Alkyl-Substituted Allylic Lithium Compounds: Structure and Dynamic Behavior[†]

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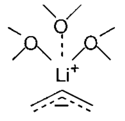
Abstract: Several methyl-substituted allylic lithium compounds have been prepared by CH_3Li cleavage of their corresponding bis(methyl)bis(allylic)stannanes. Low-temperature ^{13}C and proton NMR studies of 1:1 complexes of these allylic lithium compounds with TMEDA establish their structures. NMR line shape changes with temperature provide barriers to rotation. Results are listed in order as follows (allyl substituents, compound number, barrier to rotation in kcal·mol^{-1}, and bonds undergoing rotation): 1,1-dimethyl, **26**, 18, 2−3; endo-1-methyl, **27**, 19, 2−3; endo-1-exo-3-dimethyl, **28**, 21, 1−2 and 2−3. These observations together with the allylic ^{13}C NMR chemical shifts indicate that in the case of unsymmetrical alkyl substitution at the termini the allyl C−C bond to the more substituted terminus is of higher bond order than that to the less substituted terminus. Unsymmetrical substitution is proposed to reduce the degree of delocalization compared to the symmetrically substituted allylic lithium compounds. A mechanism is proposed for the rotation process which is consistent with the Eyring activation parameters.

Allylic lithium compounds,[1] which are the simplest of the conjugated carbanionic substances, have been extensively investigated, via X-ray crystallogaphy,[2] spectroscopy,[3] and calculations.[4] These studies show that most solvated allylic lithium compounds assume the delocalized contact ion-paired structure **1**, within which coordinated lithium lies normal to the allylic plane.[2,3] In contrast unsolvated alkane-soluble allylic lithium compounds such as **2** exhibit ^{13}C NMR shifts which are consistent with a localized structure.[5] These unsolvated species are most likely aggregated.[5] One might have expected to find examples of allylic lithium compounds, such as **3**, in which the degree of π-delocalization lies between that of **1** and **2**. We recently reported that certain internally coordinated allylic lithium compounds, **4**, exhibit such intermediate degrees of π-delocalization.[6] We proposed that the short tether of the pendant ligand restricts the stereochemistry of coordination of lithium.[6] This places lithium off the vertical above the allyl plane above C_1 thus favoring unusual partial C−Li covalency.



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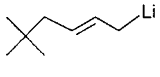

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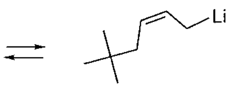

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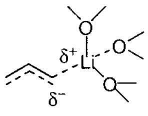

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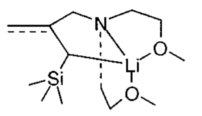

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Low-temperature NMR studies of selected solvated allylic and benzylic lithium compounds showed that contrary to prevailing opinion these ion-paired species adopt favored structures. Furthermore, below 160 K the rate of reorganization

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[†] This article is dedicated to Professor Chengxue Zhao of Shanghai Jiaotong University on the occasion of his 60th birthday.

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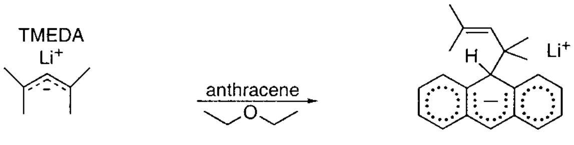
of ions within the ion pairs is slow relative to the NMR timescale.[7] Above 160 K studies of NMR line shape changes revealed and quantified for the first time the dynamics of three different ion−ion reorganization processes within the ion pair. These are (1) transfer of coordinated lithium between faces of the allyl plane, (2) rotation of coordinated lithium on one side of the allyl plane, and (3) fast reversible Li−N (of ligand) dissociation accompanied by inversion at nitrogen.

This article is addressed to the effect of alkyl substituents on the allylic lithium framework. Alkyl substituents on carbanionic carbon are believed to destablize carbanions.[8] We previously described the high reactivity of 1,1,3,3-tetramethylallyllithium, TMEDA (**5**), which adds to anthracene rapidly in THF at −90 °C (see **5** → **6**).[9] Below, we describe some efficient preparations of alkyl-substituted allylic tin compounds and their conversion to allylic lithium compounds. NMR studies of these allylic lithium compounds provide insight into their structures and dynamic behavior.



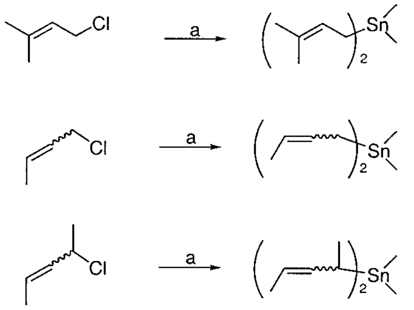
5 **6**

Results and Discussion

Preparation of Allylic Tin Compounds. Allylic lithium compounds have been prepared by metalation of alkenes,[3d] reduction of ethers[10] and sulfides,[11] and alkyllithium cleavage of lead[12] and tin[13] compounds, respectively.

