Reorientation Dynamics within Ion-Paired Allylic Lithium Compounds: Isolation of Inversion Processes

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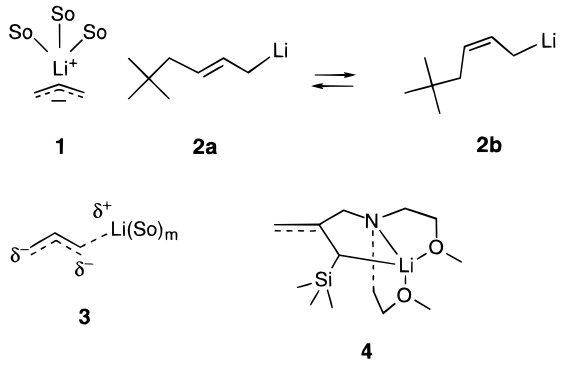
Among the several ion−ion reorientational processes that take place within several newly studied allylic lithium compounds, the dynamics of transfer of TMEDA-coordinated lithium between the two allyl faces has been determined independently by use of ^{13}C NMR line shape studies of diastereotopic geminal methylsilyl groups strategically incorporated close to the chiral lithium in the organometallic species. With increasing temperature, the ^{13}C shift between these methyls is progressively averaged due to faster rates of lithium transfer (inversion). Typical $\Delta H^{\ddagger}$ values of 5−7 kcal·mol^{-1} with $\Delta S^{\ddagger}$ = ca. −20 eu are encountered. A faster process, the reorientation of coordinated TMEDA on one side of the allyl plane, has been monitored from the NCH_3 ^{13}C resonance of TMEDA-coordinated Li^+, with $\Delta H^{\ddagger}$ = 7 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = ca. −12 eu.

Allylic lithium compounds[1] are among the simplest potentially conjugated carbanionic species. As a result of extensive spectroscopic[2,3] X-ray crystallographic[4] and calculational[5] studies, two categories of structures have been recognized. These are the delocalized contact ion-pairs with lithium normal to the allyl plane and solvated by ethers or tertiary amines **1**, and then, there are the unsolvated species, **2ab**,[6] whose ^{13}C NMR shifts are more in accord with a localized structure. Both kinds of structures have been shown to be aggregated. Possible species with structures that lie between **1** and **2**, i.e., **3**, have only recently been observed in studies of internally coordinated allylic lithium compounds, such as **4**. These were proposed to be stablized by virtue of restricted stereochemistry of lithium coordination.[7]



The structure of ion-pairs[8] has been a somewhat neglected subject, let alone the dynamics of motion of ions with respect to each other within the ion-pairs. Ion-pairs were not believed to assume energetically favored structures. Our NMR studies provided the first direct support for a sandwich structure of ion-pair dimers that contain[9] triple ions $A^-Li^+A^-$, Li^+,[9,10] in which only the outer

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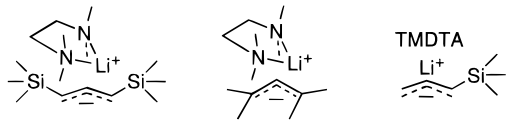
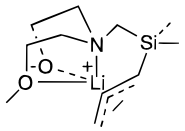
lithium is solvated.[10] Then, direct mapping of ion-pairs has been recently accomplished with careful NMR NOE experiments.[11]

Recently, we have reported that at low temperatures, 160 K, unexpected nonequivalences among ^{13}C shifts of several allylic lithium compounds implied that these ion-paired species assume quite specific structural arrangments, [12] as shown in structures **5**−**7**. Signal averaging



5 **6** **7**

effects seen in the NMR spectra with increasing temperature were ascribed to the reorientation dynamics of ions with respect to each other within the ion-pair. For example, at 150 K in diethyl ether-d_{10} **5·TMEDA** shows a small ^{13}C NMR shift between the terminal allyl carbons and two well-separated broad peaks for the *N*-methyls, which implied that complexed **TMEDA** is unsymmetrically sited with respect to the allyl moiety. With increasing temperature, these two doublets progressively average to single lines at their respective centers. Similar behavior was observed for compounds **6**−**8**.[12] NMR line



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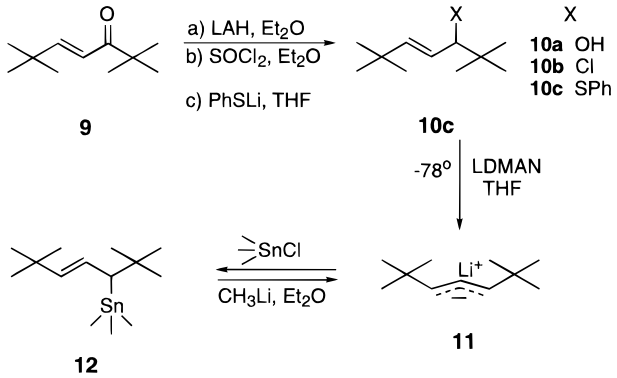
shape analysis revealed first-order processes with $\Delta H^{\ddagger}$ of 5−7 kcal·mol^{-1}, respectively. These effects were ascribed to reorientation of coordinated ligand with respect to counterion within the ion-pairs. Reorientation could result from several different processes. Thus, the averaging observed in *N*-methyl ^{13}C NMR of coordinated **TMEDA** in **5** and **6** could come from rotation of coordinated ligand on one side of the allyl plane, transfer of coordinated ligand between two faces of the allyl plane, and finally fast reversible local N−Li dissociation accompanied by inversion at nitrogen and rotation about the CH_2−N bond. To determine, independently, the rates of transfer of coordinated lithium between two sides of the allyl plane, a process that is phenomenologically inversion, we have chosen to exploit the diastereotopic properties of geminal methyls in a chiral environment.[13]

Assuming that in a 1-substituted allylic lithium compound coordinated lithium is sited normal to the allyl plane,[7] then the system is chiral. The methyls of a dimethylsilyl group near the chiral center would be magnetically nonequivalent in ^{13}C NMR. Fast transfer of coordinated lithium between the two sides normal to the allyl plane would average such a shift, so line shape analysis should provide the dynamics of face transfer alone, a process that is phenomenologically inversion of the ion-pair. Herein we report the results of such a study, the specific design and preparation of several model allylic lithium compounds that incorporate a geminal methyl silyl diastereotopic probe and how NMR line shape analysis of the geminal methyl resonances separates and identifies, the dynamics of inversion from all other intra-ion pair reorientational effects.

Results and Discussion

Evidence for the ion-paired structure and reorientation dynamics of ions with ion pairs was first obtained for **5**.[12a] To investigate whether this behavior is unique to silicon-substituted allylic lithium compounds we have now prepared the carbon analogue of **5**, the di-*tert*-butyl species **11**.



Transformation of unsaturated ketone **9**[14] via the alcohol **10a** and chloride **10b** provided the desired phenyl sulfide **10c**. Cleavage of **10c** with lithium (dimethylamino)naphthalenide, **LDMAN**, provided an impure sample of **11** together with PhSLi.

Compound **11** was purified by conversion to its trimethyltin derivative **12** and cleavage of the latter with CH_3Li in diethyl ether. Compounds **9**, **10a**−**c**, and **12** are assigned trans structures on the basis of vicinal proton coupling constants across the double bonds of ca. 15 Hz.

