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Structure of Dilithio-(*E*)-1,4-bis(trimethylsilyl)but-2-ene by X-ray Crystallography and ^{1}H–^{7}Li HOESY

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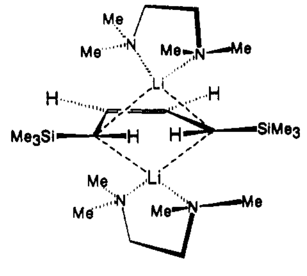
^{1}H–^{7}Li HOESY spectra of good spectral quality were obtained on $[\{Li(TMEDA)\}_2\{(Me_3SiCH{=}CH)_2\}]$ (1) and $[\{Li(TMEDA)\}_2\{(Me_3SiCH{=}CMe)_2\}]$ (2) in solution at room temperature. Fluxionality leads to motional averaging of the environment around the Li nucleus and consequently a reduction in the quadrupolar contribution to ^{7}Li relaxation. Measured ^{7}Li relaxation times in 1 and 2 were temperature dependent, but relatively long T_1 values (ca. 500 ms near ambient temperature) permitted the observation of ^{7}Li–^{1}H HOESY spectra. This is the first report of ^{7}Li–^{1}H HOESY NMR for obtaining structural information. X-ray diffraction data for 1 established a planar (*Z*)-butenediyl unit, with essentially double-bond character across C2 and C3 (1.34 (3) Å) and concentration of charge on the terminal carbons (Si–C1 = 1.76 (1) Å, C1–C2 = 1.47 Å), with the lithium atoms residing symmetrically over the vector between these carbon atoms. Crystals of 1 are orthorhombic, space group *Pbca*, $a = 10.711$ (1) Å, $b = 15.393$ (3) Å, $c = 19.941$ (3) Å, $V = 3287.8$ (9) Å^3, $Z = 4$. Cross-peak volumes for the Li-butenediyl fragment of 1 measured in ^{7}Li–^{1}H HOESY spectra in solution are consistent with the X-ray data. The combination of NMR spectroscopy and X-ray structural analysis established a double-bridging lithium structure with similar geometries for both 1 and 2.

Introduction

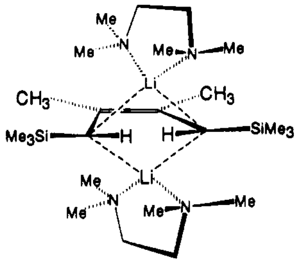
The structures of a number of lithiated carbanions, carboxylates, amines, ethers, enolates, and alkoxides have been investigated primarily by X-ray crystallography. However, lithium compounds are often fluxional in solution, and NMR methods (primarily lithium–proton HOESY: 2D heteronuclear Overhauser effect spectroscopy[1]) have proved to be powerful techniques for examining the structures of organolithium species in the solution state.[2] HOESY spectroscopy shows the nuclear Overhauser enhancement between a heteronucleus and protons where the nuclei are close in space. The size of the HOESY enhancements can be correlated to the lithium–proton distances, thus providing structural information about the position of lithiation and the geometry of the compound.

Lithium has two NMR-active isotopes ^{6}Li ($I = 1$, natural abundance 7.4%) and ^{7}Li ($I = {}^3/_2$, natural abundance 92.6%). Although ^{6}Li is the less abundant of the isotopes, it has a smaller quadrupole moment and consequently a longer relaxation time and narrower resonances than ^{7}Li. T_1 values for ^{6}Li are typically 1 order of magnitude larger than for ^{7}Li in analogous compounds. Proton–lithium HOESY studies which have been reported have employed ^{6}Li almost exclusively, with ^{6}Li enriched in most cases by chemical synthesis from labeled precursors.[3] Structural studies using ^{1}H–^{6}Li HOESY include the determination of relative distances between Li and parts of pyrrole and naphthalene compounds complexed to the lithium,[3,4] and also the location of lithium complexed with allylic systems.[4] ^{1}H–^{6}Li HOESY in conjunction with ^{13}C NMR measurements have been used to determine which of more than one possible ligating molecules in solution bind to the lithium nucleus.[5]

In most lithiated species, the observation of lithium-detected ^{7}Li–^{1}H HOESY is not possible because of rapid relaxation of the ^{7}Li nuclei. However in 1 and 2, ^{7}Li relaxation is relatively slow and it is possible to take advantage of the comparatively high natural abundance and sensitivity of ^{7}Li in recording ^{7}Li-detected NMR spectra.