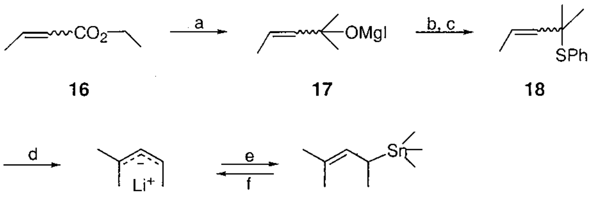
The current study required that our allylic lithium compounds be prepared in pure form from easily handled precursors. In principle alkyllithium cleavage of allylic tin compounds should be the method of choice. For example cleavage of **7** by CH_3Li proceeds in high yield yet the resulting methyltriphenylstannane (**8**), is difficult to remove from the desired product **1**. The cleavage of **9** with CH_3Li proceeds efficiently. However, **9** and other allylic trimethylstannanes are toxic, sensitive to light and O_2, and inconveniently volatile. A suitable compromise is to use diallyldimethylstannanes. They are stable if stored in a refrigerator and in darkness. They are less volatile than the allylic trimethyl stannanes and are thus easier to purify and transfer. Finally, we find they cleave cleanly to allylic lithium compounds, as shown below. The required bis(allyl)dimethylstannanes **11**, **13**, and **15** were prepared by reducing the appropriate allylic chlorides **10**,[14] **12**,[15] and **14**,[16] respectively, with Mg in the presence of dimethyldichlorostannane at room temperature in THF. Two allylic trimethyl stannanes, **20** and **25**, were prepared via their phenyl sulfide precursors; see **16**−**20** and **22**−**25**. Since LDMAN reduction of phenyl sulfides **18** and **23** gives 2-(dimethylamino)naphthalene and lithium thiophenoxide together with the desired allylic lithium compounds, **19** and **24**, these reaction mixtures were treated with $(CH_3)_3SnCl$. The resulting stannanes, **20** and **25**, were purified and then cleaved with CH_3Li to give the purified allylic lithium compounds, **19** and **24**. Interestingly sulfides **18** and **23** were formed directly by hydrolysis of magnesium salts **17** and **22** in the presence of thiophenol. Strong acid is not required for this transformation of magnesium salts to sulfides.

7 **8** **9**



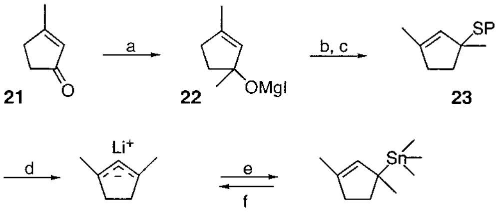
10 **11** **12** **13** **14** **15**

^{a}Mg, $(CH_3)_2SnCl_2$, THF, 25 °C



16 **17** **18** **19** **20**

^{a} CH_3MgI, Et_2O; ^{b} PhSH; ^{c} H^+, H_2O; ^{d} LDMAN, Et_2O, THF; ^{e} $\geq$SnCl; ^{f} CH_3Li



21 **22** **23** **24** **25**

$^{a-f}$ as in **16** to **20**

The structures we have assigned to the bis(allylic)dimethylstannanes, **11**, **20**, and **25**, are unambiguously determined from their NMR spectra, Table 1. Carbon-13 NMR of our preparation of dicrotyldimethylstannane (**13**) showed three lines each for CH_3Sn and CH_3C. This indicates the presence of at least three isomers which are cis/cis, cis/trans, and trans/trans. The observation of four resonances each for the two vinyl carbons is consistent with this assignment. The assignments of shifts to structures cannot be made at this time. Our preparation of **13** has properties similar to those reported by Clarke and Kwon[17a]

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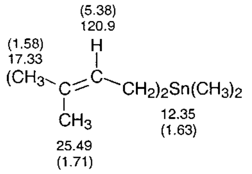
Table 1. ^{13}C and (^{1}H) NMR Shifts and Tin−^{13}C Coupling Constants for Allylic Stannanes

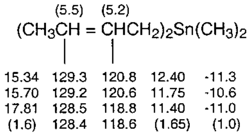
11



^{1}J (^{117}Sn, $^{13}CH_3$) = 49.6 Hz

^{1}J (^{119}Sn, $^{13}CH_3$) = 50.4 Hz

13



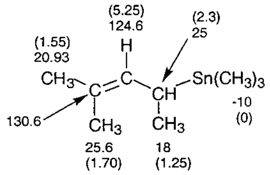
$(CH_3CH = CHCH_2)_2Sn(CH_3)_2$

15.34	129.3	120.8	12.40	-11.3
15.70	129.2	120.6	11.75	-10.6
17.81	128.5	118.8	11.40	-11.0
(1.6)	128.4	118.6	(1.65)	(1.0)

^{1}J (^{117}Sn, $^{13}CH_3$) = 34.7 Hz

^{1}J (^{119}Sn, $^{13}CH_3$) = 35.3 Hz

20



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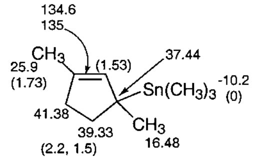
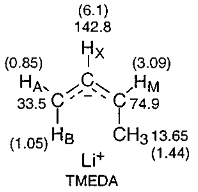


