Supporting Information

Silametallation Route to Hydrido(trialkylsilyl)silyllithiums

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• Experimental

X-ray Analysis of $[(t\text{-BuMe}_2\text{Si})_2\text{SiHLi(thf)}]_2$ (1a)

A. Crystal Data

Empirical Formula	$C_{32}H_{78}Li_2Si_6O_2$
Formula Weight	677.36
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.30 × 0.35 × 0.40 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	6635 (0.0 - 56.2°)
Lattice Parameters	a = 11.8427(4) Å b = 15.943(1) Å, β = 107.467(4)° c = 12.7700(4) Å, V = 2299.9(2) Å^3
Space Group	$P2_1/c$ (#14)
Z value	2
D_{calc}	0.978 g/cm^3
F_{000}	752.00
μ(MoKα)	2.04 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku/MSC Mercury CCD
Radiation	MoKα (λ = 0.71069 Å), graphite monochromated
Temperature	-123.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.5 mm
Detector Aperture	70 mm × 70 mm
Data Images	1000 exposures at 20.0 seconds
ω oscillation Range (χ = 0°, ϕ = 0.0°)	-75.0 - 105.0°
ω oscillation Range (χ = 45.0, ϕ = 90.0°)	-60.0 - 60.0°
Detector Position	40.00 mm
Pixel Sizes	0.137 mm
Detector Swing Angle	15.0°
$2\theta_{max}$	59.1°
No. of Reflections Measured	Total: 16981 Unique: 5185 (R_{int} = 0.020)
Corrections	Lorentz-polarization, Absorption (trans. factors: 0.754 - 1.000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	w = 1/[σ^2(Fo^2) + (0.0774P)^2 + 1.471P] where P = (Fo^2 + 2Fc^2)/3
No. of Reflections (I>2σ(I))	3959
No. Variables	199
Reflection/Parameter Ratio	19.899
Residuals: R; Rw	0.055; 0.162
Goodness of Fit Indicator	1.04
Max Shift/Error in Final Cycle	-0.01
Maximum peak in Final Diff. Map	0.65 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.46 e$^-$/Å^3

Table 1. Atomic coordinates, B_{iso}/B_{eq} and occupancy of $[(t\text{-}BuMe_2Si)_2SiHLi(thf)]_2$

atom	x	y	z	B_{eq}	occ
Si(1)	0.77995(5)	-0.14512(4)	0.10975(5)	3.12(1)	1.0000
Si(2)	0.68336(5)	-0.01614(4)	0.10689(5)	2.86(1)	1.0000
Si(3)	0.82452(5)	0.08238(4)	0.20103(5)	3.24(1)	1.0000
O(1)	0.3927(2)	-0.0360(2)	0.2107(2)	5.01(4)	1.0000
C(1)	0.5812(3)	-0.2415(3)	0.1139(4)	6.68(9)	1.0000
C(2)	0.5932(3)	-0.2040(2)	-0.0696(3)	6.49(8)	1.0000
C(3)	0.7254(3)	-0.3137(2)	0.0389(3)	6.20(8)	1.0000
C(4)	0.6649(2)	-0.2297(2)	0.0463(2)	4.01(5)	1.0000
C(5)	0.8683(3)	-0.1823(2)	0.2498(2)	5.05(6)	1.0000
C(6)	0.8844(3)	-0.1400(2)	0.0243(3)	5.38(7)	1.0000
C(7)	0.9111(3)	0.1664(3)	0.4053(3)	6.21(8)	1.0000
C(8)	0.6928(3)	0.1455(2)	0.3352(3)	5.02(6)	1.0000
C(9)	0.8246(3)	0.0223(2)	0.4089(2)	4.92(6)	1.0000
C(10)	0.8131(2)	0.1050(2)	0.3443(2)	3.79(4)	1.0000
C(11)	0.7982(3)	0.1834(2)	0.1202(3)	5.80(7)	1.0000
C(12)	0.9822(2)	0.0522(2)	0.2173(3)	5.03(6)	1.0000
C(13)	0.4537(4)	-0.0412(5)	0.3214(3)	11.5(2)	1.0000
C(14)	0.3730(4)	-0.0684(4)	0.3812(3)	9.1(1)	1.0000
C(15)	0.2645(4)	-0.0782(4)	0.3036(4)	9.9(2)	1.0000
C(16)	0.2731(4)	-0.0559(6)	0.1994(4)	13.7(3)	1.0000
Li(1)	0.4567(4)	-0.0144(3)	0.0958(3)	3.80(8)	1.0000

Table 1 (continued). Atomic coordinates, B_{iso}/B_{eq} and occupancy of [(*t*-$BuMe_2Si)_2SiHLi(thf)]_2$

atom	x	y	z	B_{eq}	occ
H(1)	0.5390	-0.1928	0.1221	6.7	1.0000
H(2)	0.6278	-0.2600	0.1893	6.7	1.0000
H(3)	0.5169	-0.2816	0.0766	6.7	1.0000
H(4)	0.5537	-0.1560	-0.0699	6.5	1.0000
H(5)	0.6441	-0.1895	-0.1142	6.5	1.0000
H(6)	0.5439	-0.2485	-0.1044	6.5	1.0000
H(7)	0.7668	-0.3294	0.1089	6.2	1.0000
H(8)	0.6648	-0.3556	0.0028	6.2	1.0000
H(9)	0.7760	-0.3011	-0.0037	6.2	1.0000
H(10)	0.8241	-0.1869	0.3002	5.0	1.0000
H(11)	0.9327	-0.1459	0.2811	5.0	1.0000
H(12)	0.9019	-0.2361	0.2502	5.0	1.0000
H(13)	0.9449	-0.1028	0.0527	5.4	1.0000
H(14)	0.8385	-0.1175	-0.0461	5.4	1.0000
H(15)	0.9189	-0.1910	0.0205	5.4	1.0000
H(16)	0.9018	0.1747	0.4779	6.2	1.0000
H(17)	0.9000	0.2239	0.3575	6.2	1.0000
H(18)	0.9859	0.1408	0.4142	6.2	1.0000
H(19)	0.6839	0.1541	0.4038	5.0	1.0000
H(20)	0.6264	0.1056	0.2959	5.0	1.0000
H(21)	0.6757	0.1999	0.2910	5.0	1.0000
H(22)	0.8223	0.0327	0.4874	4.9	1.0000
H(23)	0.7579	-0.0179	0.3763	4.9	1.0000
H(24)	0.9080	-0.0048	0.4148	4.9	1.0000
H(25)	0.8491	0.2246	0.1588	5.8	1.0000
H(26)	0.7172	0.2008	0.1068	5.8	1.0000
H(27)	0.8102	0.1763	0.0490	5.8	1.0000
H(28)	1.0321	0.0954	0.2437	5.0	1.0000
H(29)	1.0068	0.0064	0.2643	5.0	1.0000
H(30)	0.9927	0.0361	0.1484	5.0	1.0000
H(31)	0.4892	0.0104	0.3477	11.5	1.0000
H(32)	0.5169	-0.0829	0.3311	11.5	1.0000
H(33)	0.3693	-0.0269	0.4350	9.1	1.0000
H(34)	0.4002	-0.1200	0.4218	9.1	1.0000
H(35)	0.2047	-0.0458	0.3205	9.9	1.0000
H(36)	0.2390	-0.1373	0.3016	9.9	1.0000
H(37)	0.2212	-0.0097	0.1695	13.7	1.0000
H(38)	0.2461	-0.1024	0.1470	13.7	1.0000
H(39)	0.620(5)	-0.032(3)	0.186(4)	3.733(10)	0.488(4)
H(40)	0.706(5)	0.009(3)	0.004(4)	3.733(10)	0.512(4)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters of $[(t\text{-BuMe}_2\text{Si})_2\text{SiHLi(thf)}]_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si(1)	0.0327(3)	0.0474(4)	0.0388(3)	0.0051(3)	0.0114(3)	0.0028(3)
Si(2)	0.0267(3)	0.0470(4)	0.0336(3)	0.0028(2)	0.0070(2)	0.0025(2)
Si(3)	0.0336(3)	0.0481(4)	0.0429(3)	-0.0032(3)	0.0135(3)	0.0021(3)
O(1)	0.0399(9)	0.107(2)	0.047(1)	0.0021(10)	0.0188(8)	0.018(1)
C(1)	0.079(2)	0.082(2)	0.108(3)	-0.031(2)	0.050(2)	-0.019(2)
C(2)	0.087(2)	0.075(2)	0.062(2)	-0.007(2)	-0.012(2)	-0.012(2)
C(3)	0.069(2)	0.055(2)	0.102(3)	0.003(2)	0.011(2)	-0.016(2)
C(4)	0.047(1)	0.052(1)	0.053(1)	0.001(1)	0.013(1)	-0.005(1)
C(5)	0.064(2)	0.058(2)	0.054(2)	0.014(1)	-0.006(1)	0.007(1)
C(6)	0.065(2)	0.067(2)	0.090(2)	0.011(1)	0.050(2)	0.003(2)
C(7)	0.060(2)	0.098(3)	0.075(2)	-0.020(2)	0.017(2)	-0.040(2)
C(8)	0.056(2)	0.074(2)	0.068(2)	0.007(1)	0.030(1)	-0.011(2)
C(9)	0.066(2)	0.083(2)	0.037(1)	0.007(2)	0.014(1)	0.006(1)
C(10)	0.039(1)	0.060(1)	0.044(1)	-0.002(1)	0.012(1)	-0.008(1)
C(11)	0.085(2)	0.058(2)	0.072(2)	-0.016(2)	0.016(2)	0.016(2)
C(12)	0.036(1)	0.077(2)	0.084(2)	-0.011(1)	0.027(1)	-0.014(2)
C(13)	0.075(3)	0.309(8)	0.049(2)	-0.064(4)	0.012(2)	0.043(3)
C(14)	0.086(3)	0.202(6)	0.070(2)	-0.008(3)	0.038(2)	0.039(3)
C(15)	0.067(2)	0.213(6)	0.107(3)	-0.016(3)	0.041(2)	0.053(4)
C(16)	0.045(2)	0.40(1)	0.082(3)	-0.019(4)	0.024(2)	0.064(5)
Li(1)	0.035(2)	0.071(3)	0.039(2)	0.005(2)	0.013(2)	0.008(2)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths(Å) of $[(t\text{-BuMe}_2\text{Si})_2\text{SiHLi(thf)}]_2$