We previously reported that 1,1,3,3-tetramethylallyllithium added cleanly and rapidly to anthracene in diethyl ether at −90 °C.[15] Compound **11** behaves in a similar fashion, except that the reaction requires a higher temperature, −30 °C. Hydrolysis of the initial adduct **13** provided **14** in 81% yield. A vicinal proton coupling of 15.4 Hz across the allylic double bond of **14** confirms the trans relationship shown and by implication that in the precursor anion **13**; see below.

Preparation of other starting materials and their metalation (**15**−**25**) is summarized below. Four geminal dimethylsilyl allylic lithium compounds have been prepared, **16**, **18**, **21**, and **25**, via a series of metalation/silylation cycles; see **15**−**25**. Metalation has been accomplished using *n*-butyllithium in the presence of **TMEDA** in diethyl ether or THF. It is a common feature of the

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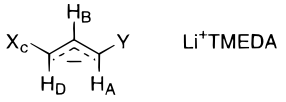
Table 1. ^{13}C and (^{1}H) NMR Shifts, Allylic Lithium Compounds Complexed to TMEDA, Diethyl Ether-d_{10} Solution, <180 K

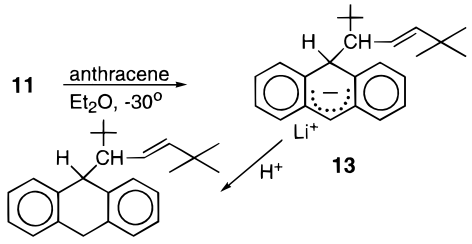
	C_1	C_2	C_3	$Si(CH_3)_2$	$SiCH_2CH_3$	$C(CH_3)_3$	NCH_3	NCH_2
16	53.1 (1.94)	149.0 (6.41)	64.3 (2.65) (2.75)	−0.441 0.001	8.6 CH_2 11.8 CH_3 (0.37) CH_2 (0.92) CH_3		46.0 49.0	58.0
18	67.43 (2.6)	155.21 (6.7)	67.43 (2.6)	0.215 −0.13 −0.32 (0.97)	8.53 CH_2 11.32 CH_3 (0.40) CH_2 (0.91) CH_3		49.4 45.0 (2.34)	58.0 (2.45)
21	50.28 (1.95)	149.7 (6.4)	65.3 (2.71) (2.83)	−2.88 −5.01		29.25 CH_3 20.0 q	50.66 46.56 (2.3)	57.86 (2.45)
25	68.8 (2.6)	155.2 (6.65)	67.1 (2.6)	−0.71 −0.35 (0.97)	8.58 CH_2 11.36 CH_3 (0.3) CH_2 (0.9) CH_3	2.12 (−0.1)	49.27 44.84	57.85 (1.94)
11	77.1 (2.54)	131.8 (6.42)	77.5 (2.54)			34.4 CH_3 33.1 q (2.33)	49.4 45.09 45.37 (2.33)	56.9 (2.45)

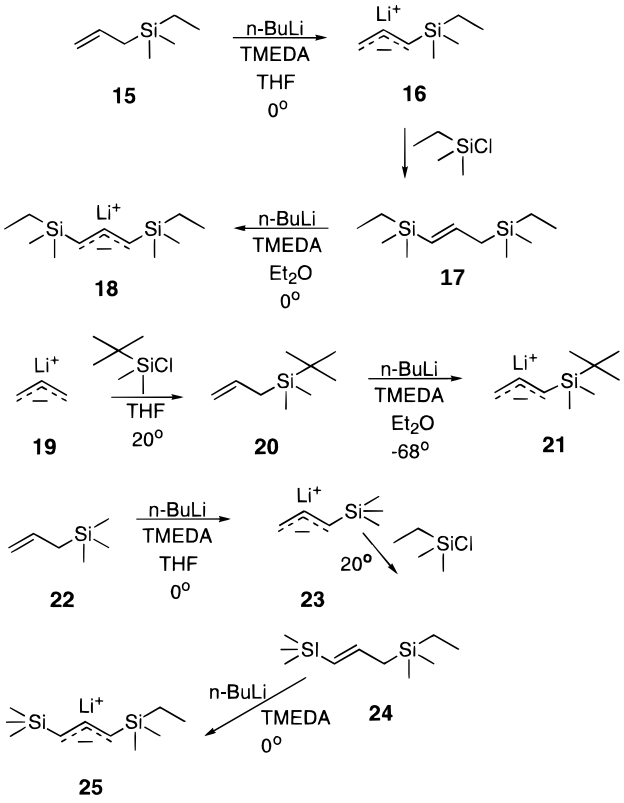
Table 2. Proton−Proton Coupling Constants, Hz, for Allylic Lithium Compounds in Ether-d_{10}



	J Hz			
no.	AB	BC	BD	CD
11	13.7		13.7	
16[a]	19.4	8.5	15	−2
18	15.6		15.6	
21[a]	15.6	8.5	14.9	−2
25	15.2		15.2	

[a] X = H_c.





chemistry reported here and previously published[16] that 1-silylallyllithiums undergo further silylation at the 3-position resulting in trans products.[16] Thus, herein **16** and **23** on silylation produce exclusively **17** and **24**, respectively, which are identified as the trans stereochemistry due to vicinal proton proton coupling constants across the double bonds of 18 and 19, Hz, respectively.

For NMR study, the solvent diethyl ether, THF, and excess **TMEDA** were removed under vacuum from the initial preparations of **11**, **16**, **18**, **21**, and **25** and replaced via bulb-to-bulb distillation by dry oxygen-free diethyl ether-d_{10} or THF-d_8.

Carbon-13 and proton chemical shifts, obtained at low temperature, using diethyl ether-d_{10} solutions, are listed in Table 1 for all of the allylic lithium compounds reported here. All of these compounds exhibit the alternating allyl ^{13}C shifts typical of delocalized carbanions.[2,3,17] The three-bond proton−proton coupling constants of ca. 15 Hz within the allyl moieties (Table 2) show that all these species are exo substituted, as drawn, and that endo isomers present are too dilute to detect. The **TMEDA** that remains in these samples is clearly bound to lithium, since the associated NMR behavior is quite different from that of the free material. Finally, geminal silyl methyls at low temperature all resolve into simple doublets. These issues are elaborated upon below; see Table 1.