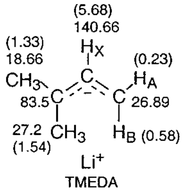
Table 2. Substituted Allylic Lithium Compounds, 200 K, TMEDA Complexes, ^{13}C and (^{1}H) NMR Shifts, and Vicinal Proton Coupling Constants

27



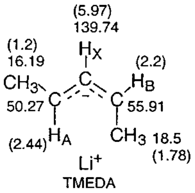
^{3}J	Hz
HA, HX	7.2
HB, HX	13.6
HM, HX	8.8
CH3, HM	7.0

26



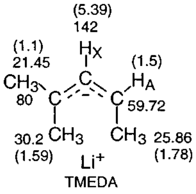
^{3}J	Hz
HA, HX	7.2
HB, HX	13.3

28



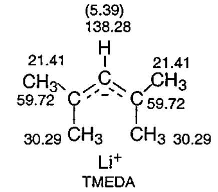
^{3}J	Hz
HA, HX	13.8
HB, HX	8.1
CH3, HA	5.8
CH3, HB	6.0

19



^{3}J	Hz
HA, HX	10.0

5

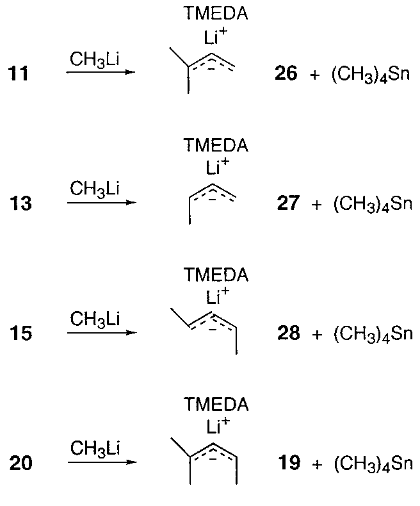


for this compound. The ^{13}C shifts we observed for the crotyl part of **13** are similar to those reported for tetracrotylstannane[17b,c,d] and for crotyltrimethylstannane.[17b]

In the case of bis(1,3-dimethylallyl)dimethylstannane (**15**) our NMR data are consistent with a complex mixture of isomers due to cis−trans isomerism around the double bonds and *R*,*S* stereochemistry at the chiral carbon. However, NMR data indicate that the species which is obtained by reacting compound **15** with CH_3Li is exclusively *exo*-*endo*-1,3-dimethylallyllithium (**28**).

Preparation and Structure of Allylic Lithium Compounds. Prior to the current study crotyllithium has been prepared by alkyllithium cleavage of tetracrotylstannane,[17b] crotyltrimethylstannane,[17b] and tetracrotylnickel.[18] Also, 1-butene was reported to undergo allylic metalation by ethyllithium in HMPT.[17c,d] On the basis of NMR studies, it has been claimed that crotyllithium consists of a mixture of the exo and endo isomers[17b,18] and that these isomers interconvert slowly.[19]

The allylic lithium compounds in this work were prepared by cleaving the allyl stannanes **11**, **13**, **15**, **20**, and **25** with CH_3Li in diethyl ether with 1 equiv of THF. In this way samples of compounds **19**, **24**, **26**, **27**, and **28** were prepared. For the NMR studies, ether and THF were replaced by THF-d_8/TMEDA to form ca. 0.5 M solutions of the allylic lithium compounds complexed to 1 equiv of TMEDA. Low-temperature ^{13}C and ^{1}H NMR for these compounds are summarized in Table 2. The structures proposed in Table 2 were assigned on the basis of their vicinal proton−proton coupling constants.



On examination of these NMR spectra it appears that, with the exception of **24**, these samples are free of starting materials