atom	atom	distance	atom	atom	distance
Si(1)	Si(2)	2.3480(9)	Si(1)	C(4)	1.915(3)
Si(1)	C(5)	1.877(3)	Si(1)	C(6)	1.881(4)
Si(2)	Si(3)	2.3453(8)	Si(2)	Li(1)	2.645(4)
Si(2)	Li(1)1)	2.667(4)	Si(2)	H(39)	1.44(6)
Si(2)	H(40)	1.47(5)	Si(3)	C(10)	1.909(3)
Si(3)	C(11)	1.887(3)	Si(3)	C(12)	1.879(3)
O(1)	C(13)	1.383(4)	O(1)	C(16)	1.416(5)
O(1)	Li(1)	1.875(5)	C(1)	C(4)	1.508(6)
C(1)	H(1)	0.95	C(1)	H(2)	1.00
C(1)	H(3)	1.00	C(2)	C(4)	1.525(4)
C(2)	H(4)	0.90	C(2)	H(5)	0.97
C(2)	H(6)	0.94	C(3)	C(4)	1.536(4)
C(3)	H(7)	0.92	C(3)	H(8)	0.99
C(3)	H(9)	0.94	C(5)	H(10)	0.95
C(5)	H(11)	0.95	C(5)	H(12)	0.95
C(6)	H(13)	0.92	C(6)	H(14)	0.97
C(6)	H(15)	0.92	C(7)	C(10)	1.538(4)
C(7)	H(16)	0.98	C(7)	H(17)	1.09
C(7)	H(18)	0.95	C(8)	C(10)	1.536(4)
C(8)	H(19)	0.92	C(8)	H(20)	1.02
C(8)	H(21)	1.02	C(9)	C(10)	1.540(4)
C(9)	H(22)	1.02	C(9)	H(23)	1.01
C(9)	H(24)	1.06	C(11)	H(25)	0.93
C(11)	H(26)	0.96	C(11)	H(27)	0.97
C(12)	H(28)	0.90	C(12)	H(29)	0.93
C(12)	H(30)	0.96	C(13)	C(14)	1.457(7)
C(13)	H(31)	0.94	C(13)	H(32)	0.98
C(14)	C(15)	1.376(6)	C(14)	H(33)	0.96
C(14)	H(34)	0.97	C(15)	C(16)	1.410(8)
C(15)	H(35)	0.95	C(15)	H(36)	0.99
C(16)	H(37)	0.96	C(16)	H(38)	0.99
Li(1)	H(39)	1.95(5)	Li(1)	H(40)	1.96(5)

Symmetry operations

(1) -X+1,-Y,-Z

Table 4. Bond Angles (deg) of $[(t\text{-BuMe}_2\text{Si})_2\text{SiHLi(thf)}]_2$

atom	atom	atom	angle	atom	atom	atom	angle
Si(2)	Si(1)	C(4)	109.16(9)	Si(2)	Si(1)	C(5)	114.9(1)
Si(2)	Si(1)	C(6)	110.8(1)	C(4)	Si(1)	C(5)	107.7(1)
C(4)	Si(1)	C(6)	107.1(1)	C(5)	Si(1)	C(6)	106.9(1)
Si(1)	Si(2)	Si(3)	108.03(3)	Si(1)	Si(2)	Li(1)	119.5(1)
Si(1)	Si(2)	Li(1)[1)]	109.5(1)	Si(1)	Si(2)	H(39)	100.8
Si(1)	Si(2)	H(40)	92.3	Si(3)	Si(2)	Li(1)	125.2(1)
Si(3)	Si(2)	Li(1)[1)]	121.0(1)	Si(3)	Si(2)	H(39)	101.4
Si(3)	Si(2)	H(40)	88.9	Li(1)	Si(2)	Li(1)[1)]	67.7(2)
Li(1)	Si(2)	H(39)	46.4	Li(1)	Si(2)	H(40)	113.5
Li(1)[1)]	Si(2)	H(39)	114.0	Li(1)1)	Si(2)	H(40)	46.3
H(39)	Si(2)	H(40)	159.7	Si(2)	Si(3)	C(10)	111.94(8)
Si(2)	Si(3)	C(11)	108.4(1)	Si(2)	Si(3)	C(12)	114.7(1)
C(10)	Si(3)	C(11)	108.4(1)	C(10)	Si(3)	C(12)	107.2(1)
C(11)	Si(3)	C(12)	106.0(2)	C(13)	O(1)	C(16)	106.9(3)
C(13)	O(1)	Li(1)	127.0(3)	C(16)	O(1)	Li(1)	126.0(3)
C(4)	C(1)	H(1)	114.8	C(4)	C(1)	H(2)	108.7
C(4)	C(1)	H(3)	110.2	H(1)	C(1)	H(2)	107.0
H(1)	C(1)	H(3)	103.1	H(2)	C(1)	H(3)	113.1
C(4)	C(2)	H(4)	111.8	C(4)	C(2)	H(5)	111.7
C(4)	C(2)	H(6)	110.0	H(4)	C(2)	H(5)	102.1
H(4)	C(2)	H(6)	113.1	H(5)	C(2)	H(6)	107.9
C(4)	C(3)	H(7)	107.6	C(4)	C(3)	H(8)	109.3
C(4)	C(3)	H(9)	103.8	H(7)	C(3)	H(8)	111.8
H(7)	C(3)	H(9)	111.9	H(8)	C(3)	H(9)	111.9
Si(1)	C(4)	C(1)	110.7(2)	Si(1)	C(4)	C(2)	109.8(2)
Si(1)	C(4)	C(3)	110.7(2)	C(1)	C(4)	C(2)	108.6(3)
C(1)	C(4)	C(3)	108.9(3)	C(2)	C(4)	C(3)	108.0(3)
Si(1)	C(5)	H(10)	114.2	Si(1)	C(5)	H(11)	110.9
Si(1)	C(5)	H(12)	113.8	H(10)	C(5)	H(11)	107.6
H(10)	C(5)	H(12)	104.1	H(11)	C(5)	H(12)	105.6
Si(1)	C(6)	H(13)	111.7	Si(1)	C(6)	H(14)	105.7
Si(1)	C(6)	H(15)	111.9	H(13)	C(6)	H(14)	106.3
H(13)	C(6)	H(15)	106.6	H(14)	C(6)	H(15)	114.5
C(10)	C(7)	H(16)	106.5	C(10)	C(7)	H(17)	107.8
C(10)	C(7)	H(18)	108.8	H(16)	C(7)	H(17)	113.0
H(16)	C(7)	H(18)	108.2	H(17)	C(7)	H(18)	112.3
C(10)	C(8)	H(19)	111.0	C(10)	C(8)	H(20)	109.7
C(10)	C(8)	H(21)	115.1	H(19)	C(8)	H(20)	105.5
H(19)	C(8)	H(21)	109.7	H(20)	C(8)	H(21)	105.2
C(10)	C(9)	H(22)	111.3	C(10)	C(9)	H(23)	113.0
C(10)	C(9)	H(24)	108.5	H(22)	C(9)	H(23)	105.1
H(22)	C(9)	H(24)	107.2	H(23)	C(9)	H(24)	111.6
Si(3)	C(10)	C(7)	110.3(2)	Si(3)	C(10)	C(8)	109.7(2)

