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Synthesis, Reactivity, and NMR Studies of Dilithiated (*E*)-1,4-Bis(trimethylsilyl)but-2-ene and (*E*)-1,4-Bis(trimethylsilyl)-2,3-dimethylbut-2-ene

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(*Z*)-1,4-Dilithio-1,4-bis(trimethylsilyl)but-2-ene and 1,4-dilithio-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene adducts of TMEDA (≡*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), [{Li(TMEDA)}$_2${(Me$_3$SiCHCH)$_2$}] (**3**) and [{Li(TMEDA)}$_2${(Me$_3$SiCHCMe)$_2$}] (**4**), respectively, have been prepared by dimetalation of the corresponding (*E*)-but-2-ene using *n*-BuLi(TMEDA) in hexane. Assignment of the *Z* configuration of the dianions with Li atoms bridging the ipso carbons ($C_{1,4}$) is based on NMR data: magnetically equivalent protons attached to the ipso carbons ($C_{1,4}$) couple to ^{7}Li ($^2J_{\mathrm{Li-H}}$ = ca. 1 Hz) in both compounds, lack of coupling of the protons attached to $C_{2,3}$ with the lithiums in **3**, and NOE enhancements for ^{1}H–^{7}Li HOESY experiments. The *Z* configuration is also consistent with the structures of two isolated silyl derivatives of **3**; treatment with ClSiMe$_3$ gives (*Z*)-1,1,4,4-tetrakis(trimethylsilyl)but-2-ene (**5**), and with Cl$_2$SiMe$_2$ it yields the (*Z*,*Z*)-1,6-disilacyclodeca-3,8-diene [{Me$_3$SiCHC(H)=C(H)CH(SiMe$_3$)SiMe$_2$}$_2$] (**6**). Compound **3** is a potent reducing agent, affording (*E*,*E*)-1,4-bis(trimethylsilyl)buta-1,3-diene (**7**) and metal when treated with HgCl$_2$ (yield of **7** 71%) or CaCl$_2$. X-ray diffraction data for **5** revealed a distorted *Z* double bond, the C–C–C angles at the sp^2 carbon centers being "opened up" to 130.2° (mean): crystals are monoclinic, space group $P2_1/n$, with a = 11.595 (4) Å, b = 12.205 (1) Å, c = 17.569 (6) Å, β = 107.33 (2)°, V = 2373 (1) Å^3, and Z = 4.

Introduction

Organolithium species are important intermediates in synthesis[2] and are found to exhibit a diverse range of structures,[3] which have been the subject of theoretical treatment.[4,5] This also includes organo*di*lithium species; many exhibit ion-pair structures, comprised of a conjugated hydrocarbon dianion with chelated lithium atoms situated symmetrically on either side of the dianion moiety, as in dilithium complexes of naphthalene,[6] stilbene,[7] anthracene,[8] acenaphthalene,[9] bifluorene,[10] hexadiene,[11] tetrakis(trimethylsilyl)ethylene,[12] 1,4-diphenylbutadiene,[13] 1,2-diphenylbenzocyclobutadienide,[14] and pentalenide[4] and dilithiated 1,2-[15] and 1,4-bis((trimethylsilyl)methyl)benzene.[16] Other conjugated systems have complex unsymmetrical structures.[17–19] Nonconjugated systems also have a diverse range of structures,[20–22] including symmetrically bridging lithium atoms as in 2,2′-dilithiobiphenyl systems.[3,22]

Ab initio and semiempirical MNDO calculations have predicted that 1,4-dilithiobut-2-ene-1,4-diyl complexes prefer to adopt dibridging structures[5] (I) with several other bonding configurations involving either delocalization of charge or multicenter bonding (II–IV) only slightly above the calculated energy surface of I.

The only crystal structure of a dilithiated butene to be elucidated to date is that of the TMEDA (≡*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) adduct of dilithio-1,4-diphenylbutadiene (V),[23] where each lithium is bound to one ipso carbon and C$_2$ and C$_3$. Related structures include dilithiated α,α'-diphenyl- or α,α'-disilyl-substituted *o*-xylenes (VI[24] and VII[15]). Unfortunately, the structure of

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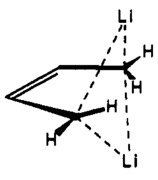

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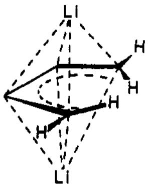

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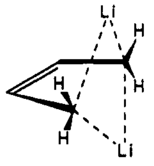

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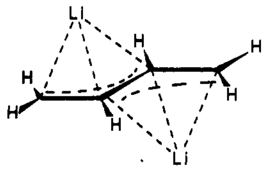

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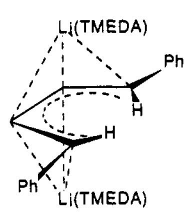

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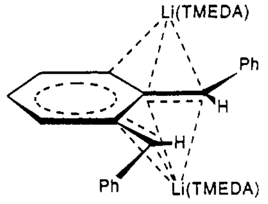

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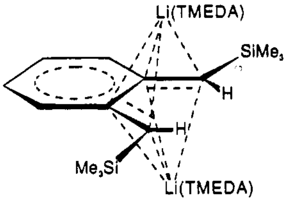

VII

VII has been misrepresented as having a bridging structure analogous to I.[3,15]

Herein we report the synthesis of dilithium species derived from the metalation of (*E*)-1,4-bis(trimethylsilyl)but-2-ene (1) and (*E*)-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene (2) and preliminary results of their structure elucidation using NMR spectroscopy. Incorporating silyl groups is noteworthy; they increase thermodynamic acidities of adjacent CH_n groups,[25] facilitating metalation with the use of strong bases such as alkyllithium reagents, and stabilize the resulting anionic centers by the high polarizability of silicon.[26] We also report (i) formation of some silyl derivatives that give insight into the assignment of the structure of the organolithium species; (ii) the X-ray structure determination of a silyl derivative that is of interest in the assignment of structure and because of the highly congested nature of the molecule, and (iii) a high-yielding synthesis of 1,4-bis(trimethylsilyl)-1,3-butadiene.