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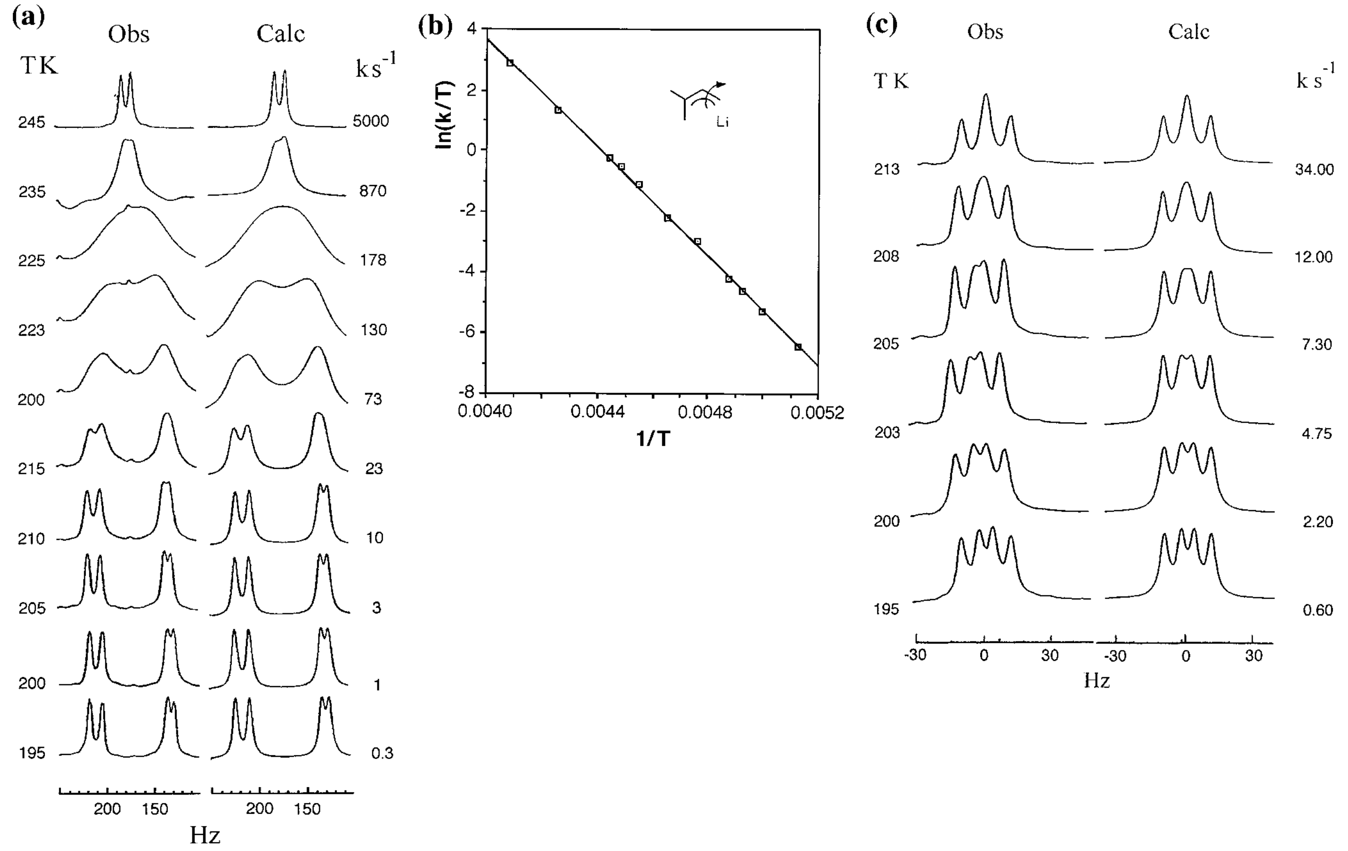

Figure 1. (a) Proton NMR of (1,1-dimethylallyl)lithium, TMEDA complex, **26**, in THF-d_8 allyl methylene resonance: (left) observed, different temperatures; (right) calculated line shapes with first-order rate constants. (b) Eyring plot for rotation around the CH−CH_2 bond of **26**, TMEDA complex, using CH_2 proton resonance. (c) Proton NMR of **26**, TMEDA complex, in THF-d_8 C_2H resonance: (left) observed, different temperatures; (right) calculated with first-order rate constants.

and hydrolysate to the limits of NMR detection. We conclude further that each sample consists of a single molecular species, which remains invariant in structure throughout the entire temperature range which was investigated.

Our sample of crotyllithium complexed to TMEDA in THF exhibited H_M, H_X vicinal coupling of 8.8 Hz indicating that the methyl group in this compound is endo, Table 2. This reflects the tendency of (1-alkylallyl)lithium compounds to favor the endo structure.[5,20] The exo isomer of crotyllithium was not detected over the entire temperature range 170−280 K.

Birch prepared (1,1-dimethylallyl)lithium (**26**) by Li cleavage of the corresponding phenyl ether.[21] Our preparation of **26** shows an array of allyl vicinal proton coupling constants (cis 7.2 Hz and trans 13.3 Hz) similar to those observed in Birch's study of crotyllithium. Analysis of the vicinal proton coupling pattern of (1,3-dimethylallyl)lithium (**28**) complexed to TMEDA shows this sample to have the *endo*,*exo*-1,3-dimethyl structure as indicated by vicinal coupling constants of 8.1 and 13.8 Hz. Finally, the single vicinal coupling constant, C_2H−C_3H of 10 Hz in (1,1,3-trimethylallyl)lithium (**19**) establishes that methyl at C_3 is endo, despite the destabilizing influence of 1-*endo*-methyl/3-*endo*-methyl repulsion, Table 2.

Qualitatively the allyl ^{13}C shifts show the alternating variation typical of delocalized carbanions.[22] While the $^{13}C_2$ allyl shifts are very similar among the compounds studied, the terminal allyl shifts exhibit interesting variations which depend on the difference in the degree of alkyl substitution at C_1 versus that at C_3. With identical alkyl substitution at the two termini (allyllithium and (1,1,3,3-tetramethylallyl)lithium) the terminal ^{13}C shifts are identical. As expected for **28**, the C_1 and C_3 shifts are very similar. With unsymmetrical alkyl substitution at the termini the ^{13}C NMR shifts become different. The δ values for the more and less alkyl-substituted terminal carbons increase and decrease, respectively, when compared to terminal shifts for the symmetrically substituted species. These shift differences increase with the difference in the degree of alkyl substitution at the allyl termini; see Table 2. We propose that these effects are the result of variations in the two allyl bond orders. The results of our NMR line shape analyses of the dynamics of allyl rotation (described below) qualitatively support this proposal. For example, throughout the entire temperature range investigated the 1,1-dimethyl ^{13}C resonances of **19** and **26** remain as well-resolved equal doublets. This shows that rotation around the CH−$C(CH_3)_2$ bond is slow relative to the NMR time scale. Meanwhile the rate of rotation around the CH−CH_2 bond of **26** is fast and lies well within the NMR time scale.