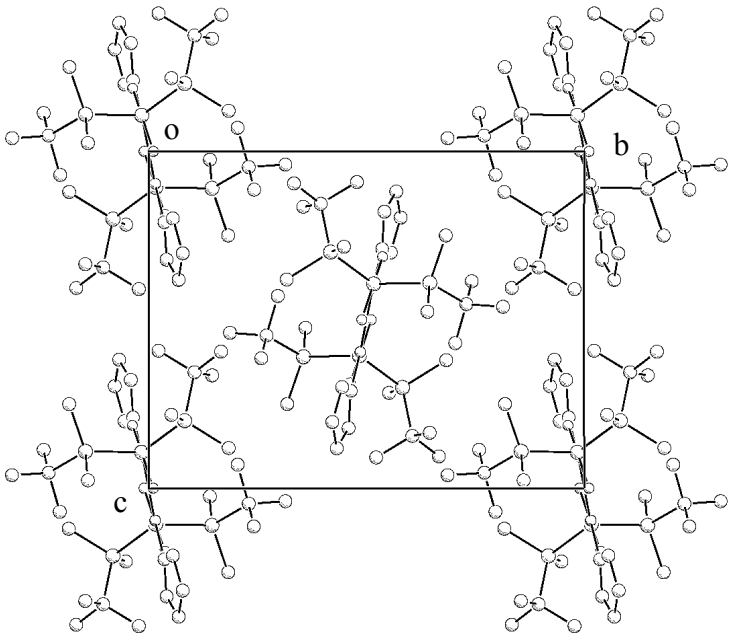
Table 4. Bond Angles (deg) of [(*t*-BuMe_2Si)$_2$SiHLi(thf)]$_2$ (continued)

Si(3)	C(10)	C(9)	109.4(2)	C(7)	C(10)	C(8)	108.2(2)
C(7)	C(10)	C(9)	109.9(2)	C(8)	C(10)	C(9)	109.3(2)
Si(3)	C(11)	H(25)	109.9	Si(3)	C(11)	H(26)	109.6
Si(3)	C(11)	H(27)	111.6	H(25)	C(11)	H(26)	110.1
H(25)	C(11)	H(27)	109.0	H(26)	C(11)	H(27)	106.7
Si(3)	C(12)	H(28)	111.2	Si(3)	C(12)	H(29)	112.3
Si(3)	C(12)	H(30)	111.4	H(28)	C(12)	H(29)	108.3
H(28)	C(12)	H(30)	107.2	H(29)	C(12)	H(30)	106.2
O(1)	C(13)	C(14)	109.3(3)	O(1)	C(13)	H(31)	110.7
O(1)	C(13)	H(32)	108.3	C(14)	C(13)	H(31)	111.6
C(14)	C(13)	H(32)	109.1	H(31)	C(13)	H(32)	107.7
C(13)	C(14)	C(15)	105.8(4)	C(13)	C(14)	H(33)	110.2
C(13)	C(14)	H(34)	111.5	C(15)	C(14)	H(33)	111.0
C(15)	C(14)	H(34)	112.1	H(33)	C(14)	H(34)	106.3
C(14)	C(15)	C(16)	109.6(5)	C(14)	C(15)	H(35)	111.8
C(14)	C(15)	H(36)	109.8	C(16)	C(15)	H(35)	110.3
C(16)	C(15)	H(36)	108.9	H(35)	C(15)	H(36)	106.2
O(1)	C(16)	C(15)	108.3(3)	O(1)	C(16)	H(37)	111.6
O(1)	C(16)	H(38)	110.5	C(15)	C(16)	H(37)	110.4
C(15)	C(16)	H(38)	110.5	H(37)	C(16)	H(38)	105.5
Si(2)	Li(1)	Si(2)1)	112.3(2)	Si(2)	Li(1)	O(1)	126.8(2)
Si(2)1)	Li(1)	O(1)	120.9(2)				

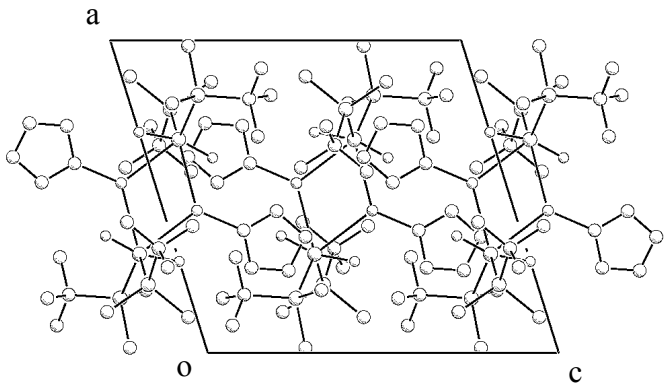
Symmetry operations

(1) -X+1,-Y,-Z

(a)



(b)



(c)

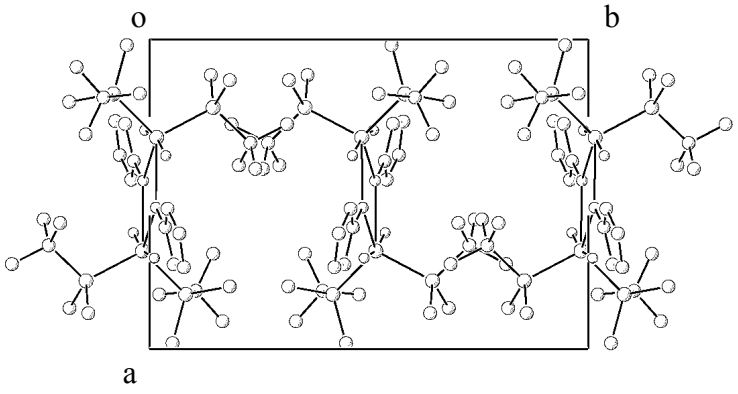


Figure. Views of Packings of $[(t\text{-BuMe}_2\text{Si})_2\text{SiHLi(thf)}]_2$. (a) along the *a* axis. (b) along the *b* axis. (c) along the *c* axis.

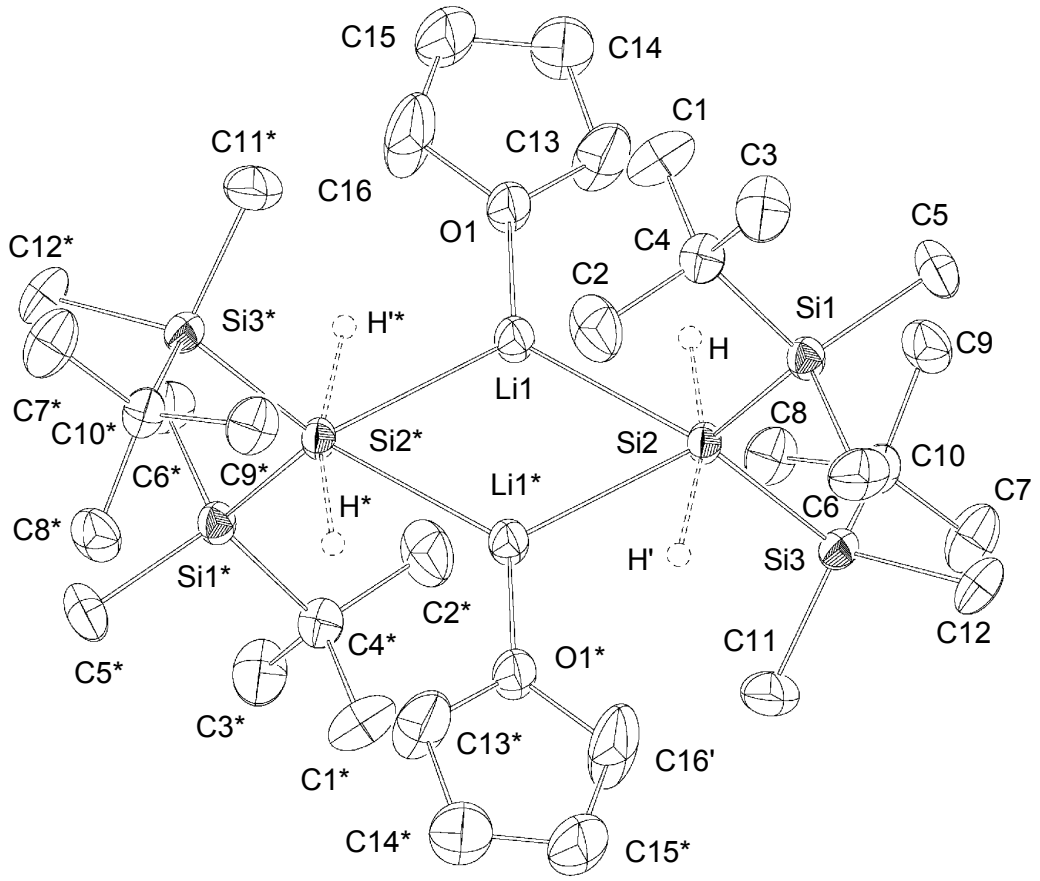


Figure. ORTEP drawing of of [(*t*-BuMe$_2$Si)$_2$SiHLi(thf)]$_2$. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms except for H(-Si) are omitted for clarity.

