hemes. Alternatively, the difference in the location of distal His between the α and β subunits is not so effective as yielding appreciable difference in the bond energy of the bound oxygen. The invariance of the ν_{OO} frequency between the α and β subunits is also seen for the tetramer containing photodissociated transient COFe subunits as shown in Figure 9. Since we failed to obtain the ν_{OO} frequency for the tetramer having the equilibrium deoxyFe subunits, the role of this hydrogen bond in a quaternary structure change is not clear at the present stage. The ν_{OO} mode for oxyCo–Ni hybrid, in which the Ni subunit mimics the deoxyFe subunit,[43] may provide important information about a change of the hydrogen bond upon a change of quaternary structure.

Acknowledgment. This work has been in part supported by Research Grant HL 14508 from the National Heart, Lung, and Blood Institute and Grant-in-Aid for Cooperative Research (60304099) from the Ministry of Education, Science and Culture.

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Dynamic Exchange and Rotational Behavior of 2-Methylallyllithium: ^{1}H, ^{13}C, and ^{6}Li NMR

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Abstract: Proton NMR of 2-methylallyllithium-^{6}*Li* (**1**) in diethyl-d_{10} ether at 150 K indicates the existence of two species, differing in aggregation, undergoing interconversion and internal rotation slowly relative to the NMR time scale. NOE experiments, ^{1}H{^{1}H} and ^{6}Li{^{1}H}, establish shifts for methylene protons syn and anti to methyl and show lithium to be closest to the anti protons. NMR line-shape analysis of **1**, in diethyl-d_{10} ether above 150 K, yields $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for rotation of 9.6 kcal and −7.3 eu, whereas for interspecie exchange these values are 7.3 kcal and −3.4 eu. In the presence, separately, of THF, TMEDA, and pentamethyldiethylenetriamine (PMDTA) the predominant form of **1** is the less associated species. It is proposed that the line broadening seen previously in low-temperature (200 K) NMR spectra of allyllithiums resulted from exchange phenomena rather than field inhomogeneities from viscosity and precipitation effects.

Allyllithium is the simplest potentially conjugated of all organometallic compounds.[1,2] It is therefore surprising that despite extensive studies NMR,[3] crystallographic,[4] and theoretical[5,6] there are still fundamental unanswered questions. These include its structure(s) in solution, especially the site(s) of lithium in relation to the allyl moiety. Most organolithium compounds exist as rapidly interconverting mixtures of different species whose distribution varies with temperature and concentration.[6] Such data are not currently available for allyllithium. In all likelihood the rates of specie interconversion have been too fast to handle with NMR methods, at the lowest temperatures used so far. Barriers to rotation of allyllithiums have been measured with NMR methods.[3a,7–9] It is not clear whether these apply to single species or are averages over some distribution of species.

This paper reports new insights into the structure and dynamic behavior of 2-methylallyllithium which we have studied using a variety of NMR methods, starting at very low temperatures.

Results and Discussion

Cleavage of tetrakis(2-methylallyl)tin by butyllithium in diethyl ether yielded clean samples of 2-methylallyllithium; see Experimental Section.

Proton NMR, 500 MHz, of **1** ca. 0.05 M in diethyl-d_{10} ether at room temperature consists of one sharp peak each for CH_2 and CH_3 at δ 2.15 and 1.7, respectively. There is no evidence of spin coupling between CH_2 and CH_3. With decreasing temperature the CH_2 resonance broadens and splits out into two δ peaks, by 205 K at δ 2.32 and 1.98, reminiscent of results attributed to slow rotation about the C_1–C_2 (C_2–C_3) bonds of other allyllithiums.[3a,7–9] However, below 205 K the δ 2.32 peak broadens, disappears into the base line, and develops by 155 K into two lines centered at δ 2.15 and 2.84, respectively; see Figure 1. Throughout this temperature range (205 to 155 K) and in other samples as low as 135 K, the δ 1.98 peak remains sharp and its shape does not change, as is also the case for the methyl resonance which is always a single line. Cooling the ether solution of **1** below 155 K brings about some line broadening but no significant changes. However, when **1** is diluted in diethyl ether (see Figure 2), the area ratio of the resonance at δ 2.15 to that at δ 2.84 increases markedly, implying the existence of at least two species, differing in aggregation. Furthermore, the summed area at δ 2.15 and 2.84 always equals that at δ 1.98. Then it appears that each of two species gives rise to two methylene proton resonances: at δ 2.84 and 1.98 for the prevailing species at higher concentrations of **1** and δ 2.15 and 1.98 for the less associated species. Note that the singlet at δ 1.98 represents methylene protons from *two* species.