(1)



(2)

In this paper we report an X-ray crystallographic study of (*Z*)-1,4-dilithio-1,4-bis(trimethylsilyl)but-2-ene (1)[6] and a structural investigation of 1 and (*Z*)-1,4-dilithio-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene (2)[6] (both as TMEDA adducts) by lithium-detected ^{7}Li–^{1}H HOESY.

Experimental Section

The compounds (*Z*)-1,4-dilithio-1,4-bis(trimethylsilyl)but-2-ene (1) and (*Z*)-1,4-dilithio-1,4-bis(trimethylsilyl)-2,3-dimethylbut-2-ene (2) were prepared by dimetalation of the corresponding but-2-ene by reaction with *n*-butyllithium in hexane in the presence of TMEDA.[6] The compounds were isolated and dissolved in deuterated solvents for NMR studies. Prismatic crystals of 1, suitable for X-ray crystallography were grown from hexane solution at −30 °C.

NMR Spectroscopy. NMR spectra were recorded using a Bruker AMX400 spectrometer, ^{1}H spectra were acquired at 400.13 MHz and ^{7}Li spectra at 155.5 MHz. The chemical shifts of ^{1}H spectra were referenced to residual solvent resonances, and ^{7}Li spectra were referenced to external LiNO$_3$ (1.0 M in H$_2$O). ^{7}Li

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† The University of Sydney.

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Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for 1[a]

bond	distance	bond	angle
C1–C2	1.49 (3)	C1–Si–C12	111.6 (6)
C2–C3	1.34 (3)	C1–Si–C11	114.7 (6)
C3–C4	1.45 (3)	C1–Si–C13	113.4 (5)
Si–C1	1.76 (1)	C12–Si–C11	104.7 (6)
Si–C12	1.87 (1)	C12–Si–C13	108.4 (6)
Si–C11	1.89 (1)	C11–Si–C13	103.4 (6)
Si–C13	1.88 (1)	Si–C1–C2	127 (1)
Li–C1	2.41 (2)	Si–C1–H1	121.4
Li–C2	2.30 (3)	C2–C1–H1	112
Li–C3	2.27 (3)	C1–C2–C3	125 (2)
Li–C4	2.36 (2)	C1–C2–H2	116
Li′–C2	2.23 (3)	C3–C2–H2	119
Li′–C3	2.23 (2)	C2–C3–C4	129 (2)
Li–N1	2.12 (2)	C2–C3–H3	116
Li–N2	2.13 (2)	C4–C3–H3	115
Li–H1	2.27	C3–C4–Si′	127 (1)
Li–H2	3.03	C3–C4–H4	114
Li–H3	2.99	Si′–C4–H4	118.7
Li–H4	2.24	N1–Li–N2	84.0 (7)
Li′–H1	2.24	C1–Li–C4	81.3 (6)
Li′–H2	2.96		
Li′–H3	2.96		
Li′–H4	2.33		
C1–H1	0.99		
C2–H2	1.02		
C3–H3	1.02		
C4–H4	1.05		

[a] C1 and C4 are symmetry related by the crystallographic inversion center.

T_1 values were measured using an inversion-recovery pulse sequence.[7] Phase-sensitive HOESY spectra were acquired using a $(\pi/2)_H$-τ_0-$(\pi/2)_H$-τ_m-$(\pi/2)_{Li}$ pulse sequence as previously described.[8] Typically, 32 scans for each of 256 experiments were acquired, with a relaxation delay of 2 s between scans. HOESY spectra were transformed with zero filling by a factor of 2 in both dimensions and exponential weighting functions in both dimensions (line broadening value of 1.0 Hz in ω_2 and 2.0 Hz in ω_1). Volume integration of cross peaks was achieved using the Bruker AMX software package.

