Notes

The Structure of (1*Z*,3*Z*)-1,4-Bis(trimethylsilyl)-1,4-bis(lithiotetramethylethylenediamine)-2,3-dimethyl-1,3-butadiene. A Double Bridged Dilithium Compound

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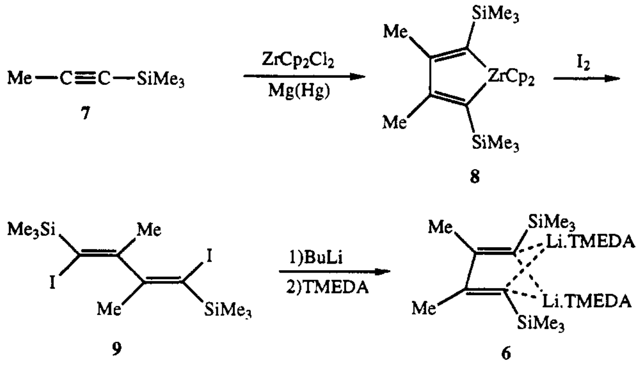
Summary: The X-ray crystal structure of the title compound shows the double bridged dilithium structure which had been predicted for the parent $C_4H_4Li_2$ by ab initio calculations. Crystal data: $C_{24}H_{56}Li_2N_4Si_2$, monoclinic, $P2_1/c$ (No. 14), $a = 12.606(3)$ Å, $b = 15.796(7)$ Å, $c = 16.096(6)$ Å, $\beta = 94.16(2)°$, $V = 3197(2)$ Å^3, $Z = 4$.

(1*Z*,3*Z*)-1,4-Dilithio-1,3-butadiene (**1**) is of substantial interest. Derivatives of **1** have been used extensively to prepare five-membered ring heterocycles and metallocycles.[1–5] There has been intrinsic interest in the bridged structures of **1** and other polylithio compounds.[6,7] In 1980 Schleyer and Kos reported the results of an *ab initio* MO study of **1** which indicated a symmetrically bridged structure **1′** which was energetically favored over nonbridged conformations.[6] Although the original paper suggested that **1′** was stabilized by a "Möbius–Hückel aromaticity", subsequent discussion has emphasized the favorable electrostatic interaction between the carbon and lithium atoms of the bridge.[7]

Solid state structures have been reported for two derivatives of **1**. *o,o′*-Dilithiobiphenyl·2TMEDA (**2**) shows the predicted symmetrical double dilithium bridge,[8] while compound **3** has a somewhat less symmetrical but essentially similar double dilithium bridge.[9,10] Bridged structures have been found for the less closely related 1,4-dilithio-2-butenediyls **4**[11] and **5**,[12] while there are a large number of organodilithium compounds which consist of two lithium atoms symmetrically disposed on either side of a conjugated hydrocarbon dianion.[13–16] Thus double dilithium bridging appears to be a common structural feature of dilithium compounds.

However it should be noted that the structures of **2** and **3** (and many other polylithium compounds) are partially disordered. In addition the "double bonds" of the butadienediyl groups of **2** and **3** are parts of benzene rings. Thus it would be desirable to have a structure of a simpler derivative of **1**. We report here on the structure of **6** which conforms in detail to the Schleyer and Kos prediction.

We have previously employed compound **6** to prepare Sb– and Bi–metallacycles.[4] It is readily available. The reaction of 1-(trimethylsilyl)-1-propyne (**7**) with zirconocene affords zirconacycle **8** which gives diiodide **9** in treatment with I_2. The diiodide is easily dilithiated using butyllithium in hexane to afford the desired dilithium compound. Addition of 2 equivalents of TMEDA followed by partial evaporation of the solvent at −10 °C gave large well-formed, blocklike yellow crystals of **6** which were suitable for X-ray diffraction. In the solid phase **6** is remarkably unreactive for an organolithium compound. Manipulation of the crystals in air for 5–10 min led to no observable changes, although **6** is oxygen sensitive in solution.