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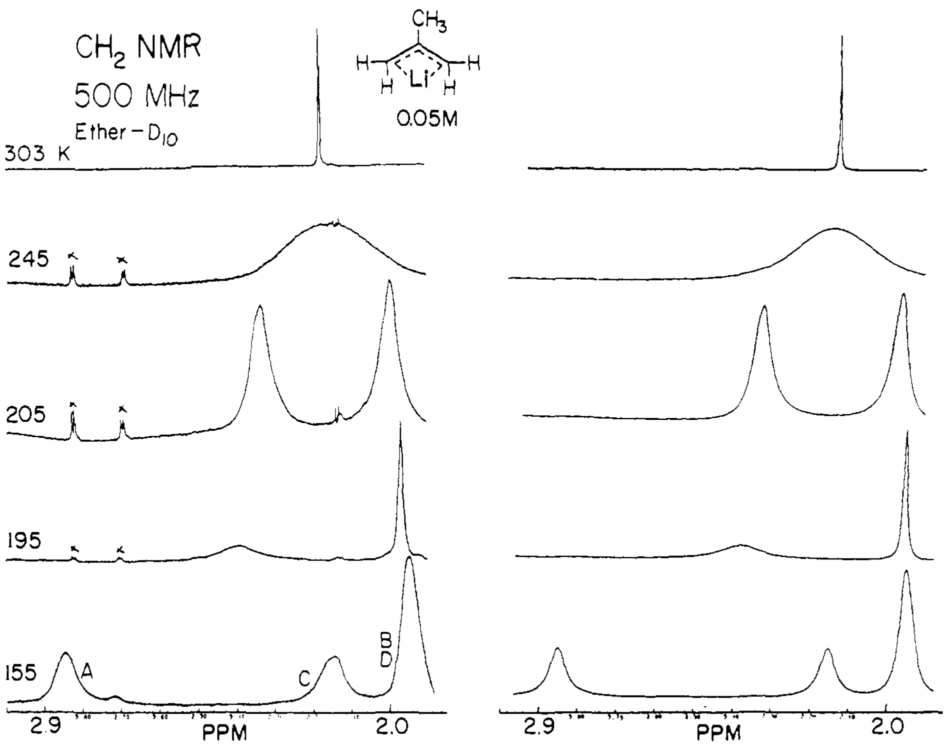


Figure 1. Left: proton NMR, 500 MHz, CH_2 region of 2-methylallyllithium-^6Li, 0.05 M diethyl-d_{10} ether, at different temperatures. Cross marks indicate minor impurities. Right: calculated for T, K, with K_{ex}, K_r s^{-1}: 155 K, 35, 3×10^{-3}; 195 K, 5500, 2.1; 205 K, 1.2×10^4, 7.5; 245 K, 2.5×10^5, 410; 303 K, 55×10^6, 2.1×10^4.

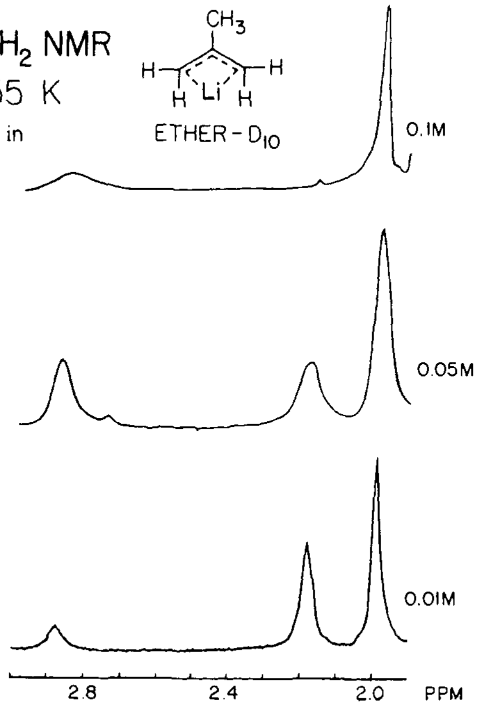
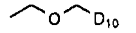
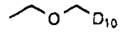
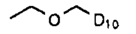
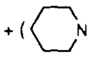
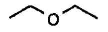