X-ray Crystallography. A unique diffractometer data set was obtained using an Enraf-Nonius CAD4 diffractometer. Reflections with $I > 2.5\sigma(I)$ were considered "observed" and used in a full-matrix 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. 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[9] were employed; computation used the XTAL program system,[10] implemented on a SUN SPARCstation 2.

Results and Discussion

X-ray Structure of [{Li(TMEDA)}$_2${(Me$_3$SiCH=CH)$_2$}] (1). Compound 1 crystallizes with discrete molecules over inversion centers such that there is 50% site occupancy disorder associated with the H1, H2, H3, H4, C2, and C3 atoms of the planar (*Z*)-butenediyl moieties (Figure 1). Data were consistently weak from several crystals, and the accuracy of the structure is poor but nevertheless provides a meaningful solution. Refinement of the structure was based on a 50% disordered molecule across an inversion center, the disorder being confined to

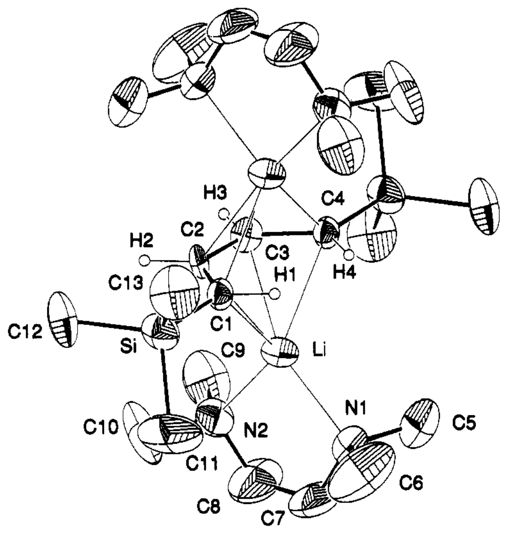

Figure 1. ORTEP (20% probability) plot of [{Li(TMEDA)}$_2${(Me$_3$SiCH=CH)$_2$}] (1). C1 and C4 are related by the crystallographic inversion center.

Table II. Atomic Coordinates, Thermal Parameters (U or U_{iso}) (Å^2) and Population Parameters (PP) for [{Li(TMEDA)}$_2${(Me$_3$SiCH=CH)$_2$}] (1)[a]

atom	*x/a*	*y/b*	*z/c*	*U*	PP
Li	0.101 (2)	0.550 (1)	0.5616 (7)	0.096 (7)*	
Si	0.1173 (3)	0.6296 (2)	0.3830 (2)	0.115 (1)*	
C1	0.056 (1)	0.5615 (8)	0.4461 (4)	0.074 (5)*	
C2	0.105 (2)	0.474 (2)	0.466 (1)	0.09 (1)*	0.5000
C3	−0.054 (2)	0.577 (1)	0.486 (1)	0.08 (1)*	0.5000
C11	0.010 (1)	0.6472 (9)	0.3087 (6)	0.230 (9)*	
C12	0.264 (1)	0.5838 (8)	0.3460 (6)	0.179 (7)*	
C13	0.151 (1)	0.7432 (7)	0.4129 (7)	0.187 (7)*	
C5	0.371 (1)	0.568 (1)	0.5450 (8)	0.21 (1)*	
C6	0.315 (2)	0.453 (1)	0.618 (1)	0.28 (1)*	
N1	0.2859 (9)	0.5399 (9)	0.5978 (5)	0.130 (5)*	
C7	0.294 (2)	0.601 (2)	0.653 (1)	0.23 (1)*	
C8	0.201 (2)	0.655 (1)	0.664 (1)	0.25 (1)*	
N2	0.083 (1)	0.6470 (7)	0.6377 (5)	0.124 (5)*	
C9	0.048 (2)	0.729 (1)	0.6082 (8)	0.20 (1)*	
C10	−0.011 (2)	0.624 (1)	0.6868 (7)	0.223 (8)	
H1	−0.0191	0.5784	0.4723	0.110	0.5000
H2	0.1821	0.4536	0.4409	0.093	0.5000
H3	−0.0974	0.6347	0.4783	0.105	0.5000
H4	0.1005	0.5019	0.4557	0.110	0.5000

[a] C1 and C4 are symmetry related by the crystallographic inversion center. Asterisks refer to U_{iso} values.