Experimental Section

Syntheses were carried out with use of standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze/thaw degassed prior to use. *n*-Butyllithium as a 1.6 M solution in hexane was obtained from Metallgesellschaft. All other reagents were obtained from Aldrich. (*E*)-1,4-Bis(trimethylsilyl)-2,3-dimethylbut-2-ene (2) was prepared according to the literature procedure.[27] ^1H NMR spectra were recorded on Bruker WM-250 or CXP-300 spectrometers in deuterated chloroform or benzene and referenced to the residual ^1H resonances of these solvents (δ 7.24 and 7.15, respectively). ^{13}C NMR spectra were recorded in the same solvents on a Bruker WM-250 spectrometer operating at 62.8 MHz using broad-band proton decoupling or DEPT pulse sequences and referenced to the ^{13}C resonances of the deuterated solvents (δ 77.00 and 128.00, respectively). ^7Li (and $^7Li\{^1H\}$) spectra were recorded on a Bruker CXP-300 spectrometer operating at 116.62 MHz and were run in deuterated benzene and measured relative to external 1 M aqueous $LiNO_3$. Elemental analyses were performed by the Canadian Microanalytical Services Ltd. and the Elemental Analysis Unit, University of Supakorn, Thailand. Melting points were determined in sealed glass capillaries under argon, where appropriate, and are uncorrected. Mass spectra were obtained on a Kratos MS25RFA spectrometer operating at 70 eV.

Synthesis of (*E*)-1,4-Bis(trimethylsilyl)but-2-ene (1). To a suspension of magnesium powder (7 g, 288 mmol) in THF (=tetrahydrofuran; 100 cm^3) and $ClSiMe_3$ (35 cm^3, 30 g, 276 mmol) was added (*E*)-1,4-dibromobut-2-ene (20 g, 94 mmol) in THF (150 cm^3) over 2 h at 0 °C with stirring. The mixture was stirred overnight at room temperature; then excess magnesium was removed by filtration and water (100 cm^3) added. The product was extracted into hexane (3 × 100 cm^3); then the combined extracts were dried (Na_2SO_4), and filtered, and the solvent was removed in vacuo. Compound 1 was distilled as a colorless liquid (9.8 g, 52%): bp 32–34 °C (ca. 1 mmHg); ^1H NMR (250 MHz, $CDCl_3$) δ 0.05 (18 H, s, $SiMe_3$), 1.33 (4 H, bd, $H^{1,4}$), 5.16 (2 H, bt, $H^{2,3}$); $^{13}C\{^1H\}$ NMR (62.8 MHz, $CDCl_3$) −2.1 ($SiMe_3$), 22.7 ($C^{1,4}$), 124.4 ($C^{2,3}$); IR $\nu_{C=C}$ 1660 cm^{-1} (w).

Synthesis of (*Z*)-1,4-Bis((*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium)-1,4-bis(trimethylsilyl)but-2-ene (3). To a stirred solution of *n*-BuLi (6.6 cm^3, 1.6 M, 10.5 mmol) and TMEDA (1.6 cm^3, 10.5 mmol) was added 1 (1 g, 5.1 mmol) over 10 min at 0 °C. After 30 min at room temperature the solution turned deep red; after 2 days the solution was concentrated in vacuo and stored at −30 °C, whereupon large deep red crystals of 3 deposited. These were collected, washed with ice-cold hexane(3 × 5 cm^3), and then dried in vacuo (1.78 g, 80%): mp 185–190 °C dec; ^1H NMR (250 MHz, C_6D_6) δ 0.38 (18 H, s, $SiMe_3$), 0.29 (2 H, bm, $H^{1,4}$), 1.81 (8 H, s, TMEDA CH_2), 2.05 (24 H, s, TMEDA CH_3), 5.07 (2 H, m, $H^{2,3}$); $^{13}C\{^1H\}$ NMR (62.8 MHz, C_6D_6) δ 4.5 ($SiMe_3$), 23.6 ($C^{1,4}$), 45.8 (TMEDA CH_3), 56.4 (TMEDA CH_2), 100.6 ($C^{2,3}$); ^7Li NMR (116.6 MHz, C_6D_6) δ −4.41 (t, $^2J_{Li-H}$ ca. 1 Hz); IR $\nu_{C=C}$ 1595 cm^{-1} (w). Anal. Calcd: C, 59.4; H, 12.24; N, 12.6. Found: C, 57.3; H, 11.83; N, 11.22.