Figure 2. Proton NMR, 500 MHz, CH_2 region of 2-methylallyllithium in diethyl-d_{10} ether, 155 K, different concentrations.

Further, according to the results of a proton proton NOE[10] experiment it is the latter protons which are syn to methyl. Thus, when the methyl peak was irradiated (5 s, 220 K, in a solution containing excess N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDTA)), the peak at δ 1.83 was enhanced 3% while the peak at δ 2.15 had a negative enhancement of 1%. This assigned the less shielded protons at δ 2.15 and 2.84 to be anti to methyl. Further, a $^6Li\{^1H\}$ NOE[11,12] experiment (irradiate protons, observe ^6Li) clearly shows ^6Li to be closest to the latter two protons (anti to methyl) and furthest from CH_3. Using a 3-s proton irradiation, the results listed in the format % ^6Li enhancement (proton irradiated) are 12% (CH_3), 25% (δ 1.98), 29.5% (δ 2.84), and 29.5% (δ 2.15). This is consistent with the observation that the shifts of protons anti to methyl are the most sensitive to aggregation.

Table I. ^{13}C NMR Shifts of 2-Methylallyllithium (ppm/TMS)

medium	T, K	CH_2	CH_3
THF-d_8	303	52.34	26.13
	303	52.9	26.1
	173	52.25	25.75
	140	52.32	29.5
THF-D_8 + ( $NCH_2)_2$	220	53.05	27.0
 PMDTA	303	52.45	
 PMDTA	173	51.11	

A temperature-dependent equilibrium distribution of species is also evident from the way the δ 2.15 and 2.84 peaks signal average. With increasing temperature the center of gravity of the signal-averaged resonance moves to lower δ values; i.e., warming favors the less associated form of **1** in diethyl ether.

In the presence of other ligands (THF with 4 to 10 equiv of diethyl ether; 1 equiv of 1,2-di-N-piperidinoethane in THF; dimethyl ether–diethyl ether–THF-d_8 (20:10:70); and 2 equiv of PMDTA in diethyl-d_{10} ether), the methylene proton NMR of **11** by 155 K consists only of two peaks of equal intensity at ca. δ 1.98 and 2.15, correlating with the data for the less associated species in diethyl-d_{10} ether. As before, increasing the temperature

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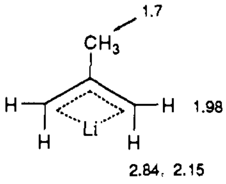
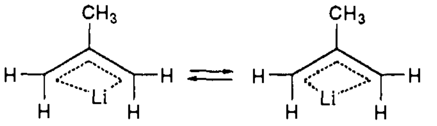
brings about signal averaging of these two resonances presumably due to bond rotation.[3a,7-9]

Proton-decoupled ^{13}C NMR of **1** in all media investigated down to as low as 135 K consists of one sharp line each for CH_2 and CH_3, with largely invariant shifts, and no detectable $^{13}C,^{6}Li$ coupling; see Table I. This is not the result of fast ^{6}Li relaxation since ^{6}Li resonance of **1** is always sharp, 2.6-Hz line width at 150 K.