In sum, it appears that differences in alkyl substitution at the termini of allylic lithium compounds lead to disproportionation of the allyl bond orders. Thus, the bond order for C_2−C (more substituted) increases while that for C_2−C (less substituted) decreases.

Compound **24** could have been of special interest to study. We previously ascribed the high reactivity of **5** to distortion from coplanarity.[9] The allylic portion of compound **24** should be constrained to be more planar than **5**. Unfortunately, due to

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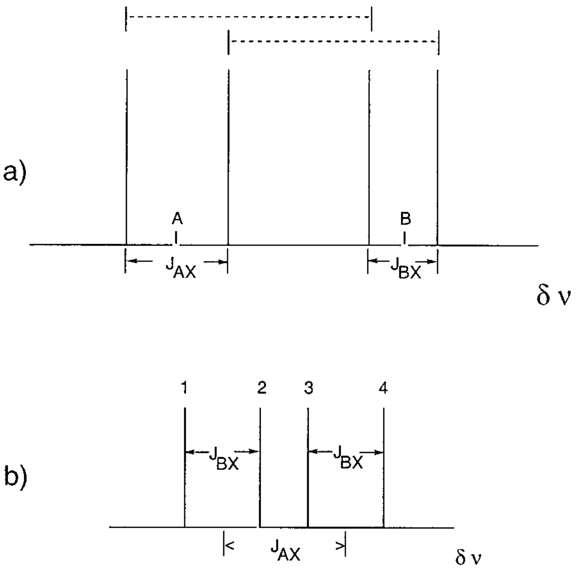
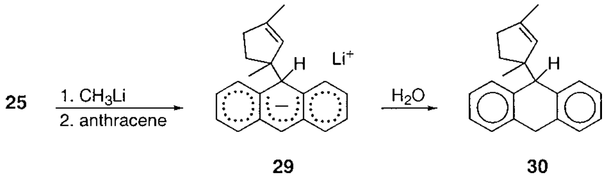


Figure 2. (a) Allyl methylene proton NMR transitions for **26**. TMEDA complex, diagrammed. (b) Proton NMR transitions diagrammed for C_2H of **26**.

the low solubility of **24** in our solvents we were unable to obtain useful NMR data for this compound. However, evidence for its formation comes from its chemistry. The product of sulfide **23** with LDMAN was reacted with trimethylchlorostannane. This gave the tin compound shown to be **25**. Reaction of **25** with CH_3Li followed by addition of anthracene and then hydrolysis gave adduct **30**. This indicated the intermediacy of **24** and anionic adduct **29**.



Dynamic Behavior of Substituted Allylic Lithium Compounds, (1,1-Dimethylallyl)lithium. As noted above, rotation around the CH−C(CH$_3$)$_2$ bond of (1,1-dimethylallyl)lithium (**26**) is slow relative to the NMR time scale over the entire temperature range investigated, from 195 to 290 K. At 195 K proton NMR shows all three allylic protons to be well resolved as are also the two vicinal proton−proton coupling constants. The geminal coupling constant $^2J(H_A, H_B)$ is too small to resolve; see Table 2.

Low-temperature proton NMR of CH_2 of **26** consists of four lines due to a shift between H_A and H_B, and each of these protons is vicinally coupled to H_X, Figure 1a. With increasing temperature the shift between H_A and H_B progressively averages out, and $^3J(H_A, H_X)$ averages with $^3J(H_B, H_X)$. By 245 K the resonance due to H_A and H_B is a 1:1 doublet, separated by 10.3 Hz. This is the average of the two vicinal coupling constants. Also as expected, by 245 K the four line resonance due to H_X has changed to a 1:2:1 triplet with a separation of 10.3 Hz. These changes in proton NMR line shapes are most likely due to the dynamics of rotation around the CH−CH$_2$ bond of **26**.

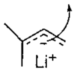
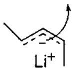
Table 3. Proton Spin Products, $\phi_X\phi_A\phi_B$, and Transitions for H_X of **26**

Number	Transition Energies	i → j	of $\rho_{i,j}$
1	$\nu_X - J_{AX} - J_{BX}$	$\alpha\alpha\alpha \rightarrow \beta\alpha\alpha$	ρ_1
2	$\nu_X - J_{AX} + J_{BX}$	$\alpha\alpha\beta \rightarrow \beta\alpha\beta$	ρ_2
3	$\nu_X + J_{AX} - J_{BX}$	$\alpha\beta\alpha \rightarrow \beta\beta\alpha$	ρ_3
4	$\nu_X + J_{AX} + J_{BX}$	$\alpha\beta\beta \rightarrow \beta\beta\beta$	ρ_4

Table 4. Definitions of Terms in Eq 1

$\Delta\nu_X$	$\nu - \nu_X$
n	freq axis of NMR spectrum
ν_X	chem shift of X in Hz
J	spin coupling constants, Hz
$1/T$	intrinsic line width, rad•s^{-1}
ρ_i	element of the density matrix
i	$\sqrt{-1}$