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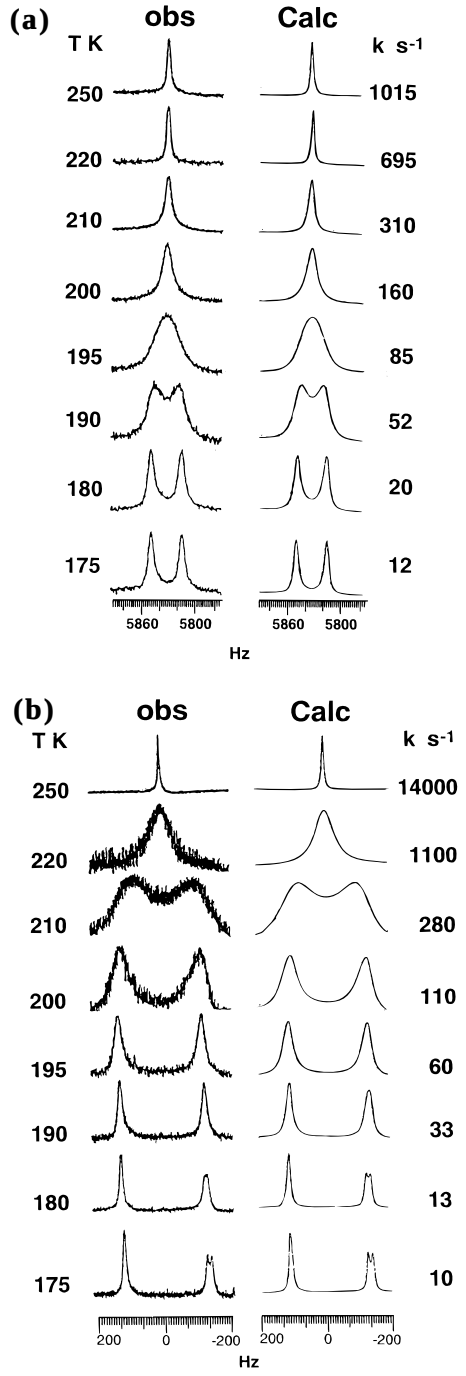

Figure 1. (a) ^{13}C NMR, **11**, 0.5 M, complexed to **TMEDA** in diethyl ether-d_{10}, C_1, C_3 allylic carbons: (left) observed, different temperatures; (right) calculated line shapes with rate constants. (b) ^{13}C NMR as in (a) NCH_3 of complexed **TMEDA**: (left) observed, different temperatures; (right) calculated line shapes with rate constants.

Consider first the behavior of *exo,exo*-1,3-di(tert-butyl)-allyllithium, **11**, complexed to **TMEDA**, which was chosen as a highly substituted species for comparison with the 1,3-disila analogue **5·TMEDA**, reported previously.[12a] NMR data indicated that the coordinated ligand in **5·TMEDA** is unsymmetrically sited with respect to the allyl loop; i.e., the system assumes a single structure. Then changes in NMR line shape were interpreted as resulting from the dynamics of reorientiation of ions with respect to each other within the ion-pair.

Compound **11·TMEDA** behaves in fashion similar to

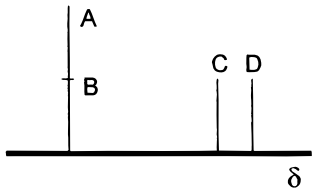

Figure 2. Pattern of ^{13}C NMR of NCH_3 of **11**, complexed to TMEDA.

5·TMEDA. At low temperature, 175 K, there is a ^{13}C NMR shift difference between the terminal allyl carbons of 0.4 ppm, Figure 1a. Further, at 175 K the *N*-methyls give rise to three singlets of relative intensities 2:1:1. With increasing temperature, the two multiplets progressively average to single lines at their respective centers, Figure 1b. We assume these resonances come from a single molecular species. The C_1, C_3 resonance was treated as a two-site equally populated uncoupled system undergoing exchange, Figure 1a. As for the *N*-methyl resonance, it was calculated as due to four equally populated uncoupled sites (the four methyls) of which two have the same shift; see Figure 2. The simplest model is for each site to exchange with all of the others, all at the same rate.[18] This model nicely matched the calculated to the observed resonances, as shown in Figure 1b. Thus, comparison of observed and calculated line shapes gave the rate constants and associated activation parameters; $\Delta H^{\ddagger}$s, kcal/mol, of 8.0 and 6.6 were derived from the *N*-methyl and C_1, C_3, ^{13}C resonances, respectively.

Entropy and enthalpy tend to balance, since over the temperature range investigated rate constants from the C_1, C_3 resonance exceed those from N-CH_3 by not more than a factor of 2; see Table 3. The Eyring plot is shown in Figure 3 for *N*-methyl ^{13}C resonances.

At low temperature, the ^{13}C NMR of geminal silyl methyls of each of the compounds **16**, **21**, and **25** consists of a single equal doublet. This is not the result of nonequivalent methyls within slowly interconverting rotamers about the allyl carbon silicon bonds since we find that the starting silylpropenes show no such effects at low temperature; their geminal silylmethyls give rise to single peaks down to 160 K. Rather, the *gem*-silylmethyl doublets for the allylic organolithium compounds are most likely due to the chiral character of these compounds. With increasing temperature, the dimethylsilyl ^{13}C doublets of **16**, **21**, and **25** progressively average to single lines at their respective centers. This behavior does not depend on concentration of the organolithium species and, hence, must be the result of a first-order process, the transfer of coordinated lithium between opposite sides normal to the allyl plane. Comparison of observed and calculated line shapes (see Figure 4 for **21**) provides the rate constants. The Eyring plot is in Figure 5; the results are given in Table 3.

Compound **18** behaves in a fashion similar to that of the others described above. The allyl ^{13}C NMR shifts are consistent with a delocalized carbanion. The C_1 and C_3 allyl resonance is a single broadened line (compared to the other carbons), implying a small shift between them. The ^{13}C NMR spectrum down to 170 K shows no evidence for more than one species. In contrast to **16**, **21**, and **25**, the geminal methyls of which give rise to 1:1 ^{13}C doublets,

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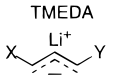
Table 3. Dynamics of Ion−Ion Reorientation within Allylic Lithium·TMEDA Complexes in Diethyl Ether-d_{10} As Obtained from NCH_3, $Si(CH_3)_2$, or C_1, C_3 ^{13}C NMR Line Shapes



$\Delta H^{\neq}$ kcal•mole^{-1}
($\Delta S^{\neq}$ eu)

#	X	Y	NCH_3	$Si(CH_3)_2$	C_1, C_3
16	H		a	4.9[b] (-21.)	—
21	H		6.5 (-10.)	5.6[b] (-19.)	
5[c]			5.3 (-1.5)	—	6.7 (-6.)
11			8.7 (-4.6)	—	6.6 (-15.)
25			5.4	4.7[b] (-25.)	d
18			5.9	6.9[e] (-12.) 7.1[b] (-22.)	d

[a] Broadened doublet. [b] Net inversion. [c] Reference 12a, recalculated. [d] Broadened line. [e] Reorientation of complexed lithium on one side normal to allyl plane.

