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[1-(Trimethylsilyl)allyl]lithium: Structure in Solution and Rotational Barriers

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Abstract: NMR data show that the title compound, **10**, exists in a variety of media exclusively in the exo form. NOE experiments, $^{6}\text{Li}\{^{1}\text{H}\}$, indicate that ^{6}Li is near the C_1 and C_3 of the allyl moiety and far from C_2. The complex of **10** with *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA) is concluded to exist as two monomeric tridentately coordinated contact ion pairs with lithium near C_1 or C_3. Rotation of coordinated Li^+ in these complexes with respect to the allyl loop is slow at 150 K and $\Delta H^{\ddagger}$ is 7.7 kcal. Barriers to rotation about the $CHCH_2$ bond depend critically on solvent varying between 11 and 17 kcal.

(Allyl)lithium and structural variations thereof are the simplest potentially conjugated of organometallic compounds. They have been variously described, leaving out aggregation, as anything from symmetrical ionic or bridged to unsymmetrical covalent with all manner of variations in between,[1] **1–4**, as inferred from the results of extensive NMR,[2,3] crystallographic[4] calculational[5] and chemical investigations.[6]


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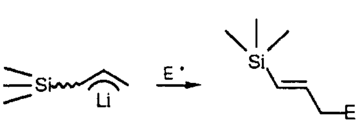
Stabilization of carbanionic species by directly bonded silicon is well known[7] though how this comes about, whether by silicon conjugation (3d or 3p) or polarization effects or some combination thereof, is still a controversial subject.

[1-(Trimethylsilyl)allyl]lithium (**5**) was first reported by the groups of Corriu[8] and Magnus[9] and Chan[10] who carried out numerous reactions with electrophiles obtaining almost always trans products,[9] **6**, addition having taken place at C_3 in contrast to (1-alkylallyl)lithiums which gave mixtures of cis, trans, and vinyl products,[11,12] **7–9**. The regiospecificity of the reactions of **5** may but does not necessarily imply that the reagent exists as the exo structure, **10**. To obtain some insight into these problems this paper reports an NMR investigation of [1-(trimethylsilyl)allyl]lithium.



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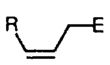
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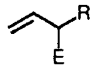
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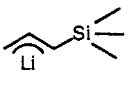
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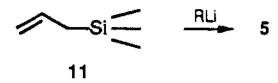
Results and Discussion

Metallation of 3-(trimethylsilyl)propene (**11**) was accomplished by (*sec*-butyl)lithium in THF at −78 °C, with or without 1 equiv of TMEDA,[9] as well as at room temperature with (butyl)lithium-^{6}Li in diethyl ether or in pentane with 1 equiv of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDTA). The reactions in THF always produced a small amount, ca. 5%, of lithium acetaldehyde enolate via cleavage of THF. The resulting solutions were evaporated at reduced pressure to remove volatile compounds and the residues dissolved in THF-d_8, diethyl-d_{10} ether, or cyclopentane-1,2-d_2 for NMR investigation.



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Proton and ^{13}C NMR data for **5** in different media are listed in Tables I and II. Below 260 K the allyl protons in all samples

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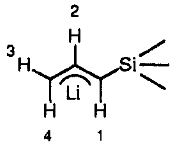
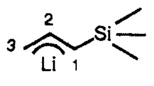
Table I. Proton NMR (300 MHz) Data for **10** at 300 K in Different Media



	δ, ppm					J, Hz			
	H_1	H_2	H_3	H_4	CH_3Si	H_1, H_2	H_2, H_3	H_2, H_4	H_3, H_4
THF, + 1 equiv of PMDTA	2.09 (7)	6.40	2.70 (3)	2.83 (6)	−0.12 (0)	15.1	8.6	15.1	2.8
diethyl ether	1.96 (5)	6.43	2.74 (3)	2.84 (4)	−0.10 (0)	15.1	8.8	15.1	2.8
diethyl ether + 1 equiv of THF	1.96 (5)	6.30	2.56 (8)	2.70 (4)	−0.13 (0)	15.7	8.6	15.1	2.8
THF + 1 equiv of TMEDA	2.08	6.37	2.470	2.68 (0)	−0.08 (0)	15.7	8.6	15.0	2.7