The molecular structure illustrated in Figure 1 shows the double dilithium bridge which had been anticipated by theory. Selected interatomic distances and angles are

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Chart I

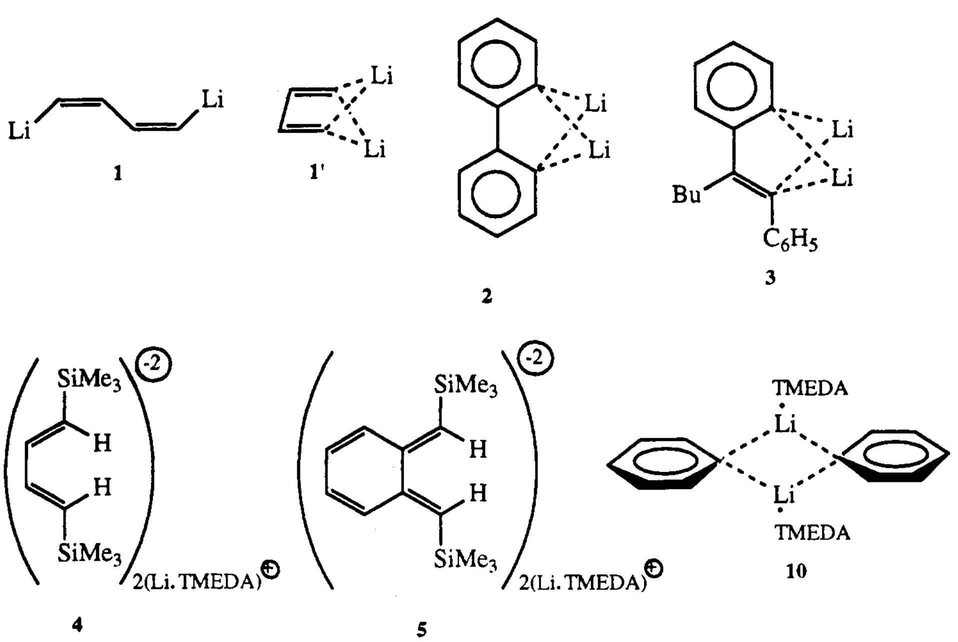

Table I. Selected Intramolecular Distances (Å) and Angles (deg) of 6

distances		angles	
Si(1)C(1)	1.833(4)	Si(1)C(1)C(2)	127.0(3)
Si(2)C(4)	1.838(4)	Si(2)C(4)C(3)	125.2(3)
N(1)Li(1)	2.197(7)	N(1)Li(1)N(2)	82.8(2)
N(2)Li(1)	2.188(7)	N(1)Li(1)C(1)	129.0(3)
N(3)Li(2)	2.214(7)	N(1)Li(1)C(4)	130.8(3)
N(4)Li(2)	2.193(7)	N(2)Li(1)C(1)	115.1(3)
Li(1)C(1)	2.180(7)	N(2)Li(1)C(4)	114.0(3)
Li(1)C(4)	2.129(7)	N(3)Li(2)N(4)	82.9(3)
Li(2)C(1)	2.165(7)	C(1)Li(1)C(4)	87.1(3)
Li(1)C(4)	2.169(7)	C(1)Li(2)C(4)	86.5(3)
Li(1)Li(2)	2.644(4)	C(1)C(2)C(3)	121.7(3)
Li(1)C(2)	2.508(7)	C(1)C(2)C(5)	123.7(3)
Li(1)C(3)	2.495(7)	C(2)C(3)C(4)	122.1(3)
Li(2)C(2)	2.537(8)	C(4)C(3)C(6)	123.8(4)
Li(2)C(3)	2.552(8)		
C(1)C(2)	1.359(5)		
C(2)C(3)	1.539(5)		
C(2)C(5)	1.538(6)		
C(3)C(4)	1.352(6)		
C(3)C(6)	1.536(6)		

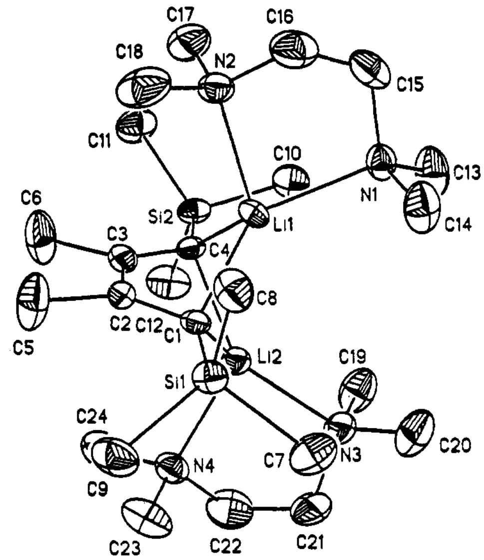

Figure 1. ORTEP diagram of 6, with hydrogen atoms excluded.

listed in Table I. The central butadienediyl group (C(1)C(2)C(3)C(4)) is coplanar within 0.01 Å, while the attached atoms of the methyl (C(5), C(6)) and TMS (Si(1), Si(2)) groups deviate only by 0.03 Å from the plane. The butadiene C–C bonds alternate in length in the usual manner: short (C(1)C(2)), long (C(2)C(3)), short (C(3)C(4)).