Synthesis of (*Z*)-1,4-Bis((*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium)-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene (4). To a stirred solution of *n*-BuLi (6.6 cm^3, 1.6 M, 10.5 mmol) and TMEDA (1.6 cm^3, 10.5 mmol) was added 2 (1.14 g, 5.1 mmol) over 10 min at 0 °C. After 2 h at room temperature the solution become pale red and was then heated to 60 °C overnight, resulting in a deep red solution. This was then concentrated in vacuo and stored at −30 °C overnight, whereupon large bright red crystals of 4 deposited. These were collected, washed with ice-cold hexane (3 × 5 cm^3), and then dried in vacuo (1.74 g, 74%): mp 174–176 °C dec; ^1H NMR (250 MHz, C_6D_6) δ 0.42 (18 H, s, $SiMe_3$), 0.37 (2 H, bs, $H^{1,4}$), 1.76 (8 H, s, TMEDA CH_2), 2.03 (24 H, s, TMEDA CH_3), 2.22 (6 H, s, Me): $^{13}C\{^1H\}$ NMR (62.8 MHz, C_6D_6) δ 6.6 ($SiMe_3$), 19.5 (Me), 27.8 ($C^{1,4}$), 46.0 (TMEDA CH_3), 56.49 (TMEDA CH_2), 103.17 ($C^{2,3}$); ^7Li NMR (116.6 MHz, C_6D_6) δ −4.63 (t, $^2J_{Li-H}$ ca. 1 Hz); IR $\nu_{C=C}$ 1590 cm^{-1} (w).

Synthesis of (*Z*)-1,1,4,4-Tetrakis(trimethylsilyl)but-2-ene (5). A solution of 3 (6.66 g, 15.0 mmol) in hexane (40 cm^3) was added over 5 min to a stirred solution of $ClSiMe_3$ (4.0 cm^3, 3.42 g, 31.5 mmol) in hexane (40 cm^3) at 0 °C over 5 min. The mixture was heated to 50 °C for 2 days, during which time the red color dissipated, yielding a pale yellow solution. Water (100 cm^3) was added, the organic layer extracted with hexane (3 × 100 cm^3), dried (Na_2SO_4), and filtered, and the solvent removed in vacuo. Crystals of 5 deposited overnight. These were collected and dried in vacuo (2.06 g, 40%): mp 92–93 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 0.03 (36 H, s, $SiMe_3$), 1.25 (2 H, m, AA'XX', $H^{1,4}$), 5.10 (2 H, m, AA'XX', $H^{2,3}$); $^{13}C\{^1H\}$ NMR (62.8 MHz, $CDCl_3$) δ 0.3 ($SiMe_3$), 17.9 ($C^{1,4}$), 123.8 ($C^{2,3}$); MS *m/e* 344 (M^+, 15.5%); IR $\nu_{C=C}$ 1640

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Table I. Selected Structural Parameters for (*Z*)-1,1,4,4-Tetrakis(trimethylsilyl)but-2-ene (5)[a]

C(1)–C(2)	1.486 (6)	C(4)–Si(41,42)	1.887 (4)–1.889 (3)
C(2)–C(3)	1.320 (6)	C(1,4)–H(1,4)	0.90 (3), 0.83 (3)
C(3)–C(4)	1.495 (6)	C(2,3)–H(2,3)	0.93 (4), 0.97 (4)
C(1)–S(11,21)	1.896 (3), 1.893 (4)		
Si(11)–C(1)–Si(12)	115.8 (2)	C(1)–C(2)–H(2)	117 (2)
Si(41)–C(4)–Si(42)	117.0 (2)	C(3)–C(2)–H(2)	113 (2)
C(1)–C(2)–C(3)	130.6 (4)	C(2)–C(3)–H(3)	118 (2)
C(2)–C(3)–C(4)	129.8 (4)	C(4)–C(3)–H(3)	112 (2)
C(2)–C(1)–H(1)	113 (2)	C(3)–C(4)–H(4)	108 (2)
Si(11)–C(1)–C(2)	110.6 (3)	Si(41)–C(4)–C(3)	111.3 (3)
Si(12)–C(1)–C(2)	111.2 (3)	Si(42)–C(4)–C(3)	110.2 (3)
Si(11)–C(1)–H(1)	100 (2)	Si(41)–C(4)–H(4)	105 (2)
Si(12)–C(1)–H(1)	106 (2)	Si(42)–C(4)–H(4)	104 (2)
C(Me)–Si (min–max)		1.838 (5)–1.883 (6)	

[a] Bond lengths are in Å and bond angles in deg.

cm^{-1} (w). Anal. Calcd: C, 55.7; H, 11.7. Found: C, 55.45; H, 10.9.