Table II. ^{13}C NMR Shifts, δ, of **10** in Different Media



	C_1	C_2	C_3	$Si(CH_3)_3$
cyclopentane-d_2 + 1 equiv of TMEDA, 297 K	55.4	148.9	61.3	2.33
diethyl ether + 1 equiv of THF, 297 K	53.8	148.3	62.0	1.3
THF-d_8 + 1 equiv of PMDTA, 297 K	53.7	149.6	62.5	2.9
THF-d_8 + 1 equiv of PMDTA, 173 K	51.7	148.19	62.1	3.22
THF-d_8 + 1 equiv of TMEDA, 297 K	54.8	149.4	62.9	2.7
THF-D_8 + 1 equiv of TMEDA, 203 K	56.8	150.1	60.0	2.9

Table III. $^6Li\{^1H\}$ NOE (%) Enhancements in **10**

	T, K	H_1[a]	H_2	H_3	H_4
THF-d_8 + 1 equiv of PMDTA	250	34	0	56[b]	56[b]
diethyl-d_{10} ether	200	21	0	28	25

[a] For numbering see Table I. [b] H_3 and H_4 together.

give rise to typical ABXY spectra for H_4, H_3, H_2, and H_1, respectively (see Table I). Shifts are assigned on the basis that H_2 is always the most deshielded proton, as widely reported in the literature:[2,3] the ^3J(vic,trans) value greatly exceeds the ^3J(vic,cis) value and both of these are larger than $^4J(H_3,H_4)$, 2.8 Hz. Note that proton geminal coupling is rarely observed among main group allylmetal compounds. Each sample gives rise to a single spectrum. The shifts vary relatively little between 150 and 350 K or among samples in different media. Within this temperature range all samples exhibit a $^3J(H_1,H_2)$ vicinal coupling of 15 to 15.8 Hz, depending on medium, implying a trans relationship between those protons and that the trimethylsilyl group is always exo with respect to the allyl skeleton, **10**. In contrast most (1-alkylallyl)lithiums are reported to consist of mixtures of exo and endo isomers with the latter favored by 2 to 3 kcal/mol.[11,12] Vicinal couplings also assign the shift of H_4 (endo), the latter always being deshielded with respect to H_3 (Table I).

The ^6Li NMR of **10** consists of one sharp line at all temperatures between 150 and 320 K. Proton-^6Li NOE experiments, $^6Li\{^1H\}$, were carried out with samples of **10** enriched 96% in ^6Li (see Experimental Section) to assign those protons nearest to lithium. As seen in Table III the only significant ^6Li resonance enhancements were observed on irradiating H_1 or H_3 and H_4, the carbon sites of maximum electron density. In the PMDTA complexes of **10** at 200 K there is a significant preference for ^6Li to be near C_3, methylene. Note that the shifts for H_3 and H_4 are close enough such that they cannot be irradiated separately. Hence ^6Li NMR shows enhancement from H_3 and H_4 together even though the larger enhancement most likely comes from H_4 alone. Also since these proton irradiations take 10 s, rotation renders enhancements for both H_3 and H_4. It is also not surprising that the ^6Li resonance is enhanced on irradiating the $(CH_3)_2N$ protons of PMDTA.

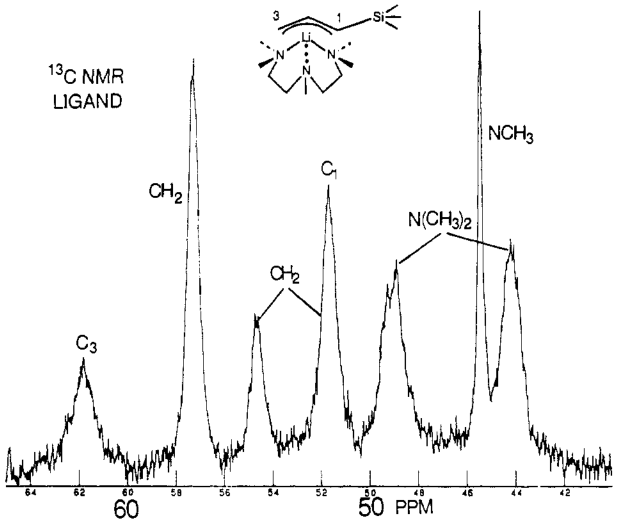


Figure 1. ^{13}C NMR, 75.44 MHz, of 0.4 M **10**·PMDTA in THF-d_8, 155 K, showing C_1, C_3 of **10** and PMDTA resonances.