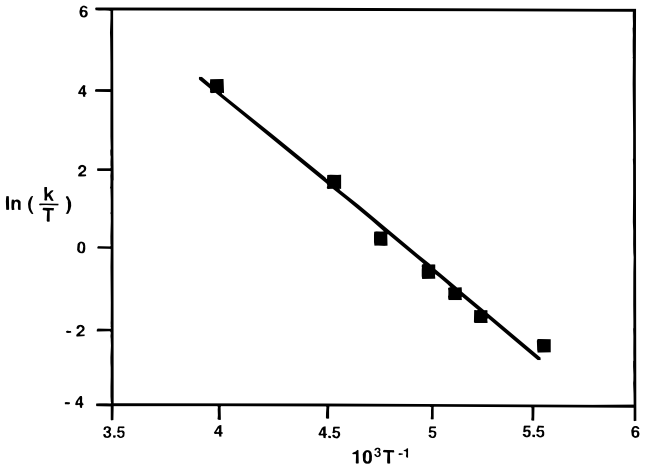


Figure 3. Eyring plot, reorientation dynamics, **11·TMEDA**, from *N*-methyl ^{13}C NMR of complexed **TMEDA** diethyl ether-d_{10} solution.

those of **18** exhibit three singlets, 2:1:1 at δ 0.215, −0.13, and −0.32, respectively. The two silicons are labeled A and B. Geminal methyls may be assigned A_1, A_2 at δ 0.215 with B_1 and B_2 at δ −0.13 and −0.34, respectively; alternatively, A_1, B_1 at δ 0.215 with A_2 and B_2 at δ −0.13 and 0.32, respectively, diagrammed in Figure 6. Of these two, only the latter assignment is consistent with the results for **25**, a compound with one less methylene than **18**. Hence, both should have similar structures and behave in a similar manner. The geminal silyl methyls of **25** give rise to a clean 1:1 doublet in ^{13}C NMR, separation 0.19 ppm. Were the first assignments for **18** correct then the ^{13}C NMR of **25** would have indicated two species, one with a geminal silylmethyl 1:1 doublet and the other with just a single line for these methyls. Clearly the second assignment must be the more correct one.

With increasing temperature above 160 K, the 2:1:1 geminal silyl multiplet of **18** progressively undergoes signal averaging, ultimately by 300 K to a single line. These line shape changes are best fitted with two different sets of rate constants, the faster set being

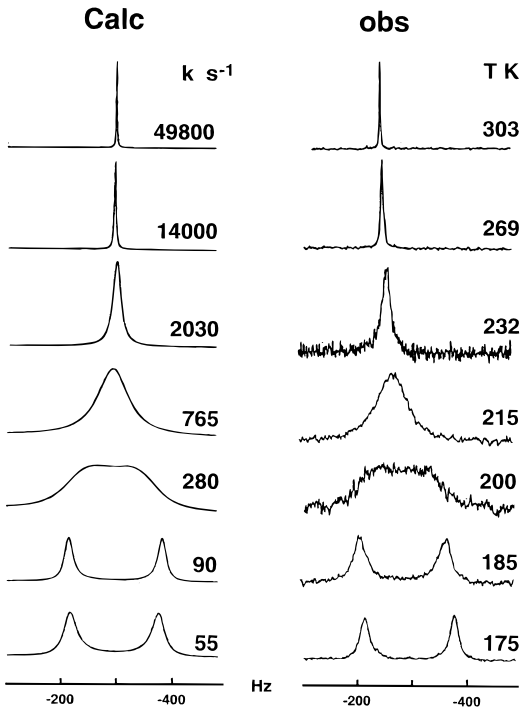


Figure 4. ^{13}C NMR, **21** complexed to **TMEDA**, *gem*-methylsilyl resonance: (right) observed, different temperatures; (left) calculated, with rate constants.

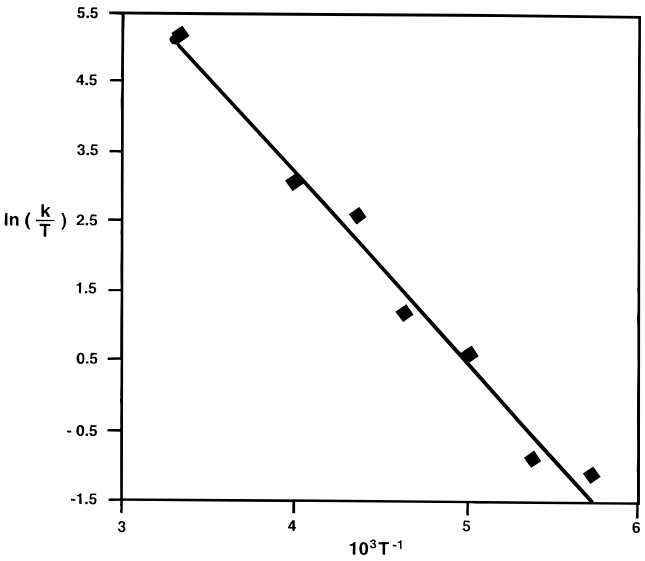


Figure 5. Eyring plot, reorientation dynamics for **21** complexed to **TMEDA** from *gem*-silylmethyl resonance.

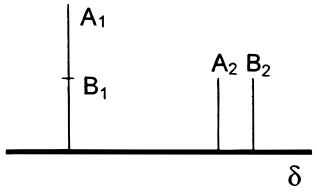


Figure 6. Assignment for *gem*-methyl ^{13}C resonances of **18** complexed to TMEDA.

responsible for averaging the 1:1 doublet (δ −0.13 and −0.34) between 170 and 200 K. In terms of our proposed model, Figure 6, that is the averaging of the two doublets, A_1A_2 with B_1B_2 to a single doublet. Above 200 K with increasing temperature, the latter doublet averages to a single line, the slower process. We would like to propose that this slower process involves transfer of coordinated lithium between opposite sides normal to the allyl plane, "inversion", while the former, detected within the lower temperature range, involves side to side motion of the coordinated ligand or its rotation on *one side of the silyl plane* only. Experimental and calculated line shapes are compared in Figure 7a,b; associated activation parameters are in Table 3.

The ^{13}C NMR of **TMEDA** in diethyl ether remains unchanged between 150 and 300 K; the *N*-methyl resonance consists of a sharp single line throughout this entire temperature range. All of the compounds reported herein, **11**, **16**, **18**, **21**, and **25**, were prepared in the presence of **TMEDA**. The **TMEDA** that remained in these samples after all volatile components had been pumped out exhibited NMR behavior quite differenct from that of the free diamine. Below 180 K, ^{13}C NMR for *N*-methyls in each of the complexes **16**, **18**, **21**, and **25** resolved into a 1:1 doublet unformally at δ 45 and 49, respectively. The exception in this work is **11**, which gave a 2:1:1 triplet; see above. These results indicate that the diamine is complexed to Li^+ in each case and that coordinated ligand is unsymmetrically sited with respect to the allyl moiety, as proposed in previous reports.[12] With increasing temperature, these *N*-methyl ^{13}C multiplets progressively average to single lines at their respective centers. NMR line shape analysis provides the associated dynamic parameters. Figure 8 shows calculated line shapes for **21**. Table 3 lists the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ derived from the *N*-methyl ^{13}C resonance for all cases analyzed.

The nature of the dynamic process responsible for these changes in the ^{13}C NMR *N*-methyl line shapes for complexed **TMEDA** in the above listed compounds is less clear than that for the *gem*-silylmethyl ^{13}C resonances of **16**, **18**, **21**, and **25**. The latter changes are most likely the result of transfer of coordinated lithium between two sides normal to the allyl plane. In contrast, changes in the TMEDA resonance may be the result of several effects, including inversion as well as lateral motion of complexed ligand and fast reversible N, Li dissociation accompanied by inversion at nitrogen and rotation around the $N-CH_2$ bond. The latter process may be much faster than the other two, fast relative to the NMR time scale, even at the lowest temperature at which acceptable NMR data could be obtained. This would account for the observation of just two *N*-methyl ^{13}C lines instead of the expected four on the basis of our proposed structures, discussed above.

