns measd	2560	4752	7262	5197
no. of unique reflns	1507	2342	7246	4883
no. of reflns used	1506	2224	7244	4879
no. of restraints	60	54	1177	522
$R_2{}^a$ (all data)	0.153	0.195	0.168	0.090
$R_1{}^a$ $F > 4\sigma(F)$)	0.054	0.068	0.063	0.033
g_1	0.043	0.067	0.080	0.041
g_2	1.69	5.81	33.43	2.78
no. of refined params	88	182	523	388

[a] $R_2 = (\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4)^{1/2}$; $R_1 = \sum|F_o - F_c|/\sum F_o$.

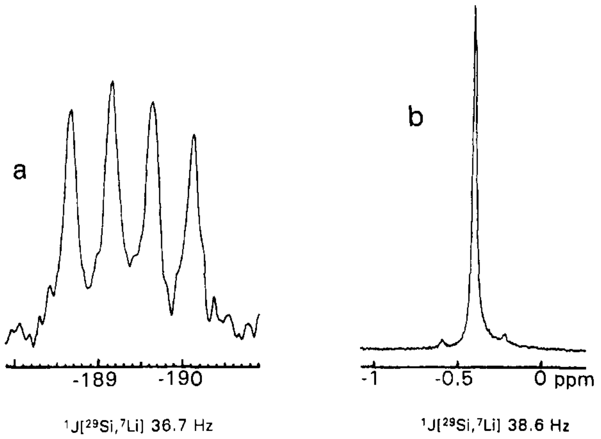

Figure 4. NMR spectra of **3**: (a) ^{29}Si NMR showing the chemical shift (δ –189.4) of the central silicon atom with the $^1J[^{29}Si,^7Li]$ coupling constant of 38.6 Hz; (b) ^{7}Li NMR at –50 °C depicting the chemical shift of 0.38 with the $^1J[^{29}Si,^7Li]$ coupling constant of 36.7 Hz.

$^1J[^{29}Si,^7Li]$ coupling constant for **3** is 38.6 Hz in the ^{29}Si NMR spectrum at room temperature and 36.7 Hz in the ^{7}Li NMR spectrum at –50 °C. Edlund, Buncel, et al.[19,20] detected a $^1J[^{29}Si,^7Li]$ coupling of 51 Hz for $PhMe_2SiLi$ in THF at –100 °C. These values are of similar magnitude to the $^1J[^{19}F,^7Li]$ couplings which we reported previously.[21] The question of whether organolithium compounds are essentially ionic, covalent, or intermediate has been vigorously debated,[22] and similar considerations clearly apply to silyllithium derivatives.

Crystal Structure of 4. Although the structure of hexakis(trimethylsilyl)disilane has been determined by other workers,[11,12] the previously reported structure was relatively imprecise[11] and was determined for a different modification (i.e. different space group and lattice solvent; Table II). The Si–Si bond (2.373 Å) in **4** is on average 0.04 Å longer than those in **1**–**3**. The central Si(1)–Si(5) bond is elongated by 0.06 to 2.390 Å (Figure 5, Table I), and the Me_3Si–Si–Si$(SiMe_3)_3$ angle across the central bond is 9° larger (113.8°) than the Me_3Si–Si–$SiMe_3$ angle (104.8°), indicating appreciable steric strain in the disilane. The mean gauche Si–Si–Si–Si torsion angles (+77.2 and –42.8°) differ substantially from the ideal values of ±60° expected for a strain-free eclipsed conformation.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

	x	*y*	*z*	*U*(eq)^a
Si(2)	7500	2500	2500	32.5(5)
Si(1)	5943.6(6)	2498.4(10)	3282.4(4)	37.3(5)
C(1)	6106(3)	3484(3)	4105(2)	50(2)
C(2)	4717(3)	2900(3)	2703(2)	48(2)
C(3)	5708(3)	1110(3)	3698(2)	50(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2**