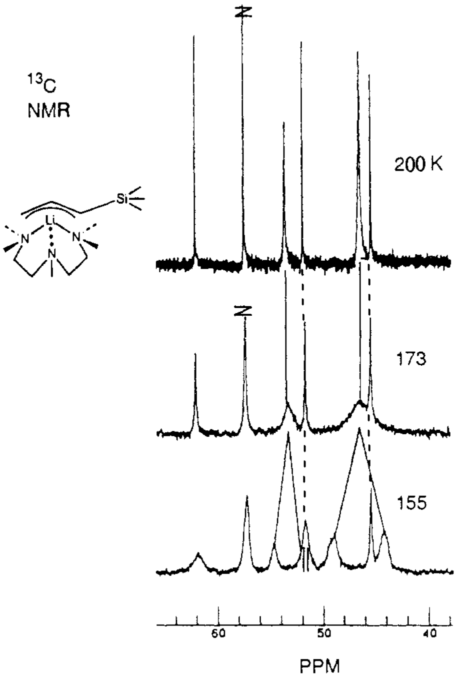


Figure 2. As in Figure 1 at different temperatures (K).

Figure 1 shows the PMDTA portion of the ^{13}C NMR spectrum, of **10** in THF with one eq of PMDTA at 155 K. Free PMDTA is not detected in this spectrum[13,14] and from the relative peak

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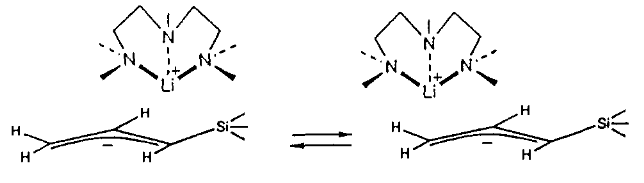
(13) ^{13}C NMR of PMDTA, 150 K, $CDCl_3$, δ, CH_2 57.36 and 58.20, NCH_3 43.05, $N(CH_3)_2$ 46.12, ref 15.

(14) Fraenkel, G.; Chow, A. S.; Winchester, W. R. *J. Am. Chem. Soc.* **1989**, in Press.

areas it is apparent that there is a 1:1 complex of **10** with PMDTA. The latter gives rise to fine structure in the ^{13}C NMR spectra, implying this ligand is unsymmetrically disposed with respect to the allyl moiety. There are two $N(CH_3)_2$ ^{13}C resonances of equal intensity at δ 44.15 and 48.83, one CH_3N peak at δ 45.38, and CH_2 peaks at δ 51.61, 54.68, and 57.16, respectively, 1:1:2. Note also that the 51.61 peak overlaps with the absorption for C_1 of **10**. As seen in Figure 2 by 173 K there is signal averaging, discussed below, of the $(CH_3)_2N$ doublet to δ 46.65 and the 1:1 methylene doublet to δ 53.22, the other resonances remaining unchanged. The PMDTA part of the spectrum undergoes no further changes up to 297 K. Then it is clear that the 1:1 complex **10**·PMDTA persists up to at least 297 K, no free PMDTA being detected at this temperature either. Taken together these results favor a tridentately complexed monomeric **10** in which the PMDTA is disymmetrically sited with respect to the silylallyl moiety and that rotation of the solvated Li^+ is slow with respect to the NMR time scale at the lower temperatures observed. Similar effects were observed by us for the monomeric TMEDA complex of [*exo*,*exo*-bis(1,3-trimethylsilyl)allyl]lithium[14] and for the monomeric complex of PMDTA with (neopentyl)lithium.[15]

A proposal for the structure of **10**·PMDTA must also take into account the proximity of Li^+ to H_1 and H_3–H_4 but not H_2 deduced from the NOE experiments and the observation that most crystallographic structures of other (allyl)lithiums[4] place lithium perpendicular to the allyl plane. Then consistent with the latter structure and the results described above, **10**·PMDTA is best described as an equilibrium ca. 1:1 mixture of two monomeric contact ion pairs (required by the NOE data) in which solvated Li^+ is located normal to the allyl plane alternately above C_1 or C_3, see **10A** ⇌ **10B**. One must assume that these species are interconverting rapidly, even at 150 K, yet in each the rotation of PMDTA-coordinated Li^+ is slow relative to the NMR time scale, i.e. the shifts among the $N(CH_3)_2$ and CH_2 carbons in complexed PMDTA. This system should still exhibit four nonequivalent $N(^{13}CH_3)_2$ methyls. That it only shows two is most likely the result of a fast inversion at the dimethylamino nitrogens (see the account of ^{13}C NMR line shape analysis below).