Table III. Summary of X-ray Data for [{Li(TMEDA)}$_2${(Me$_3$SiCH=CH)$_2$}] (1)

formula	$C_{22}H_{54}N_4Li_2Si_2$
mol wt	444.8
space group	*Pbca* (No. 61)
a, Å	10.711 (1)
b, Å	15.393 (3)
c, Å	19.941 (3)
V, Å^3	3287.8 (9)
Z	4
D(calcd), g cm^{-3}	0.899
F(000)	992
cryst dimens, mm	0.35 × 0.35 × 0.35
temp, K	296
radiation (λ, Å)	Mo Kα (0.71073, graphite monochromator)
μ, cm^{-1}	1.22 (no abs corr applied)
2θ limit, deg	40
no. of collcd reflns	2885
no. of obsd rflns [$I > 2.5\sigma(I)$]	569
R	0.052
R_w	0.052
final residue, e Å^3	0.8
s	1.74

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the C2 and C3 atoms of the butenediyl fragment and its associated H atoms. All H atoms were calculated in idealized positions at a distance close to 1.0 Å from the parent carbon atom. Molecular core geometries, atom coordinates, and crystal data are given in Tables I-III.

Important internuclear distances and angles are given in Table I. Distances within the butenediyl fragment [C2–C3, 1.34 (3) Å; C1–C2, 1.49 (3) Å; C4–C3, 1.45 (3) Å; C1–Si, 1.76 (1) Å] support localization of negative charge at C1 and C4, in accordance with the NMR data ($\delta(^{13}C)$ for C1 and C4, 23.6 ppm in 1, and similarly $\delta(^{13}C)$ for C1 and C4, 27.8 ppm for compound 2),[6] and the concentration of charge by silicon on adjacent carbon centers.[11,12] Indeed, the C–C distances are close to corresponding values for (*Z*)-1,1,4,4-tetrakis(trimethylsilyl)but-2-ene, where the comparable distances are C1–C2 1.486 (6) and 1.495 (6) Å and C2–C3 1.320 (6) Å and the angles subtended by the carbons on C2 and C3 are 130.6 (4) and 129.8 (4)°,[6] cf. 125 (2)° for C1–C2–C3 and C2–C3–C4, respectively in 1.

The overall molecular geometry approximates to C_{2v} symmetry, as expected for the so-called double-bridging dilithium structure,[12-14] being similar to established structures for dilithiated 1,4-diphenylbutadiene,[14] 1,2-bis((trimethylsilyl)methyl)benzene,[15] and also the related dilithiohexatrienyl species.[16] Concentration of charge by electropositive silicon, coupled with the direction of occupied *p* orbitals on C1 and C4, would direct lithium atoms to reside symmetrically over the internuclear vector between C1 and C4. Li–C1,C4 distances are 2.41 (2) and 2.36 (2) Å and thus provide some scope for covalency although this conflicts with the generally accepted view that lithium–carbon bonding is largely ionic.[17] Such a disposition of lithium atoms would result in intimate contact between them and C2 and C3, at 2.30 (3) and 2.27 (3) Å, respectively, with the lithiums 1.81 Å from the butenediyl plane.

NMR Spectroscopy. At 25 °C, the resonances in the ^7Li NMR spectra of both 1 and 2 are relatively narrow ($W_{1/2}$ = 2–5 Hz, at δ −4.41 and δ −4.63 ppm, respectively, in benzene-d_6 solvent). For both 1 and 2, the ^7Li resonance exhibits a resolved triplet splitting ($^2J_{Li-H} \approx 1.5$ Hz) to the terminal vinyl protons of the butadiene fragment[6] (verified by selective ^1H decoupling). The presence of the clearly resolved through-bond Li–H coupling confirms that the lithium atoms are intimately bound to the organic framework in a covalent fashion.