Li(1) and Li(2) bridge C(1) and C(4) forming a symmetrical four-membered ring, which is folded along the C(1)C(4) axis. The Li⋯Li distance is only 2.64 Å. This is comparable with the Li⋯Li distances in **2** (2.55 Å)[8] and **3** (2.63 Å).[9] Similarly, the Li⋯Li separation in the phenyllithium·TMEDA dimer (**10**) is 2.49 Å,[17] while that in the methyllithium tetramer is 2.63 Å.[18] Each lithium atom of **6** is chelated to a TMEDA molecule so that it achieves a somewhat distorted tetrahedral coordination. The coordination is very symmetrical: the approximate plane containing Li(1), Li(2), N(1), N(2), N(3), and N(4) is perpendicular (89.1(1)°) to the butadiene plane. Within each TMEDA unit there is a C_2 axis through the neighboring Li atom.

The C(1)–Li and C(4)–Li distances (2.13–2.18 Å) are quite ordinary. They are somehwat longer than had been calculated for **1** without TMEDA coordination (2.07 Å).[6] However they compare well with the corresponding C–Li distances of **2** (2.14 Å, av),[8] **3** (2.15 Å, av),[9] and **10** (2.21 Å).[17] The Li–C(2) and Li–C(3) distances of **6** are longer (2.51 Å, av), which are consistent with only a weak secondary Li–C interaction.[19]

It is particularly interesting to compare the 1,4-dilithiobutadienediyl structure of **6** with the structure of the similarly substituted 1,4-dilithiobutenediyl **4** (see Figure 2).[11] Although both types of structures have been described as examples of the "double bridged dilithium structure", they are quite different. In structure **4** the C–Li distances are greater and the lithium atoms are

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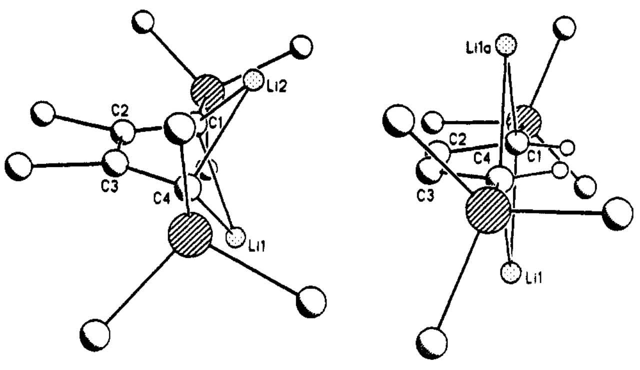
Table II. Crystallographic Data for 6

Crystal Data	
compd:	6
emp formula:	$C_{24}H_{56}Li_2N_4Si_2$
fw:	470.90 amu
cryst color and habit:	yellow, irregular
cryst dimens:	0.38 × 0.40 × 0.28 mm
cryst syst:	monoclinic
space group:	$P2_1/c$ (No. 14)
Z:	4
unit cell dimens from 25 reflns (20° ≤ 2θ ≤ 30°)	
a:	12.606(3) Å
b:	15.796(7) Å
c:	16.096(6) Å
β:	94.16(2)°
vol:	3197(2) Å^3
dens(calc):	0.983 g cm^{-3}
F(000)	1048 electrons
linear abs coeff (μ):	1.22 cm^{-1}
Data Collection	
diffractometer:	Siemens R3m/v, equipped with LT-2
radiation type:	Mo Kα λ = 0.710 73 Å, Lp corrected, graphite monochromator
temp:	−100 °C
scan type:	$\theta/2\theta$ scan
2θ scan range:	5–50°
octants used:	$+h,+k,\pm l$ (h, 0/15; k, 0/19; l, 20/20)
scan rate:	3–6°/min, variable
scan width:	0.8° below $K_{\alpha 1}$ to 0.8° above $K_{\alpha 2}$
backgd/scan ratio:	0.5
std reflns:	3 measured every 97 reflections, random variations <2%
no. of data collcd:	6370
no. of unique reflns:	5650, R_{int} = 0.0184
abs corr:	none applied
Solution and Refinement	
system used:	Siemens SHELXTL PLUS, VAXStation 3500
solution:	direct methods
refinement method:	full-matrix least squares
function minimized:	$\sum w(\lvert F_o - F_c\rvert)^2$
hydrogen atoms:[a]	riding model, d_{C-H} = 0.96, common isotropic U(H) refined to 0.078(3) Å^2
refined reflns with (F_o) ≥ $3\sigma(F)$:	3871
no. of param refined:	291
data/param ratio:	13.30
$R = \sum(\lvert F_o - F_c\rvert)/\sum\lvert F_o\rvert)$:	0.0773
$R_w = [\sum(w\lvert F_o - F_c\rvert)^2/\sum w(F_o)^2]^{1/2}$:	0.0772
$w^{-1} = \sigma^2(F_o) + 0.000442(F_o)^2$ GOF:	1.55
mean shift/error:	<0.001
max shift/error:	<0.001
secondary extinction:	2(1) × 10^{-8}
residual electron dens:	+0.48/−0.38 e/Å^3