10A **10B**

This model is also consistent with the greater sensitivity of the ^{13}C C_1 shift to ligand, compared to that for C_3, due to the proximity of the ligand in **10B** to the bulky TMS group (see Table II).

NMR spectra of **10** solvated by potential ligands such as TMEDA, diethyl ether, or THF provided less information on the nature of solvation than did those of **10**·PMDTA. The ^{13}C and proton resonance of contained TMEDA in the sample of **10** in THF with 1 equiv of TMEDA had the same spectrum as the free diamine, implying only THF is complexed to lithium. However, use of bulk THF as solvent precludes observation of a separate resonance for bound THF due to the probable fast exchange of THF between its bound and free sites.

The ^{13}C resonances for PMDTA in the **10**-PMDTA complex show a striking resemblance to those seen in the monomeric tridentate complex of PMDTA with (neopentyl)lithium.[15] In the latter species all but two ligand carbons are magnetically nonequivalent, two methylenes at δ 57.38. Thus there are four dimethylamino methyls at 43.78 (a), 44.75 (b), 47.69 (c), and 49.98 (d), two methylenes at 51.78 (e) and 54.58 (f), all of the same intensity and in δ units. Between 160 and 200 K there is signal averaging of peaks a with c and b with d as well as e with f (the 1:1 methylene peaks), all ascribed to rotation about the C–Li bond. Above 200 K there is further averaging of the resulting a–c with b–d resonances, respectively, phenomenologically, inversion at $N(CH_3)_2$, much slower than the rotation process just described. If inversion were the *faster* process then there would be averaging of peaks a with b and c with d at the lower temperature, giving rise to peaks at δ 44.27 and 48.83, respectively. These values are remarkably close to the dimethylamino methyl ^{13}C resonances of **10**·PMDTA, 155 K, at δ 44.15 and 48.83. Further the 1:1 *N*-methylene resonances of **10**·PMDTA at δ 54.68 and 51.61 match perfectly with those for (neopentyl)lithium·PMDTA at δ 54.58 and 51.78. These observations lend support to the proposal that the two broadened dimethylamino methyl resonances are the result of fast inversion at dimethylamino nitrogens, fast at 155 K.

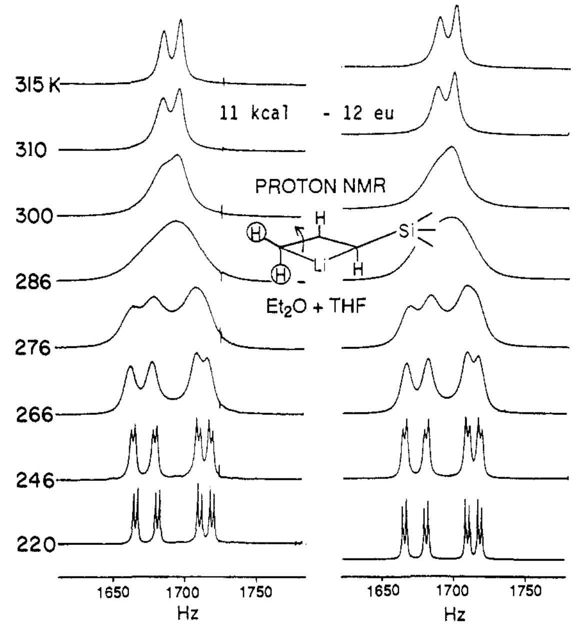


Figure 3. (Left) Proton NMR (MHz) CH_2 of **10**, 0.4 M in diethyl ether with 1 equiv of THF at different temperatures, K; (right) calculated line shapes with first-order rate constants.