Synthesis of (2*R*,3*Z*,5*S*,7*S*,8*Z*,10*R*)-1,1,6,6-Tetramethyl-2,5,7,10-tetrakis(trimethylsilyl)-1,6-disilacyclodeca-3,8-diene (6). To a stirred solution of **3** (6.66 g, 15.0 mmol) in hexane (40 cm^3) was added a solution of Cl_2SiMe_2 (1.94 cm^3, 2.06 g, 16 mmol) in hexane (20 cm^3) at 0 °C over 5 min. The solution was stirred overnight, during which time the red color dissipated, yielding a pale yellow solution. Water (100 cm^3) was added and the organic layer extracted with hexane (3 × 100 cm^3), dried (Na_2SO_4), filtered, and concentrated in vacuo. Crystals of **6** deposited overnight. These were collected and dried in vacuo (0.52 g, 10%): mp 216–217 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.03 (36 H, s, $SiMe_3$), 0.15 (12 H, s, $SiMe_2$), 1.35 (4 H, m, AA′XX′, $H^{2,5,7,10}$), 5.03 (4 H, m, AA′XX′, $H^{3,4,8,9}$); $^{13}C\{^1H\}$ NMR (62.8 MHz, $CDCl_3$) δ 1.6 ($SiMe_3$), −1.0($SiMe_2$), 17.7 ($C^{2,5,7,10}$), 123.5 ($C^{3,4,8,9}$); MS *m/e* 512 (M^+, 26.5%); IR $\nu_{C=C}$ 1635 cm^{-1} (w). Anal. Calcd: C, 56.2; H, 11.0. Found: C, 56.2; H, 10.85.

Synthesis of (*E*,*E*)-1,4-Bis(trimethylsilyl)buta-1,3-diene (7). To a solution of **3** (4.16 g, 9.34 mmol) in hexane (40 cm^3) was added $HgCl_2$ (2.60 g, 9.50 mmol) in small portions over 20 min at 0 °C. When the mixture was warmed to room temperature, only a small amount of Hg metal had deposited after 30 min. Addition of ca. 1 cm^3 of THF resulted in discharge of the red color after 10 min, yielding a pale yellow solution. The solution was repetitively washed from the mercury with hexane (3 × 50 cm^3). Water (100 cm^3) was added to the combined washings, the product extracted with hexane (3 × 100 cm^3), dried (Na_2SO_4), and filtered, and the solvent removed in vacuo. Compound **7** was distilled as a colorless liquid (1.33 g, 71%): bp 34 °C (ca. 1 mmHg); ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.07 (18 H, s, $SiMe_3$), 5.89–6.51 (4 H, AA′BB′, $H^{2,3}$ and $H^{1,4}$); $^{13}C\{^1H\}$ NMR (62.8 MHz, $CDCl_3$) δ −1.5 ($SiMe_3$), 134.9, 146.8 ($C^{1,4}$ and $C^{2,3}$); IR $\nu_{C=C}$ 1560 cm^{-1} (s).

Structure Determination. Suitable prismatic crystals of **5** were grown by slow evaporation of a hexane solution. A unique diffractometer data set was measured with use of an Enraf-Nonius CAD4 diffractometer. Reflections with $I > 2.5\sigma(I)$ were considered "observed" and used in the large-block least-squares refinement, minimizing $\sum w\Delta^2$ after solution of the structure by direct methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were constrained at estimated values (see below) except for non-methyl hydrogens, which were refined in x, y, z, U_{iso}. Conventional residuals on $[F]$ at convergence are quoted, R, R' $[(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed;[28] computation used the SHELX-86 program system.[29] Crystal data, atom coordinates, and molecular core geometries are given in Tables I–III, and a molecular projection is shown in Figure 2.

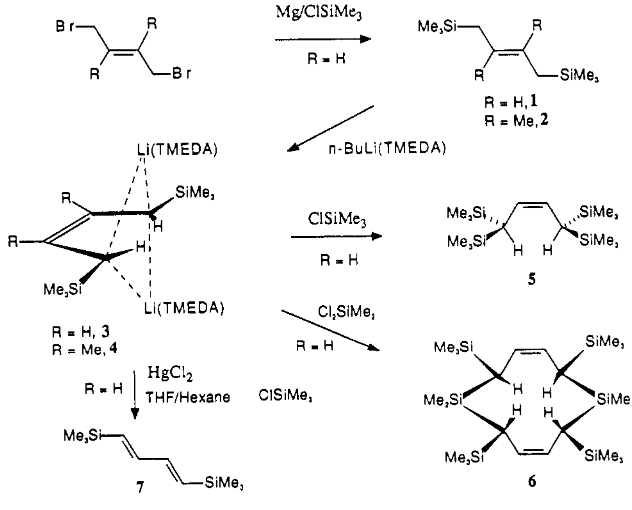
Table II. Non-Hydrogen Atom Coordinates for (*Z*)-1,1,4,4-Tetrakis(trimethylsilyl)but-2-ene (5)

atom	*x/a*	*y/b*	*z/c*
Si(11)	1356 (01)	2335 (01)	3889 (01)
Si(12)	2087 (01)	2719 (01)	5780 (01)
Si(41)	5606 (01)	2733 (01)	3517 (01)
Si(42)	6370 (01)	2042 (01)	5369 (01)
C(1)	2600 (03)	2543 (03)	4861 (02)
C(111)	106 (04)	1445 (05)	4025 (03)
C(112)	747 (05)	3668 (04)	3470 (03)
C(113)	1987 (04)	1617 (04)	3167 (02)
C(121)	3347 (04)	3270 (04)	6613 (03)
C(122)	1604 (05)	1391 (04)	6100 (03)
C(123)	818 (04)	3716 (04)	5589 (03)
C(2)	3413 (04)	3450 (04)	4784 (02)
C(3)	4459 (04)	3429 (03)	4628 (02)
C(4)	5143 (03)	2477 (03)	4445 (02)
C(411)	4482 (05)	3613 (05)	2813 (03)
C(412)	7074 (04)	3461 (05)	3758 (03)
C(413)	5712 (05)	1403 (05)	3027 (03)
C(421)	7202 (05)	3261 (04)	5869 (03)
C(422)	7441 (04)	1053 (04)	5154 (03)
C(423)	5682 (04)	1332 (04)	6055 (03)