X-ray Analysis of [(*t*-BuMe$_2$Si)$_2$GeHLi(thf)]$_2$ (5)

A. Crystal Data

Empirical Formula	$C_{16}H_{31}Si_2GeOLi$
Formula Weight	375.12
Crystal Color, Habit	Colorless, Prism
Crystal Dimensions	0.20 × 0.20 × 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit Cell Determination (2θ range)	5850 (3.6 - 55.0˚)
Lattice Parameters	a = 11.880(2) Å, b = 15.941(2) Å c = 12.802(1) Å, β = 107.2502(9)˚ V = 2315.3(5) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.076 g/cm^3
F000	792.00
μ(MoKα)	14.22 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku/MSC Mercury CCD
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
Temperature	-123.0 °C
Voltage, Current	50 kV, 40 mA
Collimator Size	0.5 mm
Detector Aperture	70 mm × 70 mm
Data Images	900 exposures × 25.0 seconds
ω oscillation Range (χ=45.0°, ϕ = 0.0°)	-75.0 - 105.0˚
ω oscillation Range (χ=45.0, ϕ = 90.0°)	-75.0 - 105.0˚
Detector Position	40.00 mm
Pixel Sizes	0.137 mm
Detector Swing Angle	15.00°
$2\theta_{max}$	55.0˚
No. of Reflections Measured	Total: 21429, Unique: 5300 (R_{int} = 0.033)
Corrections	Lorentz-polarization, Absorption (trans. factors: 0.808 – 1.000)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares (SHELXL-97)
Function Minimized	$\Sigma\, w\, (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(Fo^2) + (0.0501P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$
No. of Reflections ($I > 2\sigma(I)$)	3215
No. Variables	190
Reflection/Parameter Ratio	16.92
Residuals: R; Rw	0.045 ; 0.122
Goodness of Fit Indicator	0.91
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.71 e-/Å^3
Minimum peak in Final Diff. Map	-0.35 e-/Å^3

Table 1. Atomic coordinates, B_{iso}/B_{eq} of $[(t\text{-}BuMe_2Si)_2GeHLi(thf)]_2$

atom	x	y	z	B_{eq}
Ge(1)	0.81853(3)	0.01523(2)	0.89368(3)	3.27(1)
Si(1)	0.72014(8)	0.14626(6)	0.89173(7)	3.47(2)
Si(2)	0.67347(8)	-0.08315(6)	0.79717(8)	3.65(2)
O(1)	1.1073(2)	0.0353(2)	0.7881(2)	5.55(6)
C(1)	0.6857(3)	-0.1053(2)	0.6550(3)	4.15(7)
C(2)	0.6323(4)	0.1830(3)	0.7518(3)	5.39(9)
C(3)	0.8340(3)	0.2305(2)	0.9547(3)	4.37(7)
C(4)	0.6748(4)	-0.0229(3)	0.5900(3)	5.02(8)
C(5)	0.8045(4)	-0.1461(3)	0.6628(4)	5.51(9)
C(6)	0.6156(4)	0.1408(3)	0.9764(4)	5.72(9)
C(7)	0.7736(4)	0.3142(3)	0.9625(4)	6.5(1)
C(8)	0.5176(3)	-0.0508(3)	0.7817(4)	5.27(9)
C(9)	0.7001(4)	-0.1840(3)	0.8776(4)	6.1(1)
C(10)	1.0482(5)	0.0401(6)	0.6780(4)	11.8(3)
C(11)	0.9168(5)	0.2436(3)	0.8856(5)	7.3(1)
C(12)	0.5877(4)	-0.1645(3)	0.5926(4)	6.6(1)
C(13)	0.9069(5)	0.2037(3)	1.0699(4)	7.0(1)
C(14)	1.2260(5)	0.0553(8)	0.7983(5)	14.8(4)
C(15)	1.2358(5)	0.0773(6)	0.6953(6)	11.0(2)
C(16)	1.1261(6)	0.0673(6)	0.6181(5)	10.1(2)
Li(3)	1.0442(5)	0.0136(4)	0.9025(5)	4.4(1)

Table 1 (continued). Atomic coordinates, B_{iso}/B_{eq} of $[(t\text{-}BuMe_2Si)_2GeHLi(thf)]_2$

atom	x	y	z	B_{eq}
H(1)	0.8102	-0.0184	1.0063	9.2
H(2)	0.5741	0.1452	0.7193	5.3
H(3)	0.5941	0.2325	0.7569	5.3
H(4)	0.6852	0.1879	0.7066	5.3
H(5)	0.8100	-0.1589	0.5933	5.5
H(6)	0.8660	-0.1088	0.6940	5.5
H(7)	0.8259	-0.1980	0.7061	5.5
H(8)	0.6065	0.0029	0.5902	5.0
H(9)	0.7362	0.0112	0.6253	5.0
H(10)	0.6735	-0.0236	0.5013	5.0
H(11)	0.4767	-0.0978	0.7784	5.2
H(12)	0.5127	-0.0217	0.8423	5.2
H(13)	0.4713	-0.0146	0.7099	5.2
H(14)	0.5595	0.0983	0.9519	5.6
H(15)	0.6551	0.1325	1.0472	5.6
H(17)	0.5638	0.2029	0.9632	5.6
H(18)	0.7393	0.3093	1.0162	6.4
H(19)	0.8311	0.3593	0.9835	6.4
H(20)	0.7110	0.3303	0.8838	6.4
H(27)	0.9443	0.1884	0.8656	7.4
H(28)	0.8722	0.2712	0.8113	7.4
H(29)	0.9926	0.2805	0.9236	7.4
H(30)	0.9562	0.1597	1.0667	6.9
H(31)	0.9589	0.2470	1.1089	6.9
H(32)	0.8641	0.1845	1.1190	6.9
H(33)	0.6891	-0.1771	0.9432	6.0
H(34)	0.6479	-0.2260	0.8380	6.0
H(35)	0.7788	-0.2053	0.8857	6.0
H(36)	0.5129	-0.1396	0.5878	6.6
H(37)	0.5950	-0.1750	0.5214	6.6
H(38)	0.5991	-0.2160	0.6371	6.6
H(39)	1.0113	-0.0104	0.6564	11.3
H(40)	0.9817	0.0738	0.6709	11.3
H(41)	1.2484	0.0873	0.8470	13.7
H(42)	1.2726	0.0193	0.8277	13.7
H(43)	1.2524	0.1308	0.6900	10.6
H(44)	1.2951	0.0536	0.6791	10.6
H(45)	1.1413	0.0296	0.5726	9.8
H(46)	1.1052	0.1150	0.5729	9.8

$Beq = 8/3\ PI^2(U11(aa^*)^2 + U22(bb^*)^2 + U33(cc^*)^2 + 2U12(aa^*bb^*)\cos\gamma + 2U13(aa^*cc^*)\cos\beta + 2U23(bb^*cc^*)\cos\alpha)$