Barriers to rotation in allylic lithium compounds have been reported by several workers.[4d−f] Among the compounds described herein, **11**, **17**, and **25** appear to assume the exo-exo structures with no isomers detectable by NMR. Hence, it is not possible to determine the barrier to allyl rotation with NMR methods. However, the dynamics of allyl rotation around the C_2, C_3 bond in **21** is accessible from proton NMR. Like all compounds described here **21** is 1-exo. With increasing temperature between 290 and 330 K there is partial averaging of the cis and trans coupling constants between C_2H and the

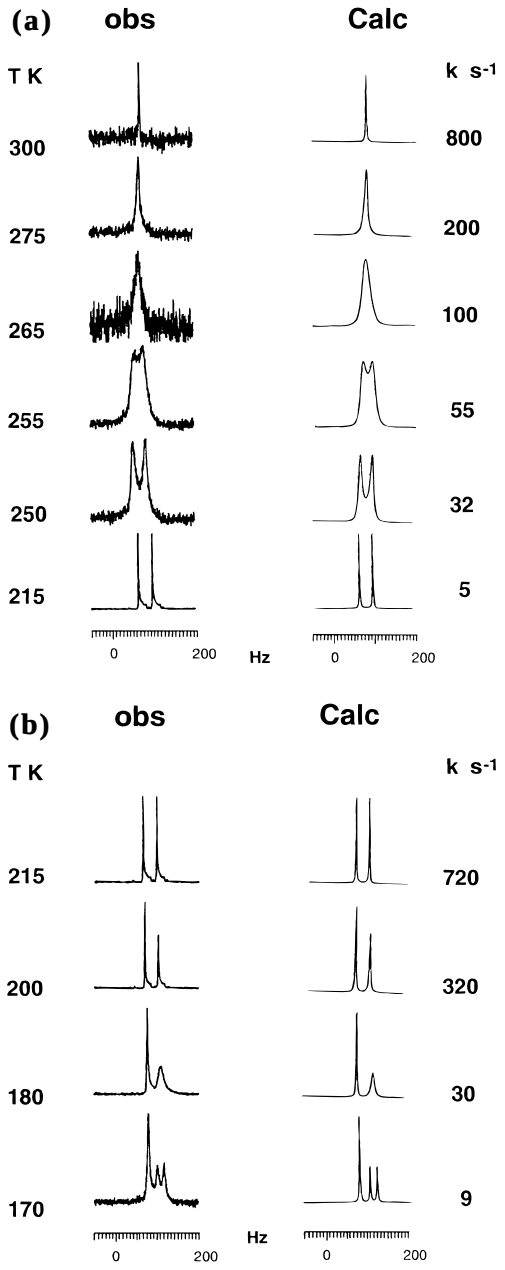


Figure 7. (a) ^{13}C NMR, *gem*-methyl resonances of **18** complexed to TMEDA, higher temperature range: (left) observed, different temperatures; (right) calculated line shapes with rate constants. (b) As in (a), lower temperature range: (left) observed with temperatures; (right) calculated with rate constants.

C_3 methylene hydrogens. Analysis of the $C_2H^{12}C$ proton resonance provides the rates of C_2, C_3 rotation and associated activation parameters. These are, in order, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for diethyl ether-d_{10} solution, 16 kcal·mol^{-1} and +4.6 eu, while for THF solution these values are 14 kcal·mol^{-1} and −2 eu. The latter are closely similar to the corresponding parameters determined for 1-trimethylsilylallyllithium using THF solutions, 14.3 kcal·mol^{-1} and ∼0 eu.[12b] Note that these barriers vary significantly with the nature of the lithium ligand present.[12b] It has been proposed that an increase in carbon lithium covalence in the transition state for rotation, compared to the ground state, is responsible for this effect.[3c]

It is now instructive to recapitulate what has been found herein and how it relates to what is generally

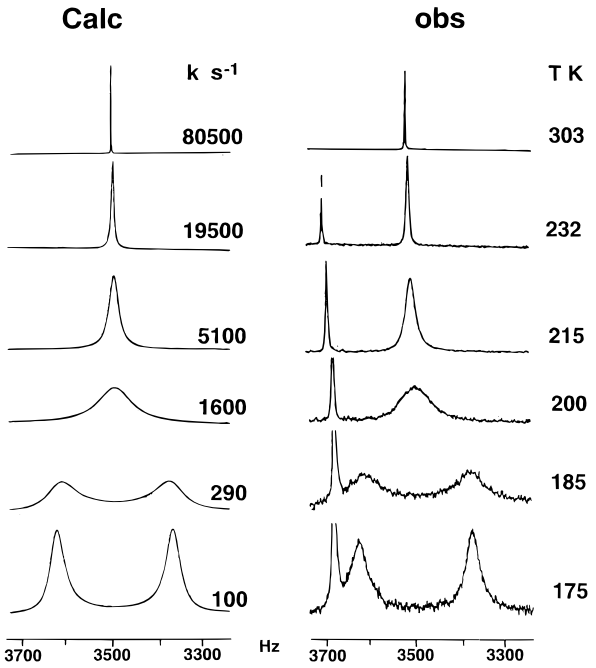


Figure 8. ^{13}C NMR **21** complexed to **TMEDA** in diethyl ether-d_{10}, *N*-methyl part: (right) observed, with temperatures; (left) calculated with rate constants.

understood about allylic lithium compounds. The examples of solvated allylic lithium compounds reported here and previously behave spectroscopically as delocalized carbanions within contact ion pairs.[3,4,6,12] Our NMR data reported here and elsewhere indicated that several of these compounds assume energetically favored structures,[12] a concept rarely applied to ion-paired salts, as evidenced by unexpected nonequivalences among the ^{13}C NMR shifts. At low temperature, 180 K, reorientation of ions *within the ion-pairs, with respect to each other*, is slow relative to the NMR time scale.

Signal averaging of nonequivalent *N*-methyl ^{13}C resonances due to bound **TMEDA** and of *gem*-methylsilyl ^{13}C resonances are due to the dynamics of ion−ion reorientation. Whereas the data from **TMEDA** methyls may be due to several effects—including inversion, rotation of the coordinated ligand on one side of the allyl plane, and fast reversible N_5Li dissociation, that from the geminal methyls on silicon comes from inversion alone, with one exception (see below). These geminal methyls are nonequivalent due to the chiral character of the ion-pair. Their averaging with increasing temperature is due to inversion of the ion-pair above and is more accurately described as transfer of coordinated lithium between two sides normal to the allyl plane. In the case of **18**, the *cis*-1,3-bis(dimethylethylsilyl) compound, the changes in the geminal methyl ^{13}C NMR line shape have been resolved to result from two processes—inversion and the faster rotation of coordinated ligand on one side of the allyl plane. This latter rate at 200 K is similar to the value obtained from the *N*-methyl ^{13}C resonance of **TMEDA**-coordinated **18**. Similar effects are seen for **5** where the *N*-methyl and C_1, C_3 ^{13}C line shapes give rise to similar rates at 200 K. In fact, the $\Delta G^{\ddagger}$ (200 K) values extracted from two sets of resonances just described for **18** and **5** are remarkably similar, $(9 \times 6) \pm 3$ kcal·mol^{-1}. Thus in cases where the dynamics of both inversion and one side reorientation have been measured, inversion is the slower process.