Table III. Summary of X-ray Diffraction Data for (*Z*)-1,1,4,4-Tetrakis(trimethylsilyl)but-2-ene (5)

formula	$C_{16}H4_0Si_4$
mol wt	344.8
space group	$P2_1/n$
a, Å	11.595 (4)
b, Å	12.205 (1)
c, Å	17.569 (5)
β, deg	107.33 (2)
V, Å^3	2373 (1)
Z	4
D(calcd), g cm^{-3}	0.962
F(000)	768
cryst dimens, mm	0.36 × 0.35 × 0.14
temp, °C	296
radiation	Mo Kα (0.710 73 Å, graphite monochromator)
μ, cm^{-1}	0.24
$A^*_{min,max}$	0.81, 0.99
2θ limit, deg	50
no. of collected rflns	4621
no. of obsd rflns $[I > 2.5\sigma(I)]$	2229
R	0.048
R_w	0.0498
final residual, e Å^{-3}	0.275
S	4.33

Scheme I



Many hydrogen atom positions were visible from Fourier difference maps, but all were calculated in idealized positions at a distance of 1.08 Å from the parent carbon atom and were restricted to "ride" along with their parent carbon atoms, except

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[28] *International Tables for X-ray Crystallography*; Ibers, J. A.; Hamilton, W. C., Eds.; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

[29] Sheldrick, G. M. SHELXS-86, Program for Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1986.

[30] O'Brien, L. C.; Bernath, P. F. *J. Am. Chem. Soc.* **1986**, *108*, 5017.

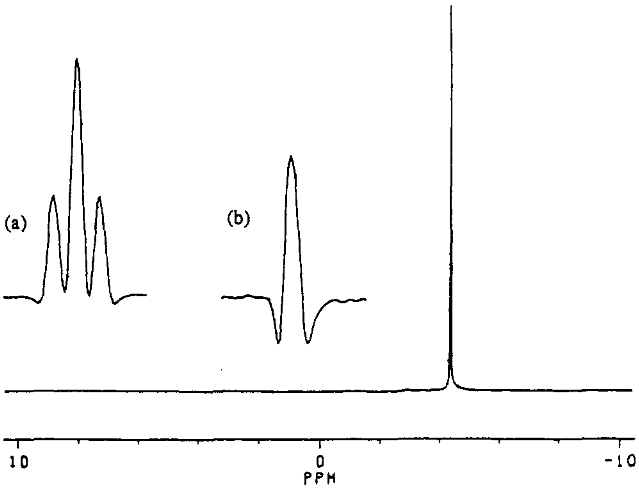


Figure 1. ^{7}Li and ^{7}Li{^{1}H} NMR spectra of (*Z*)-1,4-bis((*N*,*N*,-*N*′,*N*′-tetramethylethylenediamine)lithium)-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene (4) recorded in C_6D_6 at 35 °C.

for non-methyl hydrogens. For the methyl hydrogen atoms the isotropic hydrogen temperature factors were calculated as $1.25U_{ii}$(average) of the attached carbon atom.

Results and Discussion

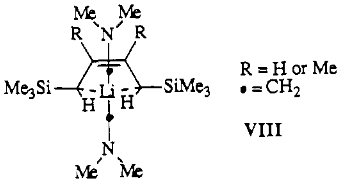
Synthesis and NMR Studies of Organolithium Reagents. Scheme I summarizes synthetic procedures. (*E*)-1,4-Bis(trimethylsilyl)but-2-ene (1) and (*E*)-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene (2) have been prepared in modest yields of 40–66% by a number of methods.[27,31,32] In this study 1 was conveniently prepared by (i) the unreported Grignard in situ reaction with (*E*)-1,4-dibromobut-2-ene, magnesium, and chlorotrimethylsilane in THF (yield 52%) and (ii) variation of a literature procedure,[31] in which "magnesium-butadiene", $Mg(C_4H_6)(THF)_2$, derived from magnesium, butadiene, and THF, was quenched directly by chlorotrimethylsilane in THF rather than in toluene (yield 43%; cf. 66%[31]) with only a trace of the *Z* isomer (^{1}H NMR). Compound 2 was prepared by a lithium reagent in situ quenching reaction involving lithium, 2,3-dimethylbutadiene, and chlorotrimethylsilane in THF;[27] "magnesium-2,3-dimethylbutadiene" derived from 2,3-dimethylbutadiene and magnesium in THF gave only a 5% yield of 2.

Metalation of 1 and 2 with use of 2 equiv of *n*-BuLi(TMEDA) in hexane afforded the corresponding (*Z*)-1,4-dilithiobut-2-ene-1,4-diyl complexes 3 and 4 as red crystalline solids, in yields of 80% and 74%, respectively. Formation of 4 required more forcing conditions than formation of 3 (ca. 60 °C; cf. ca. 20 °C), which is consistent with the added steric constraints imposed on $C_{1,4}$ by the olefinic methyl groups and the electron-releasing nature of the same methyl groups in 2. The sites of metalation are consistent with the relatively high thermodynamic acidity expected of allylic hydrogens associated with a carbon bearing a polarizing silicon center.[26] Complexes 3 and 4 are extremely air sensitive and possess good solubility in hydrocarbon solvents.