Table 2. Anisotropic Displacement Parameters of $[(t\text{-BuMe}_2\text{Si})_2\text{GeHLi(thf)}]_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge(1)	0.0302(2)	0.0497(2)	0.0427(2)	0.0030(2)	0.0081(1)	0.0018(2)
Si(1)	0.0365(5)	0.0510(6)	0.0455(5)	0.0054(4)	0.0139(4)	0.0036(4)
Si(2)	0.0377(5)	0.0517(6)	0.0508(6)	-0.0037(4)	0.0155(4)	0.0017(4)
O(1)	0.043(1)	0.121(2)	0.053(2)	0.002(2)	0.023(1)	0.021(2)
C(1)	0.042(2)	0.062(2)	0.054(2)	-0.003(2)	0.016(2)	-0.010(2)
C(2)	0.069(3)	0.059(2)	0.064(3)	0.017(2)	-0.001(2)	0.008(2)
C(3)	0.052(2)	0.057(2)	0.060(2)	0.000(2)	0.021(2)	-0.011(2)
C(4)	0.066(3)	0.083(3)	0.040(2)	0.005(2)	0.012(2)	0.007(2)
C(5)	0.059(3)	0.076(3)	0.083(3)	0.005(2)	0.034(2)	-0.016(2)
C(6)	0.067(3)	0.072(3)	0.093(3)	0.011(2)	0.047(2)	0.006(2)
C(7)	0.079(3)	0.057(3)	0.106(4)	0.003(2)	0.021(3)	-0.018(2)
C(8)	0.042(2)	0.078(3)	0.084(3)	-0.014(2)	0.025(2)	-0.014(2)
C(9)	0.091(3)	0.060(3)	0.075(3)	-0.015(2)	0.017(2)	0.015(2)
C(10)	0.071(4)	0.32(1)	0.059(3)	-0.048(5)	0.022(3)	0.050(5)
C(11)	0.084(3)	0.080(3)	0.131(4)	-0.030(3)	0.059(3)	-0.020(3)
C(12)	0.070(3)	0.093(4)	0.089(3)	-0.021(3)	0.024(3)	-0.040(3)
C(13)	0.089(3)	0.083(3)	0.074(3)	-0.006(3)	-0.006(3)	-0.015(2)
C(14)	0.050(3)	0.43(1)	0.089(4)	-0.010(6)	0.026(3)	0.080(7)
C(15)	0.075(4)	0.238(9)	0.113(5)	-0.018(5)	0.042(4)	0.064(5)
C(16)	0.097(4)	0.220(8)	0.078(4)	-0.014(5)	0.044(3)	0.038(4)
Li(3)	0.041(3)	0.076(4)	0.047(3)	0.004(3)	0.011(3)	0.011(3)

The general temperature factor expression:
$\exp(-2PI^2(a^*2U11h^2 + b^*2U22k^2 + c^*2U33l^2 + 2a^*b^*U12hk + 2a^*c^*U13hl + 2b^*c^*U23kl))$

Table 3. Bond Lengths(Å) of $[(t\text{-BuMe}_2\text{Si})_2\text{GeHLi(thf)}]_2$

atom	atom	distance	atom	atom	distance
Ge(1)	Si(1)	2.390(1)	Ge(1)	Si(2)	2.386(1)
Ge(1)	Li(3)	2.649(7)	Ge(1)	Li(3)1)	2.675(6)
Ge(1)	H(1)	1.57	Si(1)	C(2)	1.879(4)
Si(1)	C(3)	1.906(4)	Si(1)	C(6)	1.877(6)
Si(2)	C(1)	1.902(4)	Si(2)	C(8)	1.875(4)
Si(2)	C(9)	1.885(4)	O(1)	C(10)	1.378(6)
O(1)	C(14)	1.414(7)	O(1)	Li(3)	1.866(8)
C(1)	C(4)	1.539(6)	C(1)	C(5)	1.530(6)
C(1)	C(12)	1.527(6)	C(2)	H(2)	0.92
C(2)	H(3)	0.92	C(2)	H(4)	0.98
C(3)	C(7)	1.534(6)	C(3)	C(11)	1.519(8)
C(3)	C(13)	1.533(6)	C(4)	H(8)	0.91
C(4)	H(9)	0.91	C(4)	H(10)	1.13
C(5)	H(5)	0.93	C(5)	H(6)	0.94
C(5)	H(7)	0.99	C(6)	H(14)	0.94
C(6)	H(15)	0.90	C(6)	H(17)	1.15
C(7)	H(18)	0.90	C(7)	H(19)	0.97
C(7)	H(20)	1.09	C(8)	H(11)	0.89
C(8)	H(12)	0.92	C(8)	H(13)	1.09
C(9)	H(33)	0.89	C(9)	H(34)	0.95
C(9)	H(35)	0.97	C(10)	C(16)	1.43(1)
C(10)	H(39)	0.92	C(10)	H(40)	0.94
C(11)	H(27)	1.00	C(11)	H(28)	1.04
C(11)	H(29)	1.06	C(12)	H(36)	0.96
C(12)	H(37)	0.96	C(12)	H(38)	0.99
C(13)	H(30)	0.92	C(13)	H(31)	0.96
C(13)	H(32)	0.97	C(14)	C(15)	1.40(1)
C(14)	H(41)	0.79	C(14)	H(42)	0.81
C(15)	C(16)	1.392(8)	C(15)	H(43)	0.88
C(15)	H(44)	0.88	C(16)	H(45)	0.89
C(16)	H(46)	0.94	Li(3)	H(1)[1)]	1.779(5)

Symmetry operations

(1) -X+2,-Y,-Z+2

Table 4. Bond Angles(deg) of $[(t\text{-BuMe}_2\text{Si})_2\text{GeHLi(thf)}]_2$

atom	atom	atom	angle	atom	atom	atom	angle
Si(1)	Ge(1)	Si(2)	107.05(3)	Si(1)	Ge(1)	Li(3)	119.6(1)
Si(1)	Ge(1)	Li(3)1)	108.4(1)	Si(1)	Ge(1)	H(1)	98.3
Si(2)	Ge(1)	Li(3)	125.6(1)	Si(2)	Ge(1)	Li(3)1)	122.0(1)
Si(2)	Ge(1)	H(1)	91.1	Li(3)	Ge(1)	Li(3)1)	68.9(2)
Li(3)	Ge(1)	H(1)	107.2	Li(3)1)	Ge(1)	H(1)	39.8
Ge(1)	Si(1)	C(2)	114.4(1)	Ge(1)	Si(1)	C(3)	109.1(1)
Ge(1)	Si(1)	C(6)	111.0(1)	C(2)	Si(1)	C(3)	107.9(2)
C(2)	Si(1)	C(6)	106.8(2)	C(3)	Si(1)	C(6)	107.3(2)
Ge(1)	Si(2)	C(1)	111.7(1)	Ge(1)	Si(2)	C(8)	114.4(1)
Ge(1)	Si(2)	C(9)	107.4(1)	C(1)	Si(2)	C(8)	107.6(2)
C(1)	Si(2)	C(9)	108.5(2)	C(8)	Si(2)	C(9)	107.0(2)
C(10)	O(1)	C(14)	105.9(4)	C(10)	O(1)	Li(3)	127.7(4)
C(14)	O(1)	Li(3)	126.3(4)	Si(2)	C(1)	C(4)	109.9(3)
Si(2)	C(1)	C(5)	110.3(2)	Si(2)	C(1)	C(12)	110.6(3)
C(4)	C(1)	C(5)	109.1(4)	C(4)	C(1)	C(12)	108.4(3)
C(5)	C(1)	C(12)	108.5(3)	Si(1)	C(2)	H(2)	111.0
Si(1)	C(2)	H(3)	110.2	Si(1)	C(2)	H(4)	108.5
H(2)	C(2)	H(3)	105.8	H(2)	C(2)	H(4)	108.4
H(3)	C(2)	H(4)	112.9	Si(1)	C(3)	C(7)	110.7(3)
Si(1)	C(3)	C(11)	110.6(3)	Si(1)	C(3)	C(13)	109.8(3)
C(7)	C(3)	C(11)	108.3(4)	C(7)	C(3)	C(13)	108.7(4)
C(11)	C(3)	C(13)	108.6(4)	C(1)	C(4)	H(8)	108.5
C(1)	C(4)	H(9)	108.2	C(1)	C(4)	H(10)	120.5
H(8)	C(4)	H(9)	108.2	H(8)	C(4)	H(10)	105.1
H(9)	C(4)	H(10)	105.9	C(1)	C(5)	H(5)	110.8
C(1)	C(5)	H(6)	110.2	C(1)	C(5)	H(7)	118.2
H(5)	C(5)	H(6)	106.2	H(5)	C(5)	H(7)	105.9
H(6)	C(5)	H(7)	104.8	Si(1)	C(6)	H(14)	111.5
Si(1)	C(6)	H(15)	110.7	Si(1)	C(6)	H(17)	106.9
H(14)	C(6)	H(15)	109.8	H(14)	C(6)	H(17)	106.0
H(15)	C(6)	H(17)	111.8	C(3)	C(7)	H(18)	107.5
C(3)	C(7)	H(19)	110.9	C(3)	C(7)	H(20)	110.4
H(18)	C(7)	H(19)	107.1	H(18)	C(7)	H(20)	112.8
H(19)	C(7)	H(20)	108.1	Si(2)	C(8)	H(11)	106.4
Si(2)	C(8)	H(12)	110.9	Si(2)	C(8)	H(13)	118.2
H(11)	C(8)	H(12)	107.0	H(11)	C(8)	H(13)	106.0
H(12)	C(8)	H(13)	107.7	Si(2)	C(9)	H(33)	111.1
Si(2)	C(9)	H(34)	109.4	Si(2)	C(9)	H(35)	110.9
H(33)	C(9)	H(34)	109.5	H(33)	C(9)	H(35)	110.2
H(34)	C(9)	H(35)	105.5	O(1)	C(10)	C(16)	110.5(5)
O(1)	C(10)	H(39)	108.2	O(1)	C(10)	H(40)	106.9
C(16)	C(10)	H(39)	115.5	C(16)	C(10)	H(40)	115.7
H(39)	C(10)	H(40)	99.2	C(3)	C(11)	H(27)	110.2
C(3)	C(11)	H(28)	110.4	C(3)	C(11)	H(29)	114.6
H(27)	C(11)	H(28)	104.7	H(27)	C(11)	H(29)	107.9
H(28)	C(11)	H(29)	108.5	C(1)	C(12)	H(36)	109.0
C(1)	C(12)	H(37)	109.6	C(1)	C(12)	H(38)	105.1
H(36)	C(12)	H(37)	110.8	H(36)	C(12)	H(38)	110.4