	x	*y*	*z*	*U*(eq)^a
Li(1)	6667	3333	–61(6)	50(4)
O(1)	7277(3)	2587(3)	–437(2)	73(2)
C(1)	7812(17)	2720(20)	–1013(6)	80(13)
C(2)	8414(17)	2239(21)	–972(10)	93(11)
C(3)	8290(17)	1856(20)	–273(12)	84(12)
C(4)	7384(17)	1850(17)	–64(9)	77(11)
Si(1)	6667	3333	1192.8(9)	40.4(7)
Si(2)	5951.2(10)	4209.7(10)	1678.3(5)	47.4(9)
C(5)	4512(4)	3497(5)	1647(3)	74(3)
C(6)	6365(5)	5453(4)	1262(2)	76(5)
C(7)	6272(4)	4562(4)	2532(2)	59(3)
Si(3)	0	0	2611(3)	42.4(10)
Si(4)	1580(2)	319(3)	2246(2)	83(2)
C(8)	2592(13)	1371(13)	2734(13)	117(8)
C(9)	1776(9)	747(13)	1405(5)	94(7)
C(10)	1728(18)	–837(12)	2282(13)	118(20)
Si(5)	0	0	3708(2)	71(2)
C(11)	–1343(7)	–611(11)	4008(7)	95(8)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Refinement of Severely Disordered Structures. All four structure refinements were complicated by disorder. Residual electron density around the 4-fold axis in the crystals of **1** could

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Table V. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for **3**

	x	*y*	*z*	*U*(eq)[a]
Li(1)	6667	3333	5281(6)	48(5)
O(1)	6203.1(14)	3486.3(13)	5677.0(15)	68(2)
C(1)	5856(4)	3227(3)	6146(4)	72(5)
C(2)	5718(3)	3566(3)	6420(4)	71(5)
C(3)	6078(4)	4068(3)	6154(4)	70(5)
C(4)	6224(4)	3949(3)	5571(4)	75(6)
Si(1)	6667	3333	4093.0(10)	45.1(8)
Si(2)	7036.0(6)	4104.0(6)	3632.3(8)	65.8(11)
C(5)	6605(3)	4364(3)	3645(3)	97(6)
C(6)	7611(2)	4558(2)	4058(3)	88(4)
C(7)	7238(3)	4153(3)	2812(3)	107(6)
Li(2)	8949(3)	6782(3)	407(4)	60(6)
O(2)	9664.9(13)	7078.4(13)	531(2)	73(2)
C(8)	9927(4)	6825(4)	385(7)	81(3)
C(9)	10422(3)	7118(6)	627(7)	95(3)
C(10)	10419(3)	7509(6)	1022(7)	94(3)
C(11)	9920(4)	7425(4)	1009(5)	81(4)
O(3)	8889.8(12)	7274.8(14)	−42(2)	81(2)
C(12)	9297(3)	7739(5)	−237(9)	71(3)
C(13)	9107(4)	7885(5)	−757(7)	75(4)
C(14)	8561(3)	7651(5)	−640(7)	85(4)
C(15)	8441(2)	7280(4)	−174(6)	88(3)
O(4)	8871(6)	6276(4)	−169(6)	83(7)
C(16)	8966(7)	6302(3)	−805(7)	107(8)
C(17)	8721(6)	5801(4)	−1040(4)	104(8)
C(18)	8380(5)	5486(4)	−525(5)	105(8)
C(19)	8630(6)	5771(5)	26(4)	84(7)
Si(3)	8380.9(5)	6431.8(5)	1394.7(6)	45.0(7)
Si(4)	7528.2(5)	6019.4(5)	1262.2(7)	54.3(7)
C(20)	7128(2)	5661(3)	1923(3)	83(3)
C(21)	7345(2)	5566(2)	620(3)	71(3)
C(22)	7307(2)	6460(2)	1039(3)	71(3)
Si(5)	8512.1(6)	7074.1(6)	2045.9(7)	63.2(9)
C(23)	8025(3)	6969(3)	2611(3)	98(4)
C(24)	8603(3)	7614(2)	1569(3)	94(6)
C(25)	9097(2)	7300(3)	2505(3)	85(4)
Si(6)	8490.8(6)	5904.4(6)	2037.9(8)	61.7(8)
C(26)	9170(2)	6126(3)	2135(3)	87(4)
C(27)	8229(3)	5810(3)	2832(3)	96(5)
C(28)	8212(3)	5264(2)	1703(3)	92(5)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

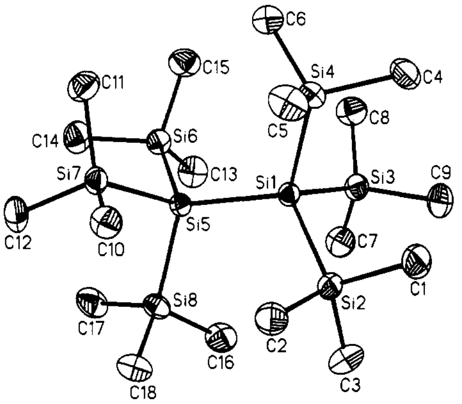

Figure 5. Structure of $(Me_3Si)_3SiSi(SiMe_3)_3$ (**4**) in the solid state. The uncoordinated THF molecule is omitted.