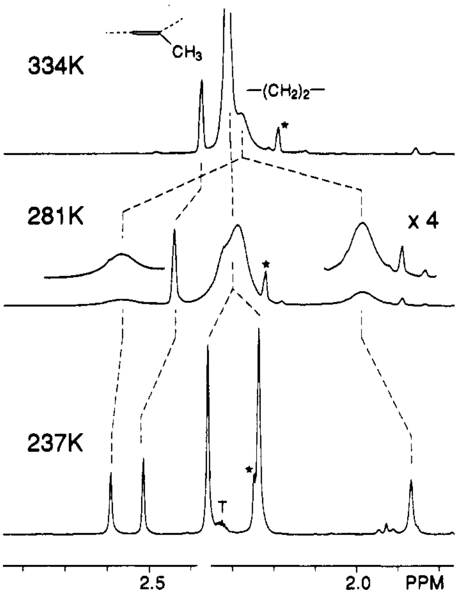
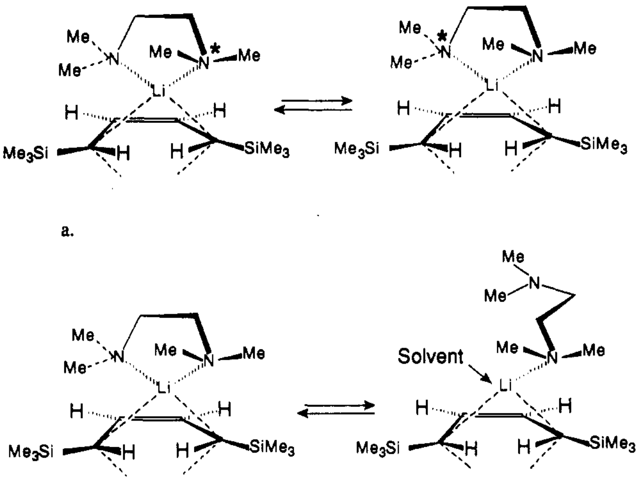


Figure 2. Section of the ^1H NMR (400 MHz, toluene-d_8 solvent) spectrum of $[\{Li(TMEDA)\}_2\{(Me_3SiCH{=}CMe)_2\}]$ (2) at various temperatures. T indicates solvent residual; * unidentified impurity.

Scheme I



The ^1H NMR spectrum of 1 in benzene-d_6 at 27 °C exhibits a strong 18-proton singlet at 0.38 ppm, a broadened 2-proton doublet at 0.29 ppm for the terminal vinylic protons, and a broadened 2-proton multiplet at 5.07 ppm for the 2,3-protons of the butadiene fragment. The resonances of two coordinated TMEDA molecules appear only as two broadened singlets at 2.05 and 1.81 ppm for the N–CH_3– and –CH_2– groups, respectively. The ^1H NMR spectrum of 2 in benzene-d_6 at 27 °C exhibits a strong 18-proton singlet at 0.42 ppm, a broadened 2-proton singlet at 0.37 ppm for the terminal vinylic protons, and a broadened 6-proton singlet at 2.22 ppm for the methyl protons at the 2,3-positions of the butenediyl fragment. As for 1, the resonances of two coordinated TMEDA molecules occur only as two broadened singlets at 2.03 and 1.76 ppm for the N–CH_3– and –CH_2– groups, respectively.

The ^1H NMR spectra of 1 and 2 acquired at ambient temperature clearly indicate exchange broadening of the resonances of the coordinated TMEDA units. The ^1H NMR spectrum of 2 was examined at several temperatures with toluene-d_8 as solvent; the resonances of the coordinated TMEDA groups broaden and split from two signals to four on cooling to −50 °C (Figure 2). This behavior is consistent with an internal process which differentiates the two ends of the coordinated TMEDA ligands, e.g. the slowing of the internal rotation of the TMEDA groups (Scheme Ia) or reversible decomplexation of one end of the TMEDA fragment (Scheme Ib), perhaps with solvent occupying the vacant coordination site on Li or with the Li atom stabilized by interaction with the π-system of the C2–C3 bond of the butenediyl fragment. Dynamic effects

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which average the NMR spectra of coordinated TMEDA groups have been noted previously in organolithium compounds.[18a-c] Lithium species undergoing reversible loss of one end of a polydentate tertiary amine ligand have been invoked previously as intermediates in ligand-exchange reactions,[18d] but this is not the favored dynamic process in the related compound *exo,exo*-[1,3-bis(trimethylsilyl)-allyl]lithium(TMEDA).[18e] At all temperatures, only one set of butenediyl proton resonances or ^{7}Li resonances is observed, indicating that the observed dynamic process is not the result of equilibration between several different species in solution.