Table 4. Bond Angles (deg) of $[(t\text{-BuMe}_2\text{Si})_2\text{GeHLi(thf)}]_2$ (continued)

atom	atom	atom	angle	atom	atom	atom	angle
H(37)	C(12)	H(38)	111.7	C(3)	C(13)	H(30)	110.7
C(3)	C(13)	H(31)	113.2	C(3)	C(13)	H(32)	117.2
H(30)	C(13)	H(31)	104.5	H(30)	C(13)	H(32)	104.5
H(31)	C(13)	H(32)	105.7	O(1)	C(14)	C(15)	109.2(5)
O(1)	C(14)	H(41)	108.2	O(1)	C(14)	H(42)	114.2
C(15)	C(14)	H(41)	118.6	C(15)	C(14)	H(42)	112.3
H(41)	C(14)	H(42)	93.9	C(14)	C(15)	C(16)	108.5(6)
C(14)	C(15)	H(43)	113.4	C(14)	C(15)	H(44)	114.3
C(16)	C(15)	H(43)	103.9	C(16)	C(15)	H(44)	115.5
H(43)	C(15)	H(44)	100.6	C(10)	C(16)	C(15)	105.8(6)
C(10)	C(16)	H(45)	115.8	C(10)	C(16)	H(46)	118.6
C(15)	C(16)	H(45)	102.3	C(15)	C(16)	H(46)	111.3
H(45)	C(16)	H(46)	102.1	Ge(1)	Li(3)	$Ge(1)^{1)}$	111.1(2)
Ge(1)	Li(3)	O(1)	127.0(3)	Ge(1)	Li(3)	$H(1)^{1)}$	143.4
$Ge(1)^{1)}$	Li(3)	O(1)	121.8(3)	$Ge(1)^{1)}$	Li(3)	$H(1)^{1)}$	34.3
O(1)	Li(3)	$H(1)^{1)}$	88.2				

Symmetry operations

(1) -X+2,-Y,-Z+2

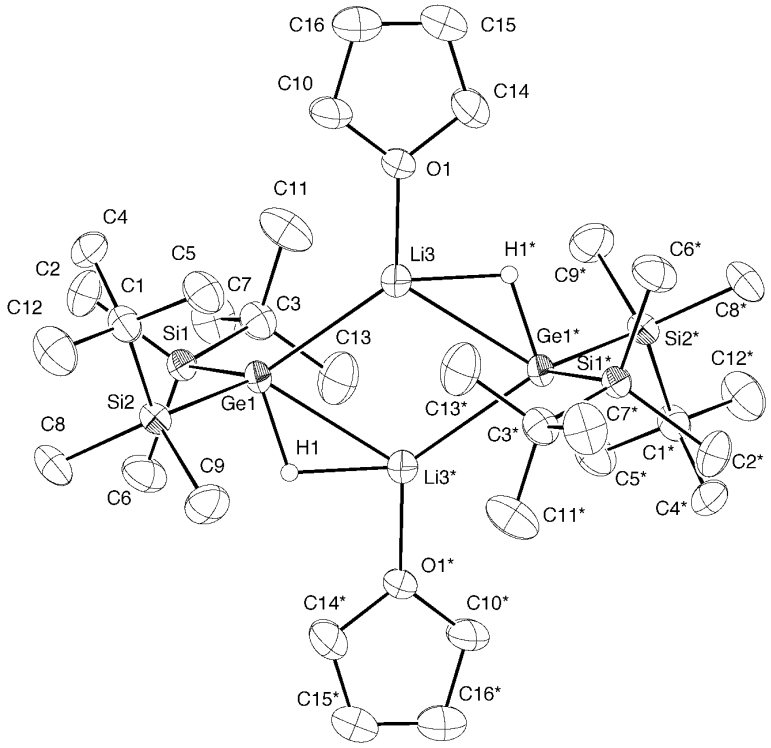
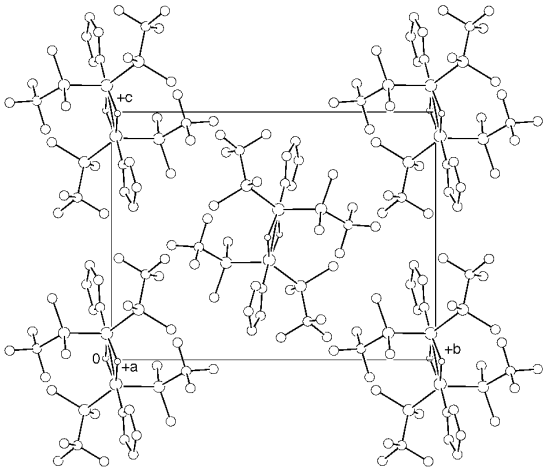
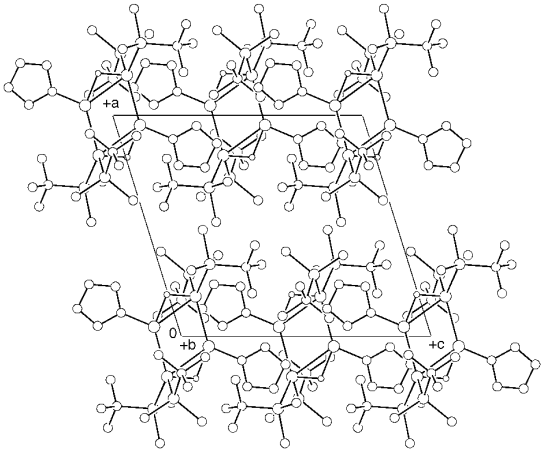


Figure. ORTEP drawing of of $[(t\text{-BuMe}_2\text{Si})_2\text{GeHLi(thf)}]_2$. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms except for H(-Ge) are omitted for clarity.

(a)



(b)



(c)

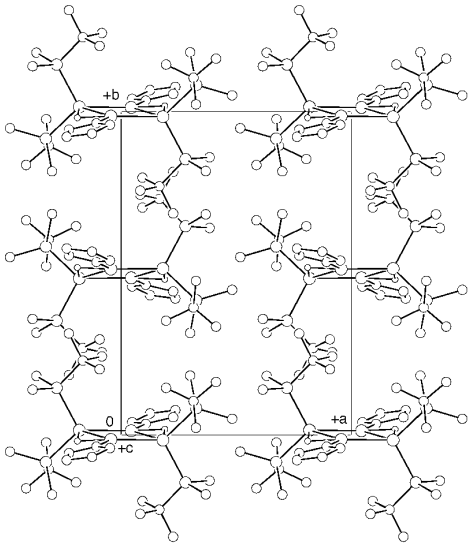


Figure. Views of Packings of $[(t\text{-BuMe}_2\text{Si})_2\text{GeHLi(thf)}]_2$. (a) along the *a* axis. (b) along the *b* axis. (c) along the *c* axis.

Experimental

Reaction of 1,3-di-*tert*-butyl-1,1,3,3-tetramethyltrisilane with *tert*-butyllithium In a Schlenk tube equipped with a magnetic stirrer bar, 1,3-di-*tert*-butyl-1,1,3,3-tetramethyltrisilane (**2a**) (0.500 g, 1.92 mmol) and dry THF (10 mL) were placed. To the solution, a pentane solution of *tert*-butyllithum (1.45 mol/L, 1.70 mL, 2.49 mmol) was added dropwise at -40 ºC. After the mixture was stirred for one hour, iodomethane (1.00 g, 7.05 mmol) was added to the mixture at -40 ºC. Then, the the mixture was stirred and allowed to warm to room temperature. After hydrolysis of the mixture and extraction with ether, the resulting organic layer was dried over anhydrous sodium sulfate. Removal of the solvent gave pure 1,3-di-*tert*-butyl-1,1,2,3,3-pentamethyltrisilane (**3a**) (0.526g, 1.92 mmol, 100%). **3a**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.11 (s, 6H), 0.14 (s, 6H), 0.24 (d, J = 5.4 Hz, 3H), 0.98 (s, 18H), 3.52 (q, J = 5.4 Hz, 1H); ^{13}C NMR (C_6D_6, δ) -9.7, -4.7, -3.7, 18.2, 27.5; ^{29}Si NMR (C_6D_6, δ) -79.4, -2.6; MS(EI, 70 eV) m/z (%) 274 (M^+, 8.4), 217 (17.3), 175 (14.1), 161 (31.6), 143 (46.2), 131 (36.9), 117 (52.0), 102 (51.7), 85 (32.7), 73 (100), 59 (98.2); HRMS calcd for $C_{13}H_{34}Si_3$: 274.1966. Found: 274.1971.