Table 5. Eyring Activation Parameters for Rotation in Substituted Allylic Lithium Compounds, Complexed to TMEDA, in THF-d_8 Solution

		Resonance Used	$\Delta H^{\ddagger}$ kcal•mol^{-1}	$\Delta S^{\ddagger}$ eu
27		CH_2	19	28
		C_2H	19	29
26		CH_2	18	32
		C_2H	18	34
28		C_2H	21	30

The H_A and H_B resonance of **26** was treated as two independently averaging equal doublets each being due to one of the spin states of H_X; see Figure 2a. The dotted lines connect the pairs of transitions which average. Comparison of the calculated NMR line shapes with the observed resonances provided the rates of rotation around the CH−CH$_2$ bond of **26** and the Eyring plot in Figure 1b. The resulting activation parameters are listed in Table 5.

Rates of rotation around the CH−CH$_2$ bond of **26** were also obtained from the resonance due to H_X. The procedures are summarized as follows. Figure 2b diagrams the four proton transitions due to H_X as described above. Table 3 lists the spin states of H_X in the spin product representation as $ø_Xø_Aø_B$, the $\Delta m_X = +1$ transitions, the transition energies, and the corresponding elements of the density matrix, $\rho_{i,j}$. Given these spectral assignments and assuming that $^3J(H_X, H_A)$ and $^3J(H_X, H_B)$ have the same sign, one can see that the effect of rotation around the CH−CH$_2$ bond is to average transition 2 with the transition 3; see Figure 2b. The coupled density matrix equations, shown in

$$\begin{bmatrix} i2\pi(\Delta\nu_X - J_{AX} - J_{BX}) - \frac{1}{T} & 0 & 0 & 0 \\ 0 & i2\pi(\Delta\nu_X - J_{AX} + J_{BX}) - \frac{1}{T} - k_1 & k_1 & 0 \\ 0 & k_1 & i2\pi(\Delta\nu_X + J_{AX} - J_{BX}) - \frac{1}{T} - k_1 & 0 \\ 0 & 0 & 0 & i2\pi(\Delta\nu_X + J_{AX} + J_{BX}) - \frac{1}{T} \end{bmatrix} \times \begin{bmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \\ \rho_4 \end{bmatrix} = iC \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} \quad (1)$$

matrix form in (1) are obtained by taking all four elements of the density matrix eq 2 $\Delta m_z = +1$ in $ø_X$.

$$\left\langle \alpha ø_A \phi_B \middle| \boldsymbol{i}[\rho, \mathrm{H}] - \frac{\rho}{T} - E\rho \middle| \beta \phi_A \phi_B \right\rangle = 0 \tag{2}$$

Terms in eq 1 are conveniently collected and defined in Table 4. Elements of $E\rho$ which incorporate the effect of H_A exchanging its site with H_B by rotation are given by (3). The coupled

$$(E\rho)_{\alpha\phi_A\phi_B,\beta\phi_A\phi_B} = k_r(\rho_{\alpha\phi_B\phi_A,\beta\phi_B\phi_A} - \rho_{\alpha\phi_A\phi_B,\beta\phi_A\phi_B}) \tag{3}$$

equations in (1) are solved for the ρ_i elements as a function of k_r and $\Delta\nu_X$. Then the H_X line shape is obtained from the sum in (4). Comparison of observed and calculated line shapes provided the rate constants for rotation, Figure 1c. The resulting

$$\mathrm{Abs}(\Delta\nu_X) = -\,\mathrm{Im}(\rho_1 + \rho_2 + \rho_3 + \rho_4) \tag{4}$$

activation parameters are listed in Table 5. As expected, the results obtained from the H_X and H_AH_B line shapes are very similar.

Some insight into the nature of lithium coordination has been obtained from NMR studies of **26** complexed to *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, PMDTA. The ^{13}C NMR of the complexed PMDTA at 170 K consists of nine well-resolved resonances of equal intensity. Their shifts are quite different from those of free PMDTA at 170 K but similar to values for PMDTA complexed to neopentyllithium[24] and mesityllithium.[25] This result implies that lithium is tridentately coordinated to PMDTA in **26**·PMDTA. Further, at 170 K the complexed ligand reorients slowly (τ > 5 s) with respect to the allylic moiety. With increasing temperature above 170 K the following sets of ^{13}C resonances each average to single lines at their respective centers: (1) the four $N(CH_3)_2$ lines; (2) the two methylene $CH_2N(CH_3)_2$ lines; (3) the two methylene CH_3NCH_2 lines. Qualitatively, these changes in the PMDTA ^{13}C NMR line shape are the result of a combination of rapid reorientation of the coordinated ligand with respect to the allyl moiety together with fast reversible N−Li dissociation accompanied by inversion at N and rotation around the CH_2–$N(CH_3)_2$ bonds.