[a] Anisotropically refined atoms are given in the form of the isotopic equivalent thermal parameter, U(eq) defined as $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

actually closer to C(2) and C(3) (2.30, 2.27 Å) than to C(1) and C(4) (2.41, 2.36 Å). The C(1), C(4), Li(1), and Li(2) are coplanar and the lithium atoms effectively sandwich the organic group. Consequently, the Li···Li separation of 4 (3.62 Å) is nearly 1 Å larger than in 6.

The differences in bonding between 4 and 6 are also reflected in their very different NMR spectra. For 6 the ^{13}C NMR signal of C(1) and C(4) is at very low field (δ = 203), which is typical for the lithiated carbon atoms of vinyl- and aryllithium compounds (vinyllithium, δ = 183.4;[20] phenyllithium δ = 188.9;[21] **3**, δ = 189, 202[9]). The ^{7}Li NMR spectrum of **6** in C_6D_6 shows a signal at δ = 0.33. This compares with δ = 0.08 for vinyllithium in ether,[22] δ = 1.03 for phenyllithium[2] in ether, and δ = 0.73 for the ^{6}Li NMR spectrum of **3**.[9] These values have been described as typical for the "more covalent organolithium compounds."[23] In contrast the ^{13}C NMR spectrum of **4** shows the signals for C(1) and C(4) at δ = 27.8. This is a very high field signal for an sp^2-hybridized carbon and is consistent with a large negative charge density at these atoms. The ^{7}Li NMR chemical shift of **4** in C_6D_6 of δ = −4.41 seems consistent with a structure in which the Li cations reside above or below a planar carbanion and are



6 4

Figure 2. A comparison of the structures of 6 and 4 drawn to the same scale. The TMEDA units and all hydrogen atoms except those at C(1) and C(4) of 4 have been excluded. The Me_3Si groups are unlabeled.

Table III. Positional Parameters and U(eq) Values for the Non-Hydrogen Atoms of 6