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for **4**

	x	*y*	*z*	*U*(eq)[a]
Si(1)	8077.2(5)	9016.3(3)	1893.0(3)	22.8(3)
Si(2)	10144.1(5)	8807.9(4)	1865.6(4)	29.1(3)
Si(3)	7657.3(6)	9998.1(4)	1036.9(4)	31.2(4)
Si(4)	7797.6(6)	9645.6(4)	2994.5(3)	27.9(4)
Si(5)	6937.3(5)	7852.9(3)	1747.2(3)	22.1(3)
Si(6)	4935.1(5)	8093.6(4)	1447.7(4)	30.1(3)
Si(7)	6899.1(6)	7035.5(4)	2752.8(3)	27.3(4)
Si(8)	7630.0(6)	7038.6(4)	835.1(3)	30.7(4)
C(1)	10922(2)	9684(2)	2239(2)	45.5(14)
C(2)	10688(2)	7954(2)	2392.7(15)	41.4(14)
C(3)	10683(2)	8666(2)	946.1(15)	47.1(15)
C(4)	8293(2)	10691.4(15)	2957.7(14)	40(2)
C(5)	8685(3)	9153(2)	3712.0(14)	44(2)
C(6)	6235(2)	9676(2)	3292.5(14)	40.9(15)
C(7)	7555(3)	9646(2)	100.4(14)	45(2)
C(8)	6235(2)	10505(2)	1233.4(15)	44(2)
C(9)	8843(3)	10761(2)	1044(2)	46(2)
C(10)	8380(2)	6873.0(15)	3179.5(13)	35.1(15)
C(11)	5875(2)	7407(2)	3440.2(14)	41(2)
C(12)	6351(2)	6042.7(14)	2481(2)	43(2)
C(13)	4741(2)	8412(2)	505.8(14)	46(2)
C(14)	4018(2)	7193(2)	1564(2)	46.5(14)
C(15)	4240(2)	8855(2)	2005(2)	46.2(14)
C(16)	8108(3)	7613(2)	53.4(13)	45(2)
C(17)	6446(3)	6353(2)	504(2)	48(2)
C(18)	8912(2)	6425(2)	1136.8(4)	43(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

be identified as a disordered THF molecule, but it was impossible to distinguish between possible O and C atoms. Because of the 4-fold symmetry, we refined one five-membered ring of carbon atoms with occupancies set to 0.25. All 1–2 and 1–3 distances were restrained to be respectively equal. To enable anisotropic refinement, we used rigid bond restraints[23–25] together with weak restraints to make the corresponding U_{ij} components of neighboring atoms similar. There were similar problems with disordered THF on a general position in structure **4**. Here we refined three five-membered rings of carbon atoms with occupancies of $^1/_3$ and applied the above restraints. In structures **2** and **3**, the coordinated THF molecules were disordered. The carbon atoms occupy two and, in one case, even three positions. Here we applied similarity restraints for all chemically equivalent 1–2 and 1–3 distances. For the anisotropic displacement parameters we used only the rigid bond restraints. The tetrakis(trimethylsilyl)silane in structure **2** lies on a position of crystallographic D_3 symmetry but has only 3-fold molecular symmetry, so the central atom (Si(3)) lies on the 3-fold axis close to the D_3 position at 0, 0, $^1/_4$, and Si(5) also lies on the 3-fold axis, but the molecule is disordered with respect to the 2-fold axes. To stabilize the refinement we used similarity restraints for the 1–2 and 1–3 Si–Si distances and for the 1–2 Si–C distances. We also tried refinement in the lower symmetry space group $P\bar{3}$, but the same disorder appeared and the refinement was less stable.

In our experience, the careful application of chemically meaningful restraints to disordered groups and solvent considerably improves the precision of the rest of the structure. The estimated standard deviations are much lower and at the same time the residual electron density is more informative, because residual features cannot be simply "mopped up" by the refinement of an excessive number of arbitrary parameters.[26] This is underlined by a comparison of our structure determination of **4** to that quoted above.[11]

Conclusion. On the one hand, the relatively small Si–Si–Si angles in **2** and **3** support the ionic character of the Si–Li bond, and on the other hand, the ^1J[Si,Li] coupling of **3** requires at least some covalency. In the disilane **4** steric factors also appear to be important.

Experimental Section

All manipulations were performed under an inert atmosphere of dry argon gas with Schlenk techniques or in an argon glovebox. The toluene, *n*-hexane, and THF solvents were dried over Na/K alloy and distilled prior to use.