Table 4. NMR Parameters

parameter	^{13}C	^{1}H
frequency, MHz	75	300
transform, K	64	16
spectral width, Hz	13514	4200
resolution, Hz/point	0.231	0.513
acquisition time, s	2.16	1.09
transients	1600−9600	1600−9600

The available data do not provide a picture as to how lithium transfers between two sides normal to the allyl plane. The transfer is not accompanied by an increase in C, Li covalence. That path would perturb the conjugation and thus facilitate rotation around the allyl carbon carbon bonds, a process already known to involve higher barriers with $\Delta H^{\ddagger}$ of 12−19 kcal·mol^{-1}, respectively. In contrast, inversion could accompany allyl rotation.

Experimental Section

Materials and Procedures. Diethyl ether, tetrahydrofuran, and pentane used in the organometallic procedures were freshly distilled from sodium and benzophenone under an argon atmosphere. Toluene was distilled from CaH_2, and TMEDA was distilled from KOH pellets and then from CaH_2, under argon or nitrogen. Organolithium compounds were analyzed using our double titration procedure, previously described.[7a] All glassware used for organometallic compounds was baked in an oven, 120 °C, overnight, flamed out under vacuum, and finally flushed out with argon.

NMR Samples. The assembly consists of a 5 mm OD NMR sample tube with an attached 2 mm straight bore stopcock, the latter protected by a rubber serum cap, the whole system previously dried with flaming in a current of argon. Within the drybox (argon), the NMR tube was loaded by syringe with ca. 1 mL of the allylic lithium solution. Solvent was removed under vacuum and the assembly flushed with argon and then attached to a high vacuum system (10^{-6} Torr) to remove remaining volatile components. After 1 h, diethyl ether-d_{10} (1 mL) was vacuum transferred into the sample. The frozen sample (liquid nitrogen) was then sealed under vacuum. Samples were stored in dry ice prior to NMR study.

NMR Equipment and Conditions. Conventional NMR spectra were obtained with a Bruker AC-200 spectrometer. All variable-temperature experiments with carried out using a Bruker MSL-300 instrument. Table 4 lists typical parameters used in this work.

2,2,6,6-Tetramethyl-4-hepten-3-one, 9. Freshly distilled 5-hydroxy-2,2,6,6-tetramethyl-3-heptanone (37 g, 0.199 mol) prepared by the method of House[14] was introduced into a three-neck round-bottom flask equipped with a reflux condensor, a stopcock, an addition funnel, and a magnetic stirbar. *p*-Toluenesulfonic acid (1.7 g, 8.5 mmol) dissolvd in 650 mL of benzene was then added and the solution refluxed for 1 h. After this time, the reflux condensor was replaced by a Vigreux distillation column, and the H_2O−benzene azeotrope was allowed to distill out at atmospheric pressure (71 °C) until no more water droplets came out. The remaining solution was concentrated by rotary evaporation and the residue extracted twice with 100 mL of CCl_4 to separate the insoluble *p*-toluenesulfonic acid. The rotary evaporator deposited 30.5 g (91.3% yield) of the trans title ketone as white needles: mp 40−41 °C; ^{1}H NMR ($CDCl_3$, 20 MHz) δ 1.0 (9H, s, tBu), 1.07 (9H, s, tBu), 6.3 (1H, d, vinyl J = 14.7 Hz), 6.8 (1H, d, vinyl J = 14.7 Hz).

2,2,6,6-Tetramethyl-4-hepten-3-ol, 10a. Into a 250 mL three-neck round-bottom flask equipped with an addition funnel, a glass stopcock, argon inlet, and a magnetic stirbar, containing $LiAlH_4$ (4.94 g, 0.13 mol) in 30 mL dry ether, was added trans ketone **14** (20 g, 0.119 mol) dropwise. This reaction mixture was stirred for 5 h and maintained at 20 °C with a water bath. Then it was hydrolyzed very carefully with 12 mL of distilled H_2O, which was added over a period of 1 h. The

reaction mixture was vacuum filtered in a Büchner funnel, and the residual slurry in the funnel was washed thoroughly with ether (50 mL). The ethereal filtrate was next dried with anhydrous $MgSO_4$ powder, concentrated in the rotary evaporator, and distilled twice to give 16.88 g (83.4% yield) of the clear title trans alcohol: bp 126−129 °C/60 Torr; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.9 (9H, s, tBu), 1.01 (9H, s, tBu), 1.4−1.5 (1H, m OH), 3.6−3.8 (1H, d, J = 7.5 Hz), 5.4 (1H, dd, J = 15.6, 7.5 Hz), 5.6 (1H, d, J = 7.5 Hz).

***trans*-2,2,6,6-Tetramethyl-3-chloro-4-heptene, 10b.** Thionyl chloride (3.5 mL, 0.048 mol, distilled) was introduced into a three-neck, 50 mL dry round-bottom flask equipped with an addition funnel, a magnetic stirbar, and a glass stopcock connected to a $CaCl_2$ drying tube. Anhydrous diethyl ether, 30 mL, was added and the mixture stirred at room temperature for 15 min, Then trans alcohol, **10a** (7.0 g, 0.041 mol), dissolved in 10 mL of diethyl ether was added dropwise from the addition funnel over a period of 30 min. The resulting solution was allowed to stir for an additional 2 h. The reaction mixture was then treated with 10 mL of 2 N KOH (aq), washed twice with 10 mL each of $NaHCO_3$ (sat.), dried with $MgSO_4$, and concentrated by rotary evaporation. Distillation afforded 5.4 g (69.6% yield) of the title chloride as a light yellow liquid: bp 108−112 °C/57 Torr; ^{1}H NMR $CDCl_3$, 200 MHz) δ 0.99 (9H, s, tBu), 1.02 (9H, s, tBu), 4.1 (1H, d, −CCl (tBu) J = 9.3 Hz), 5.46 (1H, dd, vinyl J = 15.5, 9.3 Hz), 5.65 (1H, d, vinyl J = 15.5 Hz); ^{1}H NMR ($CDCl_3$, 50 Hz); d, 26.68, 29.37, 32.98, 36.05, 75.06, 123.19, 145.11.

***trans*-2,2,6,6-Tetramethyl-5-(phenylthio)-3-heptene, 10c.** Into a flame-dried three-neck 50 mL round-bottom flask equipped with an addition funnel, magnetic stirbar, glass stopcock, and a reflux condenser connected to an argon inlet was introduced 10 mL of dry THF and thiophenol (0.58 mL, 0.0053 mol). Next, the solution was cooled with an external acetone−dry ice bath to −78 °C. When the desired temperature had been reached, *n*-butyllithium (2.12 mL, 2.5 M, 0.0053 mol) in hexanes was added very slowly from the addition funnel to the mixture, which developed a blue-gray color. It was stirred for 15 min and then allowed to warm to room temperature. The chloride **10b** (1.1 g, 0.058 mol) was then added dropwise and the mixture stirred for an additional 1 h. After this, it was refluxed for another hour, followed by the addition of 5 mL of 2 M KOH (aq), and finally it was refluxed overnight. At this point, thin-layer chromatography indicated the total conversion of the starting material to the title compound. The solution was washed twice with 10 mL portions of 2 N KOH (aq) to remove unreacted thiophenol. Then the THF was removed in vacuo, and the reaction mixture was extracted twice with ether (10 mL each), dried with $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (SiO_2, hexanes) to afford 0.8 g (62% yield) of the pure title phenyl sulfide: MS for $C_{17}H_{26}S$ m^+/e 262.1758 obsd, calcd 262.1757; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.84 (9H, s), 1.07 (9H, s), 3.27 (1H, d, J = 9.9 Hz), 5.05 (1H, d, J = 15.4 Hz), 5.24 (1H, dd, J = 15.4, 9.9), 7.18−7.38 (5H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 28.07, 29.47, 32.20, 34.53, 65.79, 123.03, 126.82, 128.36, 133.99, 135.70, 143.61.