Relaxation of the ^{7}Li Nuclei. The relaxation time of a quadrupolar nucleus is goverened by a number of factors, including the quadrupole moment, the rotational correlation time of the molecule, and the electric field gradient across the nucleus. The quadrupole moment of the ^{7}Li nucleus provides an efficient relaxation mechanism for the nucleus, and the quadrupolar contribution to relaxation (T_q) dominates T_1 for ^{7}Li (eq 1), where eq is the electric

$$1/T_q \propto (1 + \eta^2/3)(e^2qQ/h)^2\tau_c \qquad (1)$$

field gradient at the ^{7}Li nucleus, η is an asymmetry parameter which represents the distortion of the electric field gradient at the nucleus from axial symmetry, eQ is the nuclear electric quadrupole moment, and τ_c is the rotational correlation time.

The spin-lattice relaxation times for ^{7}Li nuclei are typically short (0.1–1 ms)[2] particularly when the nucleus is in an environment with a nonsymmetrical electric charge distribution. For a nucleus whose T_1 is dominated by quadrupolar relaxation, the temperature dependence of T_1 is governed essentially by the effect of temperature on τ_c, i.e. increasing monotonically as temperature increases. The measured relaxation time of the ^{7}Li nucleus in 2 shows a significant temperature dependence, with T_1 ranging from approximately 100 ms at −50 °C to more than 500 ms at 30 °C.

At temperatures above ca. 20 °C, the measured T_1 for the ^{7}Li nucleus in 2 is approximately 500 ms, which is an unexpectedly large value for a quadrupolar ^{7}Li nucleus. The slow relaxation rate at high temperature can be rationalized by a change in the symmetry of the lithium environment to one of higher average symmetry as the temperature increases.

^{1}H–^{7}Li HOESY Spectra of 1 and 2. The relative intensities of the cross peaks in a HOESY experiment are determined by the competition between the NOE buildup and the decay of signal via relaxation, so the rapid relaxation rates of most ^{7}Li nuclei in most organic compounds precludes observation of useful NOE. However, for 1 and 2, the T_1 values of ca. 500 ms at room temperature are adequate for the observation of NOEs. In HOESY experiments on 1, strong cross peaks were observed between the ^{7}Li nucleus and the vinylic protons (H2, H3) of the *cis*-butenediyl subunit as well as between the ^{7}Li nucleus and both CH_2 and CH_3 protons of the TMEDA subunits (Figure 3). The strongest interactions were with the terminal protons (H1 and H4) of the butenediyl fragment. No HOESY cross peaks were observed for the interaction of ^{7}Li and the methyl protons of the TMS substituents.