Table IV. Barrier to Rotation about the C_2C_3 Bond in **10**

	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
diethyl ether + THF	10.8	−12
diethyl ether	14	4.3
THF + 1 equiv of PMDTA	17.1	2
THF + 1 equiv of TMEDA	14.3	0

The signal averaging of the $N^{13}CH_2$ and $N(^{13}CH_3)_2$ doublets of **10**-PMDTA to single lines at their respective centers was subjected to NMR line-shape analysis. Each doublet was simulated separately as an uncoupled two-half-spin system undergoing mutual exchange. The results are necessarily approximate due to overlapping peaks from ^{13}C and $N^{13}CH_3$. Thus we find for methylene $\Delta H^{\ddagger}_{CH_2}$ = 8.7 kcal and $\Delta S^{\ddagger}_{CH_2}$ = 7 eu while for N-$(^{13}CH_3)_2$ the activation parameters are $\Delta H^{\ddagger}_{CH_3}$ = 7.7 kcal and $\Delta S^{\ddagger}_{CH_3}$ = 2 eu. The exchange rates are similar enough to imply that one mechanism must be responsible for all these just described effects. Hence we would like to propose that this process is the rotation of coordinated Li^+ with respect to the 1-(trimethylsilyl)allyl anion. Two other examples of similar effects reported from these laboratories are the rotations about the C–Li bond in (neopentyl)lithium–PMDTA monomer[15] and of coordinated lithium with respect to a 1,3-disilylallyl anion in [*exo*,*exo*-1,3-bis(trimethylsilyl)allyl]lithium–TMEDA in diethyl-d_{10} ether.[14] The $\Delta H^{\ddagger}$ for both processes are also 7.7 kcal.

Dynamic effects are also seen in the proton NMR spectra of **10** in different media. Above 260 K with increasing temperature there is progressive but not complete averaging of the shift between H_3 and H_4 and of the vicinal cis coupling, $J(H_2,H_3)$, with $J(H_2,H_4)$, vicinal trans (see Figure 3), all due to increasing rates

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[15] Fraenkel, G.; Winchester, W. R. *J. Am. Chem. Soc.* **1988**, *110*, 8720.

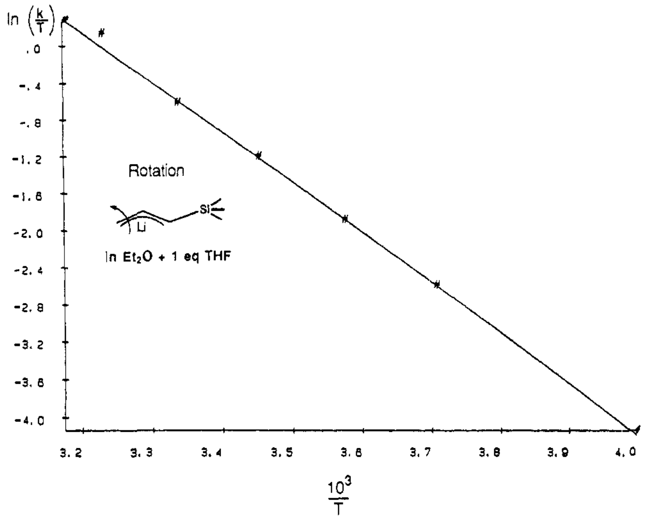

Figure 4. Eyring plot, rotation about the C_2–C_3 bond in **10**, as described in Figure 3.

of rotation about the C_2–C_3 bond. Comparison of these spectra with NMR line shapes calculated as a function of the rate of rotation about the C_2–C_3 bond yields the first-order rate constants, the activation parameters being listed in Table IV; a typical Eyring plot is shown in Figure 4.

The barriers to rotation in **10** vary widely with medium reminiscent of the barriers in allylmetal compounds in THF reported by Thompson and Ford,[3c] which increase in the progression (kcal/mol) 10.7, 16.7, and 18 for M = Li, K, and Cs. Several authors have commented[3] that the transition state for bond rotation in an allylmetal compound proceeds through a more covalent carbon metal bond or tighter ion pair than exists in the ground state. Then metals with larger effective diameters would be associated with higher barriers to rotation. Such should certainly be the case for **10**·PMDTA, most likely a monomeric ground-state ion pair wherein PMDTA has increased the effective size of the lithium. Of the other species in Table IV the THF solution most likely contains monomers, whereas that in diethyl ether is probably dimeric.[2,3,6,16] Further comment on the significance of these barriers must await definitive molecular weight measurements.