***trans*-2,2,6,6-Tetramethyl-5-(trimethylstannyl)-3-heptene, 12.** The apparatus consisted of a three-neck 50 mL round-bottom flask, previously flame dried and equipped with a glass coated stirring bar, addition funnel, a glass stopcock, and an argon inlet. It was placed in the drybox (argon) and loaded with finely cut lithium slivers (6.3 mg, 9 mg atom). Then, outside the drybox and under positive Ar pressure 10 mL of anhydrous THF was added by syringe very carefully. The flask was cooled to −50 °C with a dry ice−acetone bath, and 1-(*N*,*N*-dimethylamino)naphthalene (1.53 g, 8.9 mmol) was added dropwise from the addition funnel with stirring. The mixture was allowed to react for 12 h, developing a green-black coloration. After all the lithium slivers had disappeared, the system was cooled to −78 °C, and the sulfide **10c** (0.5 g, 1.9 mmol), previously dissolved in 0.5 mL of THF in the addition funnel, was added very slowly until the reaction mixture turned red. The resulting solution was treated with trimethyltin chloride (2.0 mL, 1 M,2 mmol) in diethyl ether. This mixture was then queched with 10 mL of H_2O, the THF was removed first in vacuo, and the remaining solution was extracted twice with 10 mL portions of diethyl ether, washed three times with 0.2 N KOH (aq) (to remove the thiophenol), once with NaCl (sat.), and twice with 1 N HCl (aq) (to remove the naphthalenamine). Next, the solution was dried ($MgSO_4$) and concentrated in the rotary evaporator. The product was purified by flash column chromatography (SiO_2, hexanes) to separate 0.45 g (75% yield) of the pure stannyl title compound: MS for $C_{14}H_{30}Sn$ m^+/e obsd 316.93965, calcd 316.9249; IR (neat) cm^{-1} 29573, 28.64.2, 1463.8, 1362.3, 1230.6, 971.0, 764.3; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.07 (9H, s, $Sn(CH_3)_3$), 0.95 (9H, s, tBu), 1.01 (9H, s, tBu), 2.0 (1H, d, −SnCH−, J = 11.0 Hz), 5.25 (1H, d, vinyl, J = 15.8 Hz), 5.44 (1H, dd, vinyl, J = 15.8, 11.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ −8.28, 30.20, 30.67, 32.87, 33.50, 49.21, 125.32, 138.04.

***exo,exo*-1,3-Di-*tert*-butylallyllithium. TMEDA, 11.** A 50 mL flame-dried Schlenk flask containing a glass-coated stirbar and a stopcock connected to an argon tube was charged by syringe with tin compound **12** (0.35 g, 0.0011 mol) and **TMEDA** (0.128 g, 0.0011 mol). After this step, the flask was cooled with an acetone−dry ice bath (−78 °C). Next, a mixture of 6.0 mL of anhydrous diethyl ether and 0.6 mL of THF was introduced for solvation, followed by the addition of methyllithium−^{6}Li (1.2 mL, 1.27 M, 1.52 mmol) in diethyl ether. The reaction mixture was stirred at −78 °C for 2 h and then slowly warmed to room temperature. By ca. −30 °C, a yellow color was observed, indicating the formation of the lithium compound. It appeared to be stable even at room temperature. To obtain NMR samples, aliquots of 0.8 and 1.2 mL were syringed out very carefully and transferred to flame-dried, argon-filled NMR tubes. The latter were attached to a vacuum system (Torr), and the solvents allowed to distill into a liquid nitrogen trap. Then when most of the solvent had been removed, the tubes were transferred to a high vacuum line (5×10^{-6} mmHg) and maintained there for 3 h to pump out completely all volatile components. Diethyl ether-d_{10}, up to 0.5 mL, was vacuum transferred into the cooled NMR tubes (liquid nitrogen). The yellow-orange NMR samples were then frozen and sealed off under vacuum with a torch. NMR samples were stored in a liquid nitrogen bath in the freezer until NMR studies began: ^{1}H NMR (Et_2O-d_{10}, 300 MHz, 3.34 ppm) δ 0.96 (9H, s, tBu), 2.20 (s, TMEDA methyls), 2.34 (s, TMEDA-methylenes), 2.5−2.6 (1H, d, J = 13.2 Hz), 6.2−6.7 (1H, t, J = 13.2 Hz); ^{13}C NMR (Et_2O-d_{10}, 75 MHz, 65.3 ppm) δ 32.676, 34.027, 46.849, 57.487, 77.814, 134.153.

9-(*tert*-Butyl-4,4-dimethyl-2-pentene)-9,10-dihydroanthracene, 14. Into a flame-dried 50 mL round-bottom flask equipped with a glass-coated stirring bar, a low-temperature thermometer, and glass stopcock, the whole flushed with argon, was introduced a mixture of 4.5 mL of diethyl ether and 0.5 mL of THF together with **TMEDA** (0.128 g, 1.1 mmol) freshly distilled from CaH_2. Next, stannane **12** (0.35 g, 1.1 mmol) was introduced into the flask. The solution was then cooled to −78 °C with a dry ice−acetone bath, and methyllithium (1.2 mL, 1.24 M, 1.52 mmol) in diethyl ether was added slowly via syringe. At −78 °C, no color change was observed, so the mixture was left to warm slowly. At −30 °C, a yellow coloration developed, and after 2 h at room temperature the bright yellow color indicated the formation of the allyllithium compound. The flask was chilled again to −78 °C, and anthracene (0.392 g, 2.2 mmol) dissolved in 2 mL of THF was added carefully from a syringe. After 1 h at −78 °C, the reaction mixture was warmed slowly to −30 °C. At this temperature, a dark orange color started to develop, which intensified by room temperature, giving a dark red solution. The reaction mixture was then quenched with 10 mL of distilled H_2O, washed twice with 10 mL each of 1 N HCl (aq), dried ($MgSO_4$), and concentrated in the rotary evaporator. Further purification by flash chromatography on SiO_2 using a 10:1 hexanes−ethyl acetate eluent system afforded 0.296 g (81.26%) of the addition product as white crystals: mp 67−68 °C; MS for $C_{25}H_{32}$ m^+/e obsd 332.3435, calcd 332.5054; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.01 (9H, s, tBu), 0.76 (9H, s, tBu), 2.07 (1H, dd, J = 9.8 and J = 3.8), 3.65 (1H, d, J = 17.7), 4.10 (1H,

d, J = 17.7), 4.28 (1H, d, J = 3.81), 4.8−4.9 (1H, dd, J = 15.4, 9.9), 5.0 (1H, d, J = 15.4), 7.1−7.4 (8H, m, ring); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 28.8, 29.11, 32.63, 34.60, 37.11, 47.58, 61.5, 124.49, 125.27, 125.68, 125.81, 127.64, 127.78, 129.15, 137.78, 138.45, 141.73.