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NMR spectra were obtained with a Bruker MSL 400 instrument. All NMR spectra were recorded in toluene-d_8 or benzene-d_6 with $SiMe_4$ or LiCl external reference.

Warning! **3** is extremely pyrophoric and should be handled in small amounts under dry inert gas atmosphere.

$(Me_3Si)_4Si$ (1). Tetrakis(trimethysilyl)silane was prepared according to the published procedure of Gilman and Smith.[1]

$[(Me_3Si)_4Si][(Me_3Si)_3SiLi(THF)_3]_2$ (2). To a solution of 30.85 g of $(Me_3Si)_4Si$ (96.4 mmol) in 400 mL of THF was added a slight excess of MeLi (69 mL; 108.8 mmol) in diethyl ether over a period of 2 h. First a pale yellow and later an orange solution was obtained. After 1 d of stirring at room temperature, the THF was condensed off and the yellow precipitate redissolved in 60 mL of diethyl ether. The product was obtained by crystallization from that solution at −18 °C as a white powder. Yield: 25.5 g (63%). X-ray-suitable crystals have also been grown from diethyl ether solution. NMR: ^1H (C_7D_8) δ 0.242 [$(Me_3Si)_3SiLi$], 0.258 [$(Me_3Si)_4Si$] (ratio 2:1); ^{29}Si (C_7H_8/C_6D_6) δ −5.21 [$(Me_3Si)_3SiLi$], −9.81 [$(Me_3\mathit{Si})_4Si$], −135.48 [$(Me_3Si)_4\mathit{Si}$], −189.4 [$(Me_3Si)_3\mathit{Si}Li$].

$(Me_3Si)_3SiLi(THF)_3$ (3). 100 mL of MeLi (160 mmol) in diethyl ether was added over a period of 3 h to a solution of 50 g of $(Me_3Si)_4Si$ (156.3 mmol) in 800 mL of THF. Approximately a quarter of the solvent was removed in vacuum, and the reaction mixture was stirred for 4 d at room temperature. The solvent was totally removed and the solid precipitate redissolved in diethyl ether. The product was crystallized from diethyl ether at −18 °C and recrystallized twice from *n*-hexane. Yield: 32.33 g (44%). X-ray-suitable crystals have also been grown from *n*-hexane. $(Me_3Si)_3SiLi(THF)_3$ was isolated as a white powder. NMR: ^1H (C_7D_8) δ 0.242 [Me_3Si], 1.458, 3.560 [THF]; ^{29}Si (C_7H_8/C_6D_6) δ −5.21 [$(Me_3Si)_3Si$], −189.4 [$(Me_3Si)_3\mathit{Si}$], $^1J[Si,Li] = 38.6$ Hz; ^7Li (C_7D_8, $T = -50$ °C) δ 0.38; $^1J[Si,Li] = 36.7$ Hz.

$(Me_3Si)_3SiSi(SiMe_3)_3$ (4). To 0.73 g of $PbCl_2$ (2.62 mmol) in 20 mL of toluene was added a solution of 2.46 g (5.24 mmol) of $(Me_3Si)_3SiLi(THF)_3$ in 20 mL of toluene over 30 min at −78 °C. The resulting solution was stirred at −78 °C for 7 h, at 0 °C for 10 h, and finally at room temperature for 7 h. The black precipitate of elemental lead was filtered off, 2 mL of THF was added to the clear solution, and after 10 d at −30 °C crystals, identified as **4**, were obtained. Yield: 0.930 g (71.8%). NMR: ^1H (C_6D_6) δ 0.361; ^{13}C (C_6D_6): δ 4.92; ^{29}Si (C_6D_6): δ −9.51 [(Me_3Si)], −130.04 [$(Me_3Si)_3\mathit{Si}$]. Mass spectrum [m/z (%)]: EI 494 (M^+, 3); FI 494 (M^+, 100).

X-ray Structure Determination of 1 to 4

Crystal data of the four structures are presented in Table II. All data were collected at −120 °C on a Stoe-Siemens-AED with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation.

The structures were solved by direct methods.[27] All non-hydrogen atoms were refined anisotropically.[26] For the hydrogen atoms, the riding model was used; the structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$. Refinement of an inversion twin parameter[28] [$x = 0.04(19)$ where $x = 0$ for the correct absolute structure and $+1$ for the inverted structure] confirmed the absolute structure of **3**. The atomic coordinates of structures **1**–**4** are given in Tables III–VI.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (23 pages). Ordering information is given on any current masthead page.

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