atom	x	y	z	U(eq), Å^2
Si1	0.78548(9)	0.17131(7)	0.35762(7)	0.0251(4)
Si2	0.71168(9)	−0.15188(7)	0.09692(7)	0.0265(4)
N1	0.9641(3)	−0.0999(2)	0.3357(2)	0.028(1)
N2	1.0095(3)	0.0052(2)	0.1949(2)	0.030(1)
N3	0.5835(3)	−0.0952(2)	0.3664(2)	0.034(1)
N4	0.4904(3)	0.0302(2)	0.2497(2)	0.032(1)
Li1	0.8601(5)	−0.0225(4)	0.2508(4)	0.023(2)
Li2	0.6540(5)	−0.0163(4)	0.2711(4)	0.024(2)
C1	0.7656(3)	0.0881(2)	0.2786(2)	0.021(1)
C2	0.7482(3)	0.0989(2)	0.1950(2)	0.024(1)
C3	0.7296(3)	0.0233(3)	0.1355(3)	0.027(1)
C4	0.7333(3)	−0.0576(3)	0.1630(2)	0.022(1)
C5	0.7445(5)	0.1860(3)	0.1521(3)	0.053(2)
C6	0.7076(5)	0.0482(3)	0.0437(3)	0.058(2)
C7	0.7388(4)	0.1322(3)	0.4595(3)	0.040(2)
C8	0.9307(3)	0.1988(3)	0.3796(3)	0.034(2)
C9	0.7167(4)	0.2777(3)	0.3425(3)	0.040(2)
C10	0.7641(4)	−0.2490(3)	0.1538(3)	0.039(2)
C11	0.7789(4)	−0.1581(3)	−0.0047(3)	0.046(2)
C12	0.5658(3)	−0.1703(3)	0.0701(3)	0.046(2)
C13	0.9310(4)	−0.1867(3)	0.3515(3)	0.046(2)
C14	0.9691(4)	−0.0538(3)	0.4141(3)	0.049(2)
C15	1.0684(4)	−0.1018(3)	0.2986(3)	0.047(2)
C16	1.0926(4)	−0.0205(3)	0.2571(3)	0.048(2)
C17	1.0124(4)	−0.0458(3)	0.1196(3)	0.046(2)
C18	1.0228(4)	0.0947(3)	0.1738(4)	0.058(2)
C19	0.5757(4)	−0.1813(3)	0.3335(3)	0.050(2)
C20	0.6408(4)	−0.0982(3)	0.4496(3)	0.051(2)
C21	0.4785(4)	−0.0580(3)	0.3749(3)	0.057(2)
C22	0.4266(4)	−0.0287(4)	0.2949(3)	0.059(2)
C23	0.4869(4)	0.1152(3)	0.2852(3)	0.055(2)

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thereby diamagnetically shielded.[23,24] Thus compound 4 and the closely related 5 are probably best described as lithium π-complexes. In contrast structures 2, 3, and 6 are effectively intramolecular dimers rather like 10.

It is striking that three derivatives of 1 (2, 3, and 6) with quite different substituents all adopt similar solid state structures involving double lithium bridging. There must be a large energetic preference for double lithium bridging, as had been insightfully predicted by Schleyer and Kos.[6,25]

Experimental Section

General Remarks. The reaction was carried out under an atmosphere of nitrogen. The NMR spectra were determined by using a Bruker AM-360 spectrometer on solutions in C_6D_6. The ^{1}H NMR and ^{13}C NMR spectra were calibrated by using signals of the solvent referenced to Me_4Si, while an external 1.0 M aqueous solution of LiCl was used to calibrate the ^{7}Li NMR spectrum.

(1*Z*,3*Z*)-1,4-Bis(trimethylsilyl)-1,4-bis(lithiotetramethylethylenediamine)-2,3-dimethyl-1,3-butadiene. A solution of 1.4 mL of hexane containing 2 mmol of butyllithium was added to a solution of (1*Z*,3*Z*)-1,4-diiodo-2,3-dimethyl-1,4-bis(trimethylsilyl)-1,3-butadiene (0.24 g, 0.5 mmol) in 1 mL of hexane at −78 °C. The reaction mixture was allowed to stir for 2 h at −78 °C, affording an orange solution. On the addition of 0.3 mL of TMEDA (2 mmol) a white precipitate formed. The mixture was allowed to warm to 25 °C, and the stirring was continued for 3 h. The clear orange liquid was canulated off and was concentrated by partial removal of the solvent at −10 °C. On standing at −10 °C, 0.1 g (91%) of yellow orange crystals formed.

^{1}H NMR (360 MHz, C_6D_6): δ 0.49 (s, *TMS*), 2.71 (s, *Me*), 2.04 (s, *TMEDA*), 2.19 (s, *TMEDA*). ^{7}Li NMR (140 MHz, C_6D_6): δ 0.33 (s). ^{13}C NMR (90.6 MHz, C_6D_6): δ 4.6 (*TMS*), 29.4 (*Me*), 46.7, 57.1 (*TMEDA*), 157.9 (CMe), 200.8 (br, *C*Li).

X-ray Structure Determination. Crystal data and data refinement parameters are summarized in Table II. An ORTEP plot of the molecular structure of 6 that shows the numbering used in the refinement is illustrated in Figure 1. Table III gives the positional values, while Table I gives the more important interatomic distances and angles. A table of the observed and calculated structure factors is available from A.J.A. on request.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the Americal Chemical Society for support of this work.

Supplementary Material Available: Tables of the anisotropic thermal parameters of the non-hydrogen atoms, positional parameters of the hydrogen atoms, and selected planes (6 pages). Ordering information is given on any current masthead page.

OM930216S

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