Dynamics of Rotation of Crotyllithium (27). As described above, methyl in crotyllithium is *endo*- and the *exo*-methyl isomer could not be detected. At low temperature all four allylic protons are magnetically nonequivalent. The vicinal coupling constants among them are similar to those for (1,1-dimethylallyl)lithium (**26**); see Table 2. The dynamics of rotation around the CH−CH_2 bond of **27** are manifested by progressive averaging of the shift between the methylene hydrogens, with concomitant averaging of J_{AX} with J_{BX}. The way the methylene proton NMR line shape changes with temperature is similar to the behavior described for **26**. Therefore, the CH_2 dynamic line shape analysis for **27** parallels that described for **26**. Regarding the H_X NMR of **27**, its eight line multiplet is the result of H_X coupling to H_A, H_B, and H_M. The procedure for calculating the H_X line shape follows that published for $C_{(2)}H$ of (1-(trimethylsilyl)allyl)lithium.[26] Observed and calculated H_X line shapes are compared in Figure 3. The Eyring parameters which result from both procedures described above are quite similar; see Table 5.

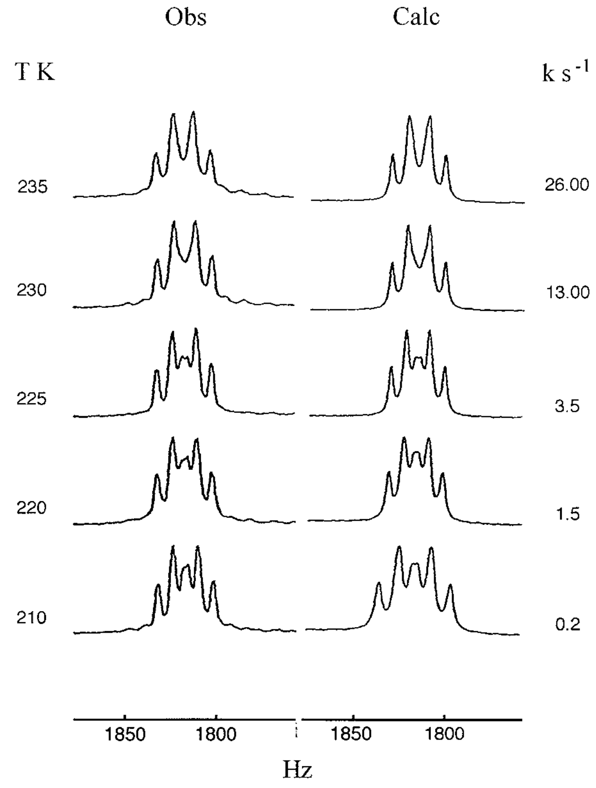
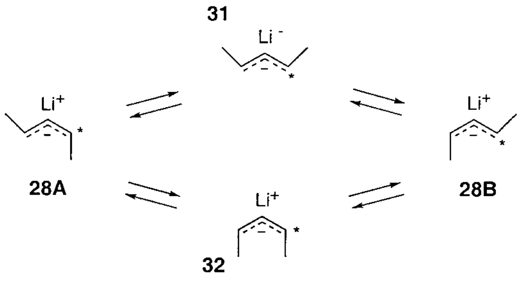


Figure 3. Proton NMR of C_2H part of **27**, TMEDA complex, in THF-d_8: (left) observed, different temperatures; (right) calculated with first-order rate constants.

***endo,exo*-(1,3-Dimethylallyl)lithium (28), Dynamics of Rotation.** As described above, the pattern of vicinal proton, proton coupling constants observed at low temperature establishes the endo, exo structure for **28**; see Table 2. Other possible isomers could not be detected. With increasing temperature there is averaging of the two C-methyl proton NMR doublets to a single doublet. Also with increasing temperature the equal quartet due to the $C_{(2)}H$ proton resonance progressively changes to a 1:2:1 triplet. The separation is the average of the two allyl vicinal proton coupling constants. NMR line shape analysis of the C_2H resonance parallels that for C_2H of **26**. Comparison of observed and calculated line shapes, Figure 4, provided the rate constants for interconversion **28A** ⇄ **28B**. The resulting activation parameters are listed in Table 5. Most likely the interconversion of **28A** to **28B** is the result of two consecutive bond rotations via one or both of the isomers **31** and **32**. Neither of the latter was detected among the NMR data for (1,3-dimethylallyl)lithium.



***endo,exo,endo*-(1,1,3-Trimethylallyl)lithium (19).** The proton and ^{13}C NMR spectra of compound **19** are invarient over the temperature range 190−300 K. Only one isomer could be observed. Under these conditions interconversion dynamics

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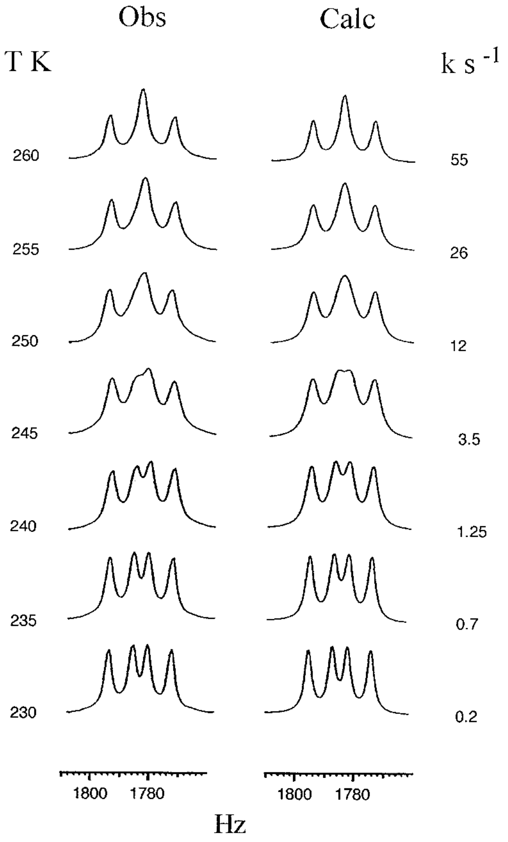