Despite 3 and 4 being highly crystalline, all crystals studied were unsuitable for X-ray structure determinations. However, NMR spectroscopy clearly establishes the mode of bonding of the metal atoms to the anions and the configuration of the anions in solution. The ^{7}Li NMR spectra of 3 and 4 consist of triplets ($^2J_{Li-H}$ ca. 1 Hz) which are clearly resolvable by Gaussian multiplication of the FID's, as shown in Figure 1 for 4. The ^{7}Li{^{1}H} NMR spectra, also shown in the same figure for 4, with the same Gaussian multiplication parameters, consist of sharp singlets. The triplets in the ^{7}Li NMR spectra of both 3 and 4 are ascribed scalar ^{7}Li–^{1}H coupling[34] involving two equivalent protons. Given the similarity of the spectra, and the lack of noticeable spectral differences between the compounds having H atoms or methyl groups attached to $C_{2,3}$, the coupling unequivocally involves the protons at $C_{1,4}$. This then dictates a Z configuration for both dianions, as in I. Moreover, the absence of any resolvable Li–H coupling to the protons at the $C_{2,3}$ in 3 indicates the interaction of the lithium atoms with these CH groups is at least weak.

Chemical shifts of the $C_{1,4}$ atoms in 3 and 4 (23.6, 27.8 ppm) differ only marginally from those of the corresponding conjugate acids 1 and 2 (22.7, 25.6 ppm). The protons on $C_{1,4}$ are shielded (0.29, 0.37 ppm) relative to those in 1 and 2 (1.33, 1.51 ppm), a common feature for ipso carbon atoms in alkyllithium species. This is consistent with the complexes having dibridging structures, for if the complexes had η^4-bound lithium atoms the protons and carbons in the 1- and 4-positions would be expected to resonate at frequencies typical of olefinic CH groups. It is consistent with the ability of silicon to localize charge by polarization.[26] The $C_{2,3}$ atoms in 3 and 4 (~105 ppm) show a marked upfield shift from those observed for 1 and 2 (~125 ppm), which is consistent with some delocalization of charge onto these carbons.

Molecules of 3 and 4 are made up of three parts, two $Li(TMEDA)^+$ units and a (*Z*)-but-2-ene-1,4-diyl unit or a (*Z*)-2,3-dimethylbut-2-ene-1,4-diyl unit. In solution at room temperature, the ^{1}H NMR spectrum of the TMEDA unit consists only of two signals, one for the four $-CH_3$ groups and one for the two $-CH_2-$ groups. At low temperature (−50 °C, toluene-d_8) these resonances broaden and resolve into four signals, two for the $-CH_3$ groups and two for the $-CH_2-$ groups. This is consistent with a structure where the planes of the TMEDA units bisect that of the butadienyl unit (VIII). At room temperature, the relaxation time of the ^{7}Li nuclei in 3 and 4 is >0.7 s and this must be a consequence of the symmetry of the environment about the quadrupolar ^{7}Li nucleus on the NMR time scale.



VIII

^{1}H–^{7}Li HOESY experiments[34] on both 3 and 4 show strong NOE enhancements of the lithium nuclei by all the protons of the TMEDA units. In addition, in 3 there are strong NOE enhancements of the ^{7}Li nuclei by the protons at $C_{1,4}$ as well as those at $C_{2,3}$. For 4 there are strong enhancements of the ^{7}Li signal from the protons at $C_{1,4}$ and the protons of the methyl groups at $C_{2,3}$. The ^{7}Li resonance was not enhanced by the protons of the $-SiMe_3$ groups of either 3 or 4.

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[31] Richter, W. J.; Neugebauer, B. *Synthesis* **1985**, 1059.

[32] Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912. Reddy, G. S.; Bhatt, M. V. *Synthesis* **1981**, 223.

[33] Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6391.

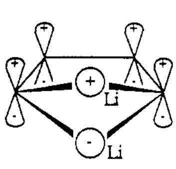
[34] Gunther, H.; Moskau, D.; Schmalz, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1212. Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. Yu, C.; Levy, G. C. *J Am. Chem. Soc.* **1984**, *106*, 6533. Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970. Bauer, W.; Muller, G.; Pi, R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1103.

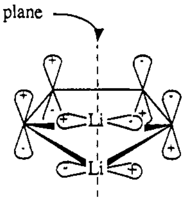
For **3**, the intensity of NOE enhancement of the ^{7}Li resonance by the protons at $C_{1,4}$ is approximately 7 times more intense than that from $C_{2,3}$. This indicates that the lithium nuclei are located significantly closer to $C_{1,4}$ than to $C_{2,3}$, consistent with a dibridging structure as in I and VIII. The relative intensities of the corresponding heteronuclear NOE enhancements in **4** indicate that the structure of **4** is analogous to that of **3**.

Observation of strong heteronuclear ^{1}H–^{7}Li NOE enhancements in this series of compounds implies that ^{1}H–^{7}Li HOESY may be a powerful method for structure elucidation of organolithium species in cases where the ^{7}Li relaxation time is sufficiently long to permit the observation of NOE enhancements. A full description of the ^{1}H–^{7}Li HOESY experiments will be presented elsewhere.