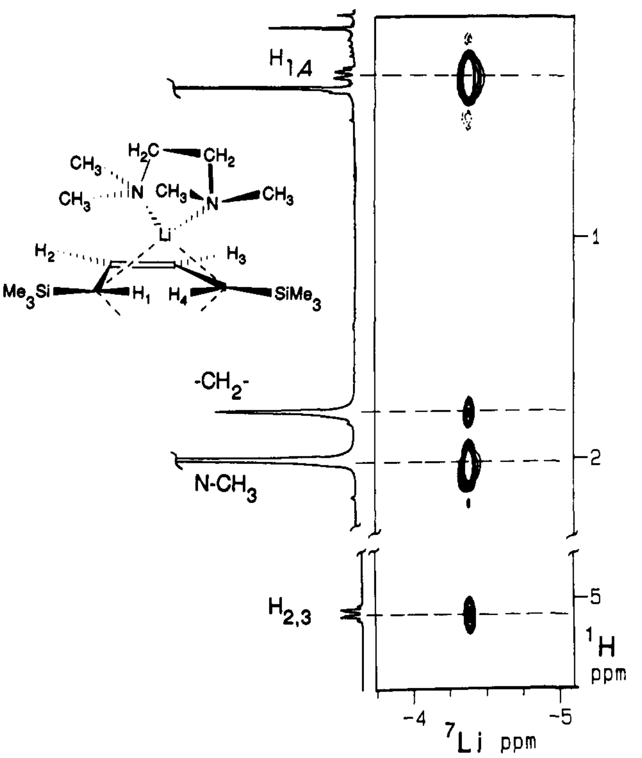

Figure 3. ^{7}Li-detected H–Li HOESY spectrum of 1 (benzene-d_6 solvent, 298 K). Solid contours are positive peaks.

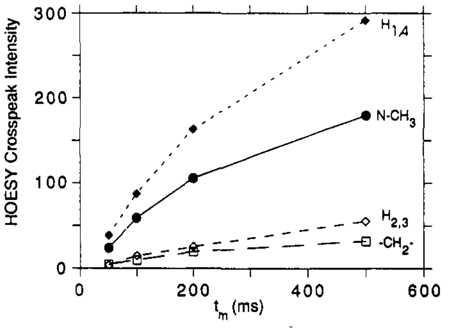

Figure 4. Buildup of HOESY cross-peak intensity as a function of mixing time (τ_m) in the ^{7}Li-detected H–Li HOESY spectrum of 1 (benzene-d_6 solvent, 298 K).

The internuclear distance between the Li nucleus and the protons of the TMS substituents is greater than 5.5 Å, and at this distance, no observable cross peaks would be expected. In Figure 3, the small negative lobes are processing artefacts.

The measured dependence of the HOESY cross-peak intensity on the mixing time (τ_m) for 1 is given in Figure 4. For values of τ_m up to 500 ms, the relative rates of buildup of HOESY cross-peak intensity are approximately constant and the same within experimental error for the various protons in the molecule. This indicates that transfer of magnetization by spin diffusion is negligible.[19]

Strong HOESY cross peaks for 2 were observed between ^{7}Li and the terminal protons (H1 and H4) as well as between ^{7}Li and the methyl substituents at C2 and C3 of the *cis*-butenediyl fragment. All protons on the TMEDA subunits gave rise to HOESY cross peaks using a mixing time of 200 ms.

Internuclear Li–H Distance Ratios Derived from ^{1}H–^{7}Li HOESY. NOESY (HOESY) cross-peak intensities

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Table IV. Experimental HOESY Cross-Peak Volumes for 1 and 2

	rel cross-peak vol[a]	scaled cross-peak vol[b] (σ_{ij})
	Compound 1	
H(1,4) → Li	871	871
H(2,3) → Li	135	135
CH_2 → Li	100	62.5
N–CH_3 → Li	556	301
	Compound 2	
H(1,4) → Li	1348	1348
CH_3(2,3) → *Li*	138	92
CH_2 → Li	100	62.5
N–CH_3 → Li	688	373

[a] Arbitrarily normalized to CH_2 → Li = 100 units; for 1 relative cross-peak volumes are the average over τ_m = 50, 100, 200, and 500 ms; for 2 relative cross-peak volumes are from a single experiment with τ_m = 200 ms. [b] Scaling factor $N_IN_S/(N_I + N_S)$ (see text).

(σ_{ij}) are inversely proportional to the sixth power of the internuclear distances (r_{ij}),[19] and the measured cross-peak volumes are given in Table IV. The intensities of the HOESY cross peaks were scaled to account for symmetry in the molecule which dictates that different numbers of nuclei contribute to different cross peaks.[19,20] For N_I spins of type *I* interacting with N_S spins of type *S*, the intensity of a NOESY cross peak due to interaction between *I* and *S* is proportional to $N_IN_S/(N_I + N_S)$.[20] For 1, the relative cross-peak volumes are the mean values determined from experiments with four different mixing times, and for 2, the results quoted are derived from a single experiment with a mixing time of 200 ms. Although the internal motion of the TMEDA subunits in 1 and 2 makes the quantitative interpretation of HOESY cross peaks to nuclei in that part of the molecule difficult, the Li-butenediyl core shows no evidence of fluxionality or exchange.