Reaction of trisilane 2a with lithium diisopropylamide (LDA) According to the procedure used for the reaction with *t*-butyllithium, reaction of **2a** (0.194 g, 0.745 mmol) with a LDA solution (2.00 mol/L, 0.64 mL, 2.88 mmol) in THF (7 mL) was carried out. After addition of an excess amount of iodomethane to the mixture and then aqueous workup, **3a** (0.161 g, 0.587 mol, 79%) was obtained.

Reaction of trisilane 2a with *n*-butyllithium According to the procedure used for the reaction with *t*-butyllithium, reaction of **2a** (0.500 g, 1.92 mmol) with *n*-butyllithum (1.65 mol/L, 1.70 mL, 2.88 mmol) was carried out. After addition of an excess amount of iodomethane to the mixture and then aqueous workup, 2-butyl-1,3-di-*tert*-butyl-1,1,3,3-tetramethyltrisilane (**4a**) (0.535 g, 1.69 mol, 88%) was obtained. **4a**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.13 (s, 6H), 0.15 (s, 6H), 0.87~0.95 (m, 4H), 0.98 (s, 18H), 1.29~1.51 (m, 5H), 3.43 (t, J = 3.9 Hz, 1H); ^{13}C NMR (C_6D_6, δ) -3.8, -2.8, 8.9, 14.0, 18.2, 26.9, 27.6, 31.4; ^{29}Si NMR (C_6D6, δ) -73.0, -2.4; MS (EI, 70 eV) *m*/*z* (%) 316 (16, M^+), 259 (24), 203 (38), 144 (34), 129 (24), 73 (100); HRMS calcd for $C_{16}H_{40}Si_3$: 316.2438. Found: 316.2437.

Reaction of 1,1,1,3,3,3-hexamethyltrisilane (2b) with *tert*-butyllithium According to the procedure used for the reaction of **2a** with *t*-butyllithium, the reaction of 1,1,1,3,3,3-hexamethyltrisilane **2b** (1.00 g, 5.67 mmol) with *tert*-butyllithium (1.36 mol/L, 3.30 mL, 2.64 mmol) was carried out. After addition of an excess amount of iodomethane to the mixture and

then aqueous workup, pure 1,1,1,2,3,3,3-heptamethyltrisilane (**3b**) (1.08 g, 5.67 mmol, 100 %) was obtained. The spectral data were agreed with the literature (Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478-484).

Reaction of 1,3-dimethyl-1,1,3,3-tetraisopropyltrisilane (2c) with *tert*-butyllithium According to the procedure used for the reaction of trisilane **2a**, reaction of 1,3-dimethyl-1,1,3,3-tetraisopropyltrisilane (**2c**) (0.50 g, 1.73 mmol) with *tert*-butyllithum (1.54 mol/L, 1.7 mL, 2.60 mmol) was carried out. After addition of an excess amount of iodomethane to the mixture and then aqueous workup, 1,1,3,3-tetraisopropyl-1,2,3-trimethyltrisilane (**3c**) (0.508 g, 1.68 mol, 97 %) was obtained. **3c**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.10 (s, 6H), 0.27 (d, J = 5.5 Hz, 3H), 1.06 ~ 1.11 (m, 24H), 1.12 - 1.14 (m, 4H), 3.56 (q, J = 5.5 Hz, 1H); ^{13}C NMR (C_6D_6, δ) -9.6, -7.3, 13.5, 13.8, 19.00, 19.03, 19.3, 19.5; ^{29}Si NMR (C_6D_6, δ) -84.1, 0.9; MS (EI, 70 eV) m/z(%) 302 (M^+, 13.1), 259 (11.9), 217 (12.9), 175 (17.7), 129 (32.8), 101 (23.4), 87 (39.0), 73 (83.7), 59 (100); HRMS calcd for $C_{13}H_{34}Si_3$: 274.1966. Found: 274.1971.

Reaction of 1,1,1,3,3,3-hexaisopropyltrisilane (2d) with *tert*-butyllithium According to the procedure used for the reaction of trisilane **2a**, reaction of 1,1,1,3,3,3-hexaisopropyltrisilane (**2d**) (1.00 g, 2.90 mmol) with a pentane solution of *tert*-butyllithium (1.36 mol/L, 1.7 mL, 2.32 mmol) in THF (10 mL) was carried out. After addition of iodomethane (0.500 g, 3.52 mmol) to the mixture at -40 ºC, usual aqueous workup gave a colorless oil (0.816 g). ^{1}H NMR of the oil showed that the starting material was recovered quantitatively.

Reaction of 1-*t*-butyl-1,1-dimethyl-2-(4-methylphenyl)disilane (2e) with LDA According to the procedure used for the reaction of trisilane **2a**, reaction of 1-*t*-butyl-1,1-dimethyl-2-(4-methylphenyl)disilane (**2e**) (0.480 g, 2.03 mmol) with a heptane/THF/ethylbenzene solution of LDA (2.0 mol/L, 1.05 mL, 2.10 mmol) in THF (5 mL) at -40 ºC was carried out. After addition of excess iodomethane, 1-*t*-butyl-1,1,2-trimethyl-2-(4-methylphenyl)disilane (**3e**) (0.488 g, 1.95 mmol, 96%) was obtained. **3e**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.04 (s, 3H), 0.08 (s, 3H), 0.42 (d, J = 4.7 Hz, 3H), 1.09 (s, 9H), 2.12 (s, 3H), 4.53 - 4.58 (m, 1H), 6.97 - 7.04 (m, 2H), 7.50 - 7.59 (m, 2H); ^{13}C NMR (C_6D_6, δ) -6.6, -5.8, -5.6, -5.2, 19.2, 23.0, 29.2, 129.3, 132.7, 136.1, 138.9; ^{29}Si NMR (C_6D_6, δ) -37.3, -6.7; MS (EI, 70 eV) *m*/*z* (%) 250 (25.1), 193 (100), 149 (41.9), 73 (36.0); HRMS calcd for $C_{14}H_{20}Si_2$, found 250.1596.

Reaction of 2e with *tert*-butyllithium According to the procedure used for the reaction of trisilane **2a**, reaction of **2e** (0.500 g, 2.11 mmol) with a pentane solution of *tert*-butyllithium (1.45 mol/L, 1.50 mL, 2.11 mmol) in THF (10 mL) at -40 ºC was carried out. After addition of an

excess amount of iodomethane to the mixture at -40 ºC, usual aqueous workup gave a mixture of **3**e (0.354 g, 1.41 mmol, 67%) and 1,2-di-*t*-butyl-1,1-dimethyl-2-(4-methylphenyl)disilane (**4e**) (0.130 g, 0.440 mmol, 21%) was obtained. **4e**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.18 (s, 3H), 0.25 (s, 3H), 0.90 (s, 9H), 1.11 (s, 9H), 2.10 (s, 3H), 4.30 (s, 1H), 6.97 - 7.04 (m, 4H), 7.50 - 7.59 (m, 4H); ^{13}C NMR (C_6D_6, δ) -3.9, -3.4, 18.0, 18.9, 21.5, 27.5, 29.5, 129.0, 132.6, 136.5, 138.6; ^{29}Si NMR (C_6D_6, δ) -15.7, -7.8; MS (EI, 70eV) m/z (%) 292 (M^+, 73), 235 (97), 179 (27), 149 (100), 135 (34), 73 (47); *Anal. Calcd* for $C_{10}H_{20}Si$: C, 79.93%; H, 8.38%. Found: C, 79.91%; H, 8.63%.

Reaction of dipropylsilane (2f) with *tert*-butyllithium According to the procedure used for the reaction of trisilane **2a**, reaction of dipropylsilane (**2f**) (1.00 g, 8.61 mmol) with a pentane solution of *tert*-butyllithium (1.45 mol/L, 5.9 mL, 8.61 mmol) in THF (10 mL) at -40 ºC was carried out. After addition of an excess amount of iodomethane to the mixture at -40 ºC, usual aqueous workup gave *tert*-butyldipropylsilane (**4f**) (1.48 g, 8.57 mmol, 100%) was obtained. **4f**: a colorless oil; ^{1}H NMR (C_6D_6, δ) 0.51-0.64 (m, 4H), 0.96 (s, 9H), 0.98 (t, J = 5.0 Hz, 6H), 1.39-1.47 (m, 4H), 3.70-3.74 (m, 1H); ^{13}C NMR (C_6D_6, δ) –3.3, 12.7, 18.4, 19.1, 25.9, 27.8; ^{29}Si NMR (C_6D_6, δ) 4.2; MS (EI, 70 eV) m/z (%) 172 (M^+, 76), 157 (9), 129 (12), 115 (100); HRMS calfc for $C_{10}H_{24}Si$: 172.1647. Found: 172.1638.