1-(Dimethylethylsilyl)allyllithium, TMEDA Complex, 16. *n*-Butyllithium in pentane (1.36 mL, 2.5 M, 3.4 mmol) was slowly added by syringe to a solution of **TMEDA** (0.39 g, 3.4 mmol) and 3-dimethylethylsilylpropene (0.43 g, 3.4 mmol) in 3 mL of THF at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. A 0.5 M solution of the title compound in dimethyl ether-d_{10} was prepared for NMR study, as described above.

***trans*-1,3-Bis(dimethylethylsilyl)propene, 17.** To a solution of 3-(dimethylethylsilyl)propene (5 g, 0.039 mol) and **TMEDA** (4.54 g, 0.039 mol) in 70 mL of THF was added at 0 °C *n*-butyllithium (16 mL, 2.5 M, 0.039 mol) in pentane. The mixture was warmed to room temperature and stirred for 3 h. Then 3-dimethylethylchlorosilane (4.8 g, 0.039 mol) was added dropwise over 10 min. Hydrolysis with excess water followed by ether extraction and drying the ether extracts with sodium sulfate gave, after removal of solvent and vacuum distillation of the residue, 4.0 g of the title compound in 48% yield: bp 126−127 °C/40 Torr; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.02 (m, 1H), 5.47 (m, 1H), 1.61 (m, 2H), 0.97 (t, 6H), 0.51 (q, 4H), 0.08 (s, 6H), −0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 50.0 MHz) δ 144.2, 126.6, 26.7, 7.7, 7.4, 7.2, 6.7, −3.3, −4.2.

1,3-Bis(dimethylethylsilyl)allyllithium, TMEDA Complex, 18. *n*-Butyllithium-^{6}Li in pentane (4.5 mL, 0.616 M, 2.77 mmol) was slowly added by syringe to a solution of **TMEDA** (0.31 g, 0.41 mL, 2.7 mmol) and *trans*-1,3-bis(dimethylethylsilyl)propene (0.58 g, 2.7 mmol) in 2 mL of diethyl ether at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. A 0.5 M solution in diethyl ether-d_{10}, degassed in a 5 mm OD NMR tube, was prepared for NMR studies, as described above.

3-(Dimethyl-*tert*-butylsilyl)propene, 20. Allyllithium[19] (2.4 g, 0.05 mol) was placed in an addition funnel and dissolved in 10 mL of dry, degassed THF. Under an argon atmosphere and at room temperature, this solution was added dropwise over 30 min to chloro-*tert*-butyldimethylsilane (7.53 g, 0.05 mol) dissolved in 30 mL of dry THF contained in a 250 mL round-bottom Schlenk flask. After the addition was complete, the reaction was allowed to continue for 2 h, after which it was quenched by addition of 5 mL of 3% NaOH solution saturated with NaCl. The organic phase was extracted with diethyl ether and dried over Na_2SO_4. Solvents were removed by rotary evaporation, and the residue was distilled at 132 °C/760 Torr to give 6.56 g of the title compound in 84% yield: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (s, 9H, $C(CH_3)_3$), −0.068 (s, 6H, $Si(CH_3)_2$), 1.518 (d, 2H, CH_2Si, $^3J(CH_2{-}CH{=}CH_2)$ = 8.1 Hz), 5.78 (m, 1H, $CH_2{=}CH$, $^3J(CH_2{=}CH)$ = 16.6, 10 Hz), 4.78 and 4.87 (m, 2H, $^2J(CH_2{=})$ = −1.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 6.59 ($Si(CH_3)_2$), 26.56 ($C(CH_3)_3$), 16.78 ($C(CH_3)_3$), 20.7 (CH_2Si), 135.69 (−CH=), 112.68 (CH_2=).

1-Dimethyl-(*tert*-butylsilyl)allyllithium, 21. Compound **20** (0.035 g, 0.23 mmol) and **TMEDA** (0.023 g, 0.2 mmol) were dissolved in 2 mL of dry diethyl ether in a 50 mL Schlenk tube under an argon atmosphere. With external cooling to −68 °C, *n*-butyllithium-^{6}Li (3.5 mL, 0.57 M, 0.2 mmol) in pentane was then added dropwise to the reaction mixture with stirring. After the reaction was allowed to warm to room temperature, 4 h, neutral silane and diethyl ether were removed under high vacuum and the residue dissolved in 1 mL of pentane. This solution was transferred in a Schlenk tube to the drybox (argon atmosphere) and then syringed into a 5 mm OD NMR tube. Volatile components were removed under high vacuum, and the NMR sample in diethyl ether was prepared as described above: ^{1}H NMR (diethyl ether-d_{10}, 200 MHz, 293 K) δ 0.859 (s, 9H, $C(CH_3)$), −0.036 (s, 6H, $Si(CH_3)_2$), 1.94 (1, CHSi), 6.46 (m, 1H, $CHCH_2$), 2.81 (m, 2H, CH_2CH), 2.71 (s, 6H, NCH_3), 2.46 (s, 4H, NCH_2); ^{13}C NMR (75 MHz) δ −3.1 ($Si(CH_3)_2$), 27.85 ($C(CH_3)_3$), 50.87 (CHSi), 149.98 ($CHCH_2$), 65.21 ($CHCH_2$), 46.97 (NCH_3), 57.93 (NCH_2).

***trans*-1-(Trimethylsilyl)-3-(dimethylethylsilyl)propene, 24.** To a solution of 3-(trimethylsilyl)propene (2.1 g, 0.018 mol) and **TMEDA** (2.05 g, 0.018 mol) in 30 mL of THF was added at 0 °C *n*-butyllithium in pentane (7.1 mL, 2.5 M, 0.018 mol). The mixture was then warmed to room temperature and stirred for 3 h. Dimethylethylchlorosilane (2.17 g, 0.018 mol) was added dropwise over 1 min. Hydrolysis (excess water) followed by ether extraction and drying of the extracts with sodium sulfate yielded after rotary evaporation of solvent and vacuum distillation of the residue 1.5 g of the title compound in 42% yield: bp 97−98 °C/40 Torr; proton NMR ($CDCl_3$, 200 MHz) δ 6.04 (m, 1H), 5.44 (m, 1H), 1.63 (m, 2H), 0.94 (t, 6H), 0.51 (q, 4H), 0.018 (s, 9H), 0.0 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.7, 127.9, 26.6, 73, 6.7, −0.98, −4.19.

***exo,exo*-1-(Trimethylsilyl)-3-(dimethylethylsilyl)allyllithium, 25.** *n*-Butyllithium-^{7}Li (0.5 mL, 2.5 M, 1 mmol) in pentane was slowly added by syringe to a solution of **TMEDA** (0.168 mL, 1.12 mmol) and *trans*-1-(trimethylsilyl)-3-(dimethylethylsilyl)propene (0.223 g, 1.12 mmol) in 2 mL of diethyl ether at 0 °C. The mixture was warmed to room temperature over 3 h. An NMR sample tube of the title compound in diethyl ether-d_{10} was prepared, as described above. This sample was stored in dry ice prior to the NMR studies.

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