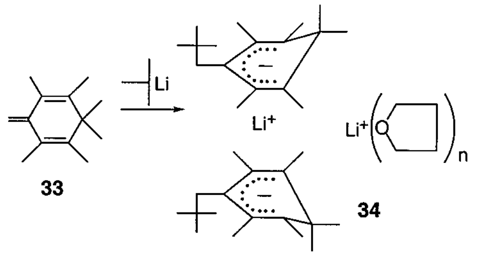
Figure 4. Proton NMR of C$_{(2)}$H part of *endo,exo*-(1,3-dimethylallyl)-lithium, TMEDA complex, **28**: (left) observed, different temperatures; (right) calculated with first-order rate constants for rotation.

between the predominant species, **19**, and isomers in low concentration could not be detected among the NMR spectral data.

Conclusions

The effect of alkyl substitution on carbanion structure and reactivity has been a neglected subject compared to the influence of alkyl groups on free radicals and on carbocations.

We previously showed that the (peralkylcyclohexadienyl)-lithium compound **34**, formed by addition of *tert*-butyllithium to **33**, is far more stable than cyclohexadienyllithium.[27] We proposed that periplanar steric repulsions between the ring methyls in **34** render the transition state for aromatization energetically inaccessible under ordinary conditions[27] thereby stabilizing the ground state. By contrast, our preparation of (1,1,3,3-tetramethylallyl)lithium (**5**) was far more reactive than allyllithium. We proposed that distortion from coplanarity due to methyl−methyl repulsion in **5** was responsible for its reactivity.



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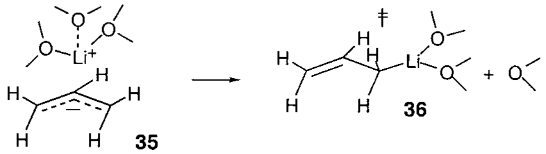
The present study confirms the predilection of terminal methyl in an allylic lithium compound to occupy the endo site. Unsymmetrical alkyl substitution at the allylic termini results in disproportionatioan of the π allylic bond orders and of the terminal carbon electron densities. The π bond order to the more substituted terminus is larger and that to the less substituted terminus is smaller, both compared to the uniform bond orders in symmetrically substituted allylic lithium compounds.

It is already known that the barrier to rotation in allylic lithium compounds depends strongly on the mode of solvation of lithium.[26] A mechanism for the rotation process has been proposed which involves the development of increased C−Li covalency in the transition structure (**36**) compared to the ground state (**35**). This would necessarily accompany a decrease in Li−O(ether) coordination thereby releasing a molecule of ether. Such a desolvation rationalizes the large positive values of $\Delta S^{\ddagger}$.



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Experimental Section

Materials and Procedures. Ethers and pentane used in these procedures were freshly distilled from sodium and benzophenone under an argon atmosphere. Toluene was distilled from CaH$_2$. TMEDA was distilled from KOH and then from CaH$_2$ under argon. Organolithium compounds were analyzed using the double titration procedure. All glassware used for organometallic compounds was baked in an oven overnight, flamed out under argon, and finally flushed with argon.

NMR Equipment. Conventional NMR spectra were obtained with a Bruker AC-200 spectrometer. All variable-temperature experiments were carried out using a Bruker MSL-300 or the Bruker Avance 300 instrument.

Preparation of Stannanes. General Procedure. Compounds **11** and **13** were prepared by reducing a mixture of the allylic chloride (150 mmol) and dimethyldichlorostannane with magnesium turnings (0.2 gatom) in 100 mL of dry THF at 5 °C. Hydrolysis and extraction of this reaction mixture into hexanes followed by drying the latter extract and removal of solvent gave, after distillation, an 88% yield of **11** and separately **13** in 77% yield. Compounds **20** and **25** were obtained by LDMAN (80 mmol) reduction of the corresponding phenyl sulfide, **18** or **23** (41 mmol) in 50 mL of THF at −78 °C, followed by slow addition of trimethylation chloride. After workup as described above this procedure gave an 81% yield of **20** and, separately, **25** in 80% yield.

Allylic Lithium Compounds. General Procedure. Samples of allylic lithium compounds for NMR study were prepared by methyllithium (1.4 mmol) cleavage of the allylic tin compound (1.4 mmol) in 10 mL of diethyl ether with TMEDA (4 mmol) at 0 °C. An aliqot of 3 mL of the product solution was syringed into the NMR tube. All volatile components were removed under vacuum and replaced by 1.0 mL of THF-d_8. The sample tube was sealed off under vacuum.

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Supporting Information Available: NMR line shapes plotted versus temperature, Eyring plots NMR spectra, and text giving preparations of new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[26] Reference 7b, p 2584.

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