Reaction of diphenylsilane (2g) with *tert*-butyllithium According to the procedure used for the reaction of trisilane 2a, reaction of diphenylsilane (2g) (1.00 g, 5.43 mmol) with a pentane solution of *tert*-butyllithium (1.36 mol/L, 3.20 mL, 4.34 mmol) in THF (10 mL) at -40 ºC was carried out. After addition of iodomethane (1.00 g, 7.05 mmol) to the mixture at -40 ºC, usual aqueous workup gave *tert*-butyldiphenylsilane (4g) (1.15 g, 4.80 mmol) was obtained in 88% yield by Kugelrohr distillation. These spectral data were agreed with the literature (Hassler, K.; Weidenbruch, M. *J. Organomet. Chem.* 1994, *465*, 127-135).

Reaction of 2g with LDA According to the procedure used for the reaction of trisilane **2a**, reaction of **2g** (0.520 mg, 2.82 mmol) with a heptane/THF/ethylbenzene solution of LDA (2.0 mol/L, 1.50 mL, 3.00 mmol) was carried out. After addition of excess iodomethane to the mixture at -40 ºC, the sovent was distilled off. After dry hexane was introduced into to the mixture, the resulting salt was filtered off. Removal of hexane and Kugelrohr distillation gave pure (diisopropylamino)diphenylsilane (**4g'**) (0.641 g, 2.26 mmol, 80%) was obtained. **4g'**: bp 80 °C/ 0.1 Torr; ^{1}H NMR (C_6D_6, δ) 1.07 (d, J = 6.8 Hz, 12 H), 3.22 (sept, J = 6.8 Hz, 2 H), 7.19 - 7.23 (m, 6 H), 7.69 -7.73 (m, 4 H); ^{13}C NMR (C_6D_6, δ) 24.4 ($CH(\underline{C}H_3)_2$), 45.8 ($\underline{C}HMe_2$), 128.3, 129.7, 135.7, 136.6 (Ph); ^{29}Si (C_6D_6, δ) -25.8 (J(Si-H) = 200 Hz); MS (EI, 70 eV) *m*/*z* (%)

283 (8.1, M^+), 268 (100), 183 (55.6), 105 (14.3); *Anal. Calcd* for $C_{18}H_{15}NSi$: C, 76.26%; H, 8.89%, N, 4.94%. Found: C, 76.53%; H, 8.89%, N, 4.72%.

Isolation of 1,3-di-*tert*-butyl-2-lithio-1,1,3,3-tetramethyltrisilane (1a) In a round-bottomed Schlenk flask (50 mL) equipped with a stirring bar, trisilane **2a** (1.00 g, 3.84 mmol) and dry THF (10 mL) were placed. To the mixture a pentane solution of *tert*-butyllithium (1.36 mol/L, 4.24 mL, 5.76 mmol) was added dropwise at -40 ºC. The color of solution turned pale yellow gradually. The mixture was stirred for more one hour at -40 ºC. Then, addition of dry hexane (10 mL) to the mixture gave an off-white powder. After the supernatant was removed by decantation, the solvent was removed in vacuo. Recrystallization from hexane provided pure 1,3-di-*tert*-butyl-2-lithio-1,1,3,3-tetramethyltrisilane (**1a**) (0.683 g, 2.02 mmol) in 53% yield. **1a**: colorless crystals; ^{1}H NMR (C_7D_8, δ) 0.20 (s, 1H, Si-H), 0.24 (brs, 6H, SiMe), 0.32 (brs, 6H, SiMe), 1.04 (s, 18H, *t*-Bu), 1.22-1.31 (m, 4H, THF), 3.50-3.54 (m, 4H, THF); ^{13}C NMR (C_7D_8, δ) 0.3, 1.4 (SiMe), 18.2 ($\underline{C}(CH_3)_3$), 25.3 ($C(\underline{C}H_3)_3$), 28.2 (THF), 69.0 (THF); ^{29}Si NMR (C_7D_8, δ) –188.8 (J(Si-H) = 75 Hz), 4.5 (*t*-BuMe_2Si); ^{7}Li NMR (C_7D_8, □) 2.01 (brs, □$_{1/2}$ = 9.3 Hz).

Preparation of 1,1-di(*tert*-butyldimethylsilyl)-2,2-di(diisopropylmethylsilyl)disilane In a Schlenk flask equipped with a magnetic stirring bar, a THF/pentane solution of hydrosilyllithium **1a**, which was prepared by the reaction of **2a** (3.00 g, 11.5 mmol) and a pentane solution of *tert*-butyllithium (1.45 mol/L, 11.9 mL, 17.3 mmol) in THF (40 mL), was placed. To the solution, 2-chloro-1,3-dimethyl-1,1,3,3-tetraisopropyltrisilane (3.72 g, 11.5 mmol) was added at –78 ºC and the mixture was stirred overnight with allowing to warm to room temperature. After hydrolysis and extraction with ether, the organic layer was separated and dried over anhydrous sodium sulfate. Removal of the solvent in vacuo gave a viscous colorless oil. The title compound (4.46 g, 8.15 mmol, 71%) was obtained by Kugelrohr distillation.
a colorless oil; bp 120-140 ºC / 3.0 □10^{-3} Torr; ^{1}H NMR (C_6D_6, δ) 0.29 (s, 6H, SiMe), 0.30 (s, 6H, SiMe), 0.34 (s, 6H,SiMe) 1.07 (s, 18H, *tert*-Bu), 1.16-1.18 (m, 24H, CHMe_2), 1.20-1.27 (m, 4H, CHMe$_2$), 3.11 (s, 1H, SiH), 3.17 (s, 1H, SiH); ^{13}C NMR (C_6D_6, δ) –4.8 , -1.6, -1.4, 14.9, 15.0, 19.0, 19.3, 19.6, 19.87, 19.91, 27.7; ^{29}Si NMR (C_6D_6, δ) –128.9 (*Si*H), -125.9 (*Si*H), 1.5, 5.0; MS (EI, 70 eV) *m*/*z* (%) 546 (19, M^+), 431 (83), 416 (61), 73 (87), 57 (100). ; Anal. Calcd for $C_{26}H_{66}Si_6$: C, 57.06%; H, 12.15%. Found: C, 56.81%; H, 12.19%.

Synthesis of 1,1-di(*tert*-butyldimethylsilyl)-2,2-di(diisopropylmethylsilyl)disilene (6) In a two-necked flask equipped with a magnetic stirring bar and a dropping funnel, disilane **5** (1.10 g, 2.01 mmol) and dry dichloromethane (30 mL) were placed. To the solution, bromine (0.642 g, 4.02 mmol) was added dropwise at 0 ºC in the dark. After removal of the solvent in vacuo, the

resulting solid of 1,2-dibromodisilane was dissolved in dry THF. The THF solution was the added to the suspension of potassium graphite (0.452 g, 3.34 mmol) and THF (5 mL) at –78 ºC through a canulla. The solution turned yellow immediately. The mixture was stirred overnight with allowing to warm to –10 ºC. The solvent was removed in vacuo and dry hexane was introduced to the mixture. After filtration of the resulting salt and graphite, recrystallization from hexane gave the title compund (0.760 g, 1.40 mmol, 70%). **6**: air- and moisture sensitive orange crystals; mp 110 °C (decomp.); ^{1}H NMR (C_6D_6, δ) 0.29 (s, 6H), 0.40 (s, 12H), 1.14 (d, J = 9.3 Hz, 12H), 1.19 (d, J = 7.3 Hz, 12H), 1.40 (sept, J = 7.3 Hz, 4H); ^{13}C NMR (C_6D_6, δ) –6.9, 7.3, 16.7, 21.6, 28.8; ^{29}Si NMR (C_6D_6, δ) 5.9 (*t*-BuMe$_2$*Si*), 11.7 (*i*-Pr$_2$Me*Si*), 132.4 (Si=Si binding to *i*-Pr$_2$MeSi), 156.6 (Si=Si binding to *t*-BuMe$_2$Si); MS (EI, 70 eV) m/z (%) 544 (25, M^+), 129 (66), 73 (100); HRMS calcd for $C_{26}H_{64}Si_6$: 544.3624. Found: 544.3629.