The infrared spectra of **3** and **4** have single, weak, olefinic $\nu_{C=C}$ bands at 1595 cm^{-1} (**3**) and 1590 cm^{-1} (**4**) at a frequency lower than those of **1** and **2**, 1660 and 1665 cm^{-1}, respectively, but at a frequency higher than that of (*E*,*E*)-1,4-bis(trimethylsilyl)buta-1,3-diene (**7**), 1560 cm^{-1} (s) (see below). The weakness of these absorptions for **3** and **4** is an indication of the complexes having 1,4-dilithiobut-2-ene-1,4-diyl structures (I) rather than being considered as η^4-butadienediyl complexes (II), which would be expected to show an intense olefinic carbon–carbon bond stretching frequency typical of the asymmetric stretching mode of conjugated olefins. Nevertheless, a lower $\nu_{C=C}$ value for **3** (and **4**) relative to that of the oxidized form **7** is consistent with some conjugation across the C_4 unit in **3**.

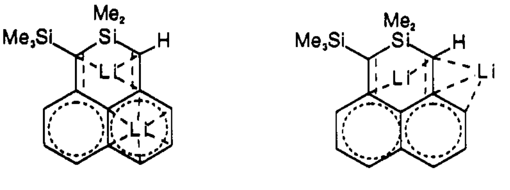
Thus ^{1}H, ^{13}C, and ^{7}Li NMR and IR data suggest that the structures of **3** and **4** have dibridging lithium atoms, and the electronic structures of the dianions are best described as being (*Z*)-but-2-ene-1,4-diyls, although with some delocalization of charge through the $C_{2,3}$ "double bonds". Overall this gives credence to the molecular orbidal description (structure I), which proposed the involvement of lithium orbitals in cyclic six-π-electron molecular orbitals of (*Z*)-1,4-dilithiobut-2-ene-1,4-diyl structures (IX and X).[5]


IX



X

The related complex VII has the lithium atoms bound almost equidistant to the ipso carbon atoms and adjacent ring carbons (range 2.32 (2)–2.41 (2) Å.[15] This is consistent with charge delocalization onto the otherwise aromatic ring, with the actual location of the metal centers matching location of nodes in the highest occupied orbital of the dianion, as is the case for the isomeric para complex.[16] Another related organodilithium complex where adjacent ipso carbons bear silyl groups crystallizes in two modifications that differ in the mode of interaction of the lithium centers with the dianion (XI; TMEDA's are not shown, and for each isomer the lithium atoms are on either side of the "naphthalene" plane).[18] Presumably, in this case extensive delocalization of charge results in a flat potential energy surface such that crystal-packing effects can influence the actual position of the lithium centers.



XI

Organolithium Reactions. Compounds **3** and **4** have potential as transfer agents of their dianions. In a test of this compound **3** was treated with $ClSiMe_3$ and Cl_2SiMe_2, yielding compounds **5** and **6**, respectively (Scheme I). Both of these derivatives exhibit a (*Z*)-butene configuration, in accordance with **3** having a *Z* configuration and in agreement with spectroscopic data for **3**. In addition, silylation of **3** at the $C_{1,4}$ positions serves to confirm that **1** is metalated in these positions. Treatment of **3** with $HgCl_2$ in hexane with a small amount of THF results in oxidation rather than transfer of the dianion, the product being (*E*,*E*)-1,4-bis(trimethylsilyl)butadiene (**7**). Assignment of the *E*,*E* isomer was on the basis of the product being identical with that derived from other syntheses (IR, ^{1}H NMR, and $n^{25}{}_D$).[35] To date this reaction represents the quickest and highest yielding (71%) synthesis of **7**. Oxidation even occurred with a chloride salt of highly electropositive metal, namely calcium, in diethyl ether. Thus, compound **3** is seemingly a potent reducing agent but has scope as a source of a dinucleophile. The related organodilithium reagent VII is also a potent reducing agent, yielding Sn(II) species from $SnCl_4$[36] and Zr(III) species from zirconocene dichloride,[37] most likely yielding the corresponding unstable substituted *o*-xylylene.

The benefits of using crystalline alkali-metal complexes to deliver exact stoichiometric amounts of reagent are documented.[15] In the foregoing oxidation involving $HgCl_2$, the benefits were 2-fold. First, reaction yields were increased consistently by ca. 30% compared to reacting **3** in situ, and second, the reactions were much "cleaner". Without isolation of **3** purification of **7** was hampered by the codistillation of a "mercury complex", which slowly decomposed, depositing mercury over several days. The identification of this complex was not obvious by ^{1}H and ^{13}C NMR spectroscopy, and no attempt was made to further characterize it.

Compounds **5** and **6** were isolated as air-stable, colorless crystalline solids in modest yields. Assignment of structure came from NMR and IR spectroscopy, mass spectrometry, and, for **5**, a crystal structure determination (see below). For **6** the NMR equivalence of the four $SiMe_3$ groups and equivalence of the two $SiMe_2$ groups and of the methyls within each $SiMe_2$ group, together with a single AA′XX′ spin system for the ring CH groups and equivalence of all olefinic and allylic carbon centers, uniquely defines the stereochemistry of **6**, with overall molecular symmetry C_{2v} as shown in Scheme I. The weak olefinic $\nu_{C=C}$ bands of **5** and **6** at 1640 and 1635 cm^{-1}, respectively, also indicate *Z* double bonds. Both **5** and **6** give molecular ion peaks with relative intensities of 15.5% and 26.5%, respectively, for the most abundant isotopic form (that is, all ^{28}Si nuclei) and show characteristic fragmentation patterns for the loss of $SiMe_3$ and Me groups.