In sum this work has established that a (1-silylallyl)lithium exists in the exo structure and that solvated lithium is located near the ends of the allyl loop in two ion paired species that are in rapid equilibrium. In the case of **10** solvated by triamine PMDTA the rotation of coordinated Li^+ with respect to the allyl loop inside the ion pair is slow relative to the NMR time scale at 150 K, as previously observed for [1,3-bis(trimethylsilyl)allyl]lithium in diethyl ether with 1 equiv of TMEDA[14] and in monomeric (neopentyl)lithium complexed to PMDTA.[15] These (silylallyl)lithiums are the first examples of contact ion pairs in which the rotation of one solvated ion is slow with respect to the counterion. Such effects are only clearly seen below 160 K.

Finally the barriers to rotation about the C_2–C_3 bond in **10** vary between 10 and 17 kcal/mol, respectively.

Experimental Section

The NMR instruments used for ^1H, ^{13}C, and ^6Li spectra used in this work were Bruker AM 250, MSL 300, and AM 500 spectrometers, respectively. Typical parameters used in our experiments are listed in a previous paper.[15] The NOE experiments were carried out as follows: The sample was cooled to the lowest feasible temperature, slowing possible averaging due to dynamic affects, and a proton NMR spectrum was obtained. From this a list of chemical shifts was obtained and then each shift was irradiated for 10 s. The decoupler was then turned off and ^6Li NMR observed via a 45° pulse on lithium and accumulation. This was repeated to ensure instrument stability, with 5 cycles of 8 pulses at each proton shift. Following this procedure led to the NOE enhancements described above (Table III).

[1-(Trimethylsilyl)allyl]lithium (10). Under an atmosphere of argon, 1-(trimethylsilyl)propene (**1**, 2 g, 17.5 mmol) was introduced by syringe into a 250-mL Schlenk flask containing a magnetic stirbar and the flask was sealed with a rubber septum. The alkene, **1**, was degassed by the freeze–pump–thaw procedure. THF (50 mL) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, 3 mL) were syringed in and the system cooled to −78 °C with a dry ice–acetone bath. Then (*sec*-butyl)lithium in pentane (13.5 mL, 1.3 M, 17.6 mmol) was added dropwise by syringe to produce a yellow solution. This mixture was stirred for ca. 30 min at −78 °C and then allowed to warm up to room temperature. Solvent was removed in vacuo. Samples (0.11 g) of the resulting viscous residue were dissolved in THF-d_8 (5 mL), methylcyclohexane-d_{14}, and diethyl-d_{10} ether, creating ca. 1 M solutions.

A second sample was prepared in an identical fashion to the above sample except no TMEDA was used. Samples prepared in THF contained small amounts of lithium acetaldehyde enolate.

[1-(Trimethylsilyl)allyl]lithium–PMDTA Complex (10·PMDTA). An oven-dried Schlenk tube flushed with argon containing a magnetic stir bar and closed with a septum was moved into the glovebox under an argon atmosphere. Therein, 3-(trimethylsilyl)propene (1.0 g, 8.8 mmol) was weighed, mixed with 20 mL of pentane, and syringed into the Schlenk tube. (Butyl)lithium-*⁶Li* (2 mL, 4.4 M, 8.8 mmol) was added followed by *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (1.59 g, 2 mL, 9.2 mmol). This mixture was stirred overnight in the glovebox at room temperature. It was removed from the glovebox and cooled with ice while being concentrated in vacuo. After ca. 70% of solvent had been evaporated crystals formed. The excess solvent was removed with a syringe and the tube was evacuated. There was obtained 1.9 g of crystals of the title compound in 74% yield, based on (alkyl)lithium. The material, initially white, turned red on standing. An NMR sample was prepared by dissolving 50 mg in 0.4 g of THF-d_8, a 0.4 M solution.

[1-(Trimethylsilyl)allyl]lithium in Diethyl-d_{10} Ether. With use of the apparatus described above, under an atmosphere of argon, compound **1** (2.3 g, 20 mmol) was weighed and dissolved in 20 mL of diethyl ether. (Butyl)lithium-*⁶Li* (4 mL, 4 M, 10 mmol) in pentane was added to this mixture at room temperature and the solution was stirred for 4 days. The solvent was removed in vacuo. A sample for NMR study was prepared by dissolving 20 mg of **10** in 0.5 mL of diethyl-d_{10} ether, ca. 0.3 M. A solution of **10** in THF-d_8, 0.3 M, was prepared in a similar fashion.

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