In complex 1, the ratio of $(\sigma_{\text{Li-H1(4)}})^{1/6}:(\sigma_{\text{Li-H2(3)}})^{1/6}$ (inversely proportional to the ratio of distances $r_{\text{Li-H1(4)}}:r_{\text{Li-H2(3)}}$) is 1.36, in excellent agreement with the value of 1.31 derived from distances in the X-ray crystal structure (Table I). This result suggests that the ^{1}H–^{7}Li HOESY can provide useful geometric information about the location of the ^{7}Li nucleus with respect to organic fragments in organolithium complexes. The HOESY cross peaks between Li and protons of the TMEDA are also consistent with the distances of a lithium-coordinated TMEDA. It is not possible to confidently assign quantitative significance to any distance information derived from the TMEDA part of the molecule since it is obviously fluxional and an interpretation of the HOESY cross-peak intensity would require a detailed knowledge of the exchange process.

In complex 2, the ratio of $(\sigma_{\text{Li-H1(4)}})^{1/6}:(\sigma_{\text{Li-Me2(3)}})^{1/6}$ (which is inversely proportional to ratio of distances $r_{\text{Li-H1(4)}}:r_{\text{Li-Me2(3)}}$) is 1.55. With the assumption that the Li–H1(4) distance in 2 is similar to that in 1, (2.27 Å; Table I) the intensity of the HOESY cross peak between the Li nucleus and the 2,3-methyl groups of the *cis*-butenediyl subunit indicates a Li–CH_3 distance of approximately 3.5 Å. The position of CH_3 groups is difficult to define from NOE data, but it has been shown in small molecules that the methyl position determined by NOE measurements is approximately that of the centroid of the methyl protons.[20,21] The geometry and dimensions of the methylated derivative 2 are essentially the same as those in the parent complex 1.

Conclusions

^{1}H–^{7}Li HOESY spectra of good spectral quality have been obtained on [{Li(TMEDA)}$_2${(Me$_3$SiCH=CH)$_2$}] (1) and [{Li(TMEDA)}$_2${(Me$_3$SiCH=CMe)$_2$}] (2) in solution near room temperature. Although ^{7}Li is typically a difficult nucleus on which to obtain nuclear Overhauser enhancements, fluxionality in this type of molecule leads to motional averaging of the environment around the Li nucleus and consequently a reduction in the quadrupolar contribution to ^{7}Li relaxation. Measured ^{7}Li relaxation times in 1 and 2 were temperature dependent, but relatively long T_1 values (ca. 500 ms near ambient temperature) permit the observation of HOESY spectra.

X-ray structural data on 1 clearly established a double-bridging lithium structure. ^{1}H–^{7}Li HOESY experiments indicate that the solution structure of 1 is consistent with the structure found in the solid-state X-ray structure and that 1 and 2 have similar structures. For the related compound, [1,2-C$_6$H$_4$(CHSiMe$_3$)$_2${Li(TMEDA)}$_2$],[15] the Li–C distances (2.37 (2) and 2.38 (2) Å for C1–C4 and C2–C3, respectively) are significantly longer than in 1, indicating more ionic character. This is also reflected in C–C distances of the dianion which is consistent with greater charge delocalization, C1–C2 1.43 (2) Å (cf. 1.47 Å (mean) in 1) and C2–C3 1.45 (1) Å (cf. 1.34 (3) Å in 1), with other C–C distances in the ring ranging from 1.36 (2) to 1.43 (2) Å. This structure is best described as a contact ion pair system with the lithium atoms residing over nodes in the HOMO of the dianion.[22] The position of the Li nuclei relative to the four carbon atoms of the bridging *cis*-but-2-ene-1,4-diyl subunit indicates that the 1,4-dilithiobut-2-ene-1,4-diyl complexes prefer dibridging structures, as predicted by ab initio and semiempirical MNDO calculations.[13,14]

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Supplementary Material Available: Lists of hydrogen atom parameters, U_{ij} values, and bond distances and angles for compound 1 (4 pages). Ordering information is given on any current masthead page.

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