Compound **6** was the only product isolated from the reaction of **3** with Cl_2SiMe_2 and is based on the condensation of two units of the dianion. The analogous reaction involving **4** gave an intractable mixture of compounds and

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(35) Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415. Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1978**, *144*, 1.

(36) Lappert, M. F.; Leung, W.-P.; Raston, C. L.; Thorne, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1982**, *233*, C28.

(37) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 893.

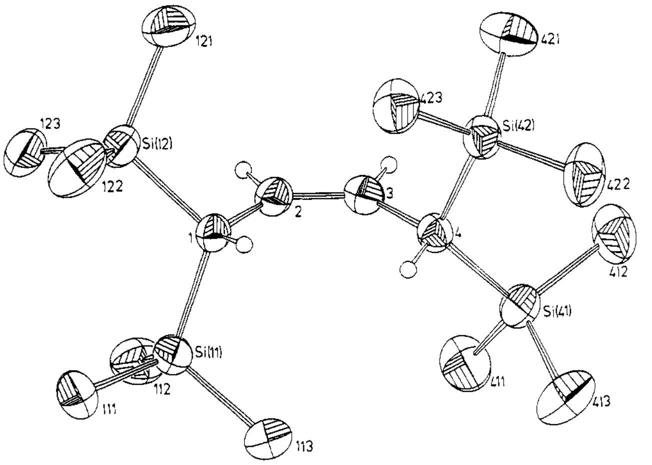
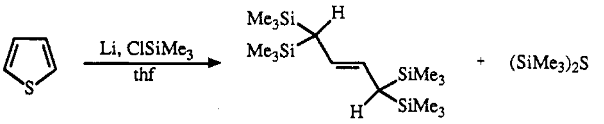


Figure 2. Molecular projection of (*Z*)-1,1,4,4-tetrakis(trimethylsilyl)but-2-ene (**5**) showing the labeling scheme of selected atoms for crystallographic purposes. Thermal ellipsoids are drawn at 20% probability level. Methyl hydrogens are omitted for clarity.

was not pursued further. It may be that high dilution is required for condensation of both **3** and **4** with Cl_2SiMe_2 to circumvent the formation of dimers, such as in **6**, trimers, and higher order products. The formation of oligomers from similar reactions with both dilithiated butenes and magnesium-butadienes have been noted elsewhere.[27]

The corresponding *E* isomer of **5** has been prepared[38] by the method

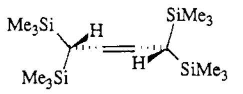


(mp 68 °C, cf. 92–93 °C for **5**); assignment of the *E* configuration was made solely on the basis of proton coupling constants observed in the non-first-order ^1H NMR spectra of the compound.

X-ray Structure. Compound **5** crystallizes with one molecule as the asymmetric unit, but close to C_2 symmetry (Figure 2). Important internuclear distances and angles are given in Table I. Considerable deviations are observed from the idealized (*Z*)-butene configuration as a result of the steric hindrance about the "cup" of the butene caused by the four large trimethylsilyl substituents. The sp^2 bond angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are both "opened up" to 130.6 (4) and 129.8 (4)°, respectively, with the dihedral angle C(1)–C(2)–C(3)–C(4) = 2.8°. The deviation of the H(1) and H(4) protons from the least-squares plane defined by C(1)–C(4) is measurable as the dihedral angles H(1)–C(1)–C(2)–C(3) and C(2)–C(3)–C(4)–H(4) (14.3 and 14.5°, respectively). The above three dihedral angles combine constructively to relieve steric buttressing of the trimethylsilyl substituents which is associated with H(1) and H(4) being in close proximity (2.49 (6) Å).

Both the Si(11)–C(1)–Si(12) and Si(41)–C(4)–Si(42) bond angles (115.8 (2) and 117.0 (2)°, respectively) are significantly larger than the standard sp^3 bond angle. This is a common feature of carbons bearing two trimethylsilyl groups[25] and is again in a consequence of relief from steric crowding. Of note is that all of the methyl carbon–silicon bond lengths are significantly shorter than the carbon–silicon bonds from the C(1) and C(4) carbons, and this is a consequence of the high thermal motion of these groups. All other geometries, including the C=C bond distance (1.320 (6) Å), are unexceptional.

The conformation of the carbons in $C_{1,4}$ positions of **5**, which is related to **6** in terms of the degree of steric hindrance around the allylic carbons, has repercussions for the structure of **6**. The most likely conformation of **6** is as shown, which despite the appearance would not contain notably short distances between the "internal" hydrogens and the π electrons of the double bonds.



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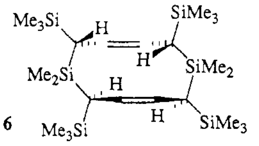

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Acknowledgment. We gratefully acknowledge support of this work by the Australian Research Council.

Supplementary Material Available: Lists of U_{ij} values, hydrogen atom parameters, and bond distances and angles for compound **5** (3 pages); a list of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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[38] Laguerre, M.; Dunogues, J.; Calas, N. D. e. R. *J. Organomet. Chem.* **1980**, *193*, C17.