The explanation most consistent with all the above results is that **1** exists in diethyl-d_{10} ether as a mixture of at least two different aggregates, the less associated of which prevails at lower concentrations and higher temperatures, and is found exclusively when better lithium ligands than diethyl ether are employed, such as THF or PTMEDA. Since allyllithium is dimeric at the freezing point of THF,[13] the less associated form of **1** in diethyl ether is most likely a solvated dimer. The 2-methylallyl moiety is either symmetrical, **2s**, or unsymmetrical, **2a**, and undergoing end-to-end lithium transfer, fast relative to the NMR time scale, even at 135 K; see eq 1. Note that a slight dissymmetry in allyllithium in THF was indicated from a deuterium perturbation of equilibrium experiment carried out by one of us.[13]



2s, proton NMR



(1)

2a

Finally in both aggregates lithium is closer to the anti (to methyl) methylene hydrogens than to the syn hydrogens. The change in the proton NMR line shape of **1** in diethyl ether must result from two dynamic processes: the exchange of allyls between different aggregates which averages the two CH_2 doublets to one, and the slower rotation about C_1–C_2 (C_2–C_3) which averages syn with anti hydrogen shifts, respectively.

It is instructive to show how the methylene proton NMR line shapes of **1** in diethyl ether were calculated, taking into account both bond rotation and transfer of 2-methylallyls between species.[14] Since the proton NMR of **1** is first order, with no discernible proton–proton spin coupling, not even geminal coupling,[15] the two methylene groups are magnetically independent so the four hydrogens can be simulated as a single uncoupled pair, one pair for each species. For convenience we label the CH_2 protons for the more associated species X as A and B (shielding direction), and in species Y (less associated) as C and D; see Figure 1. Their corresponding density matrix elements are written, for example, as ρ_A^X. The effect of exchange (e) and rotation (r) on two of these elements is

$$\rho_A^X(r) = \rho_B^X \qquad \rho_B^X(r) = \rho_A^X \qquad \rho_A^X(e) = \rho_C^Y \qquad \rho_B^X(e) = \rho_D^Y \tag{2}$$

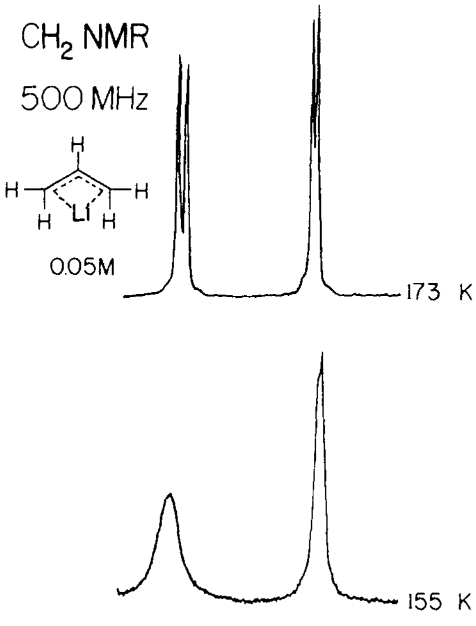


Figure 3. Proton NMR, 500 MHz, allyllithium, in diethyl-d_{10} ether, at two temperatures, K.

Table II

	^{1}H	^{13}C	^{6}Li
frequency, MHz	500.139	75.436	44.148
transform, K	32	32	8
spectral width, Hz	5000	15151.5	833.39
Hz/point	0.305	0.925	0.216
pulse width, μs	8	8	5
aquisition time, s	3.277	2.0	2.325
transients	16	1000	32

The resulting density matrix equations take the form

$$(\mathrm{DI} + R)\rho_{col} = iB_{col} \tag{3}$$

with the ρ elements ordered as ρ_A^X, ρ_B^X, ρ_C^Y, ρ_D^Y; B_{col} is 1,1,1,1; diagonal elements $i\Delta\omega_S - T^{-1} - k_r - \tau(s\rightarrow s')^{-1}$; and R, the reorganization matrix, is shown in eq 4. Comparison of the experimental spectra with calculated line shapes gives rise to a barrier to rotation, $\Delta H^{\ddagger}{}_r$, of 9.6 kcal with $\Delta S^{\ddagger}{}_r$ of −7.3 eu, similar to published values for other simple allyllithiums.[3a,7-9] For the faster interaggregate exchange observable only below 160 K, $\Delta H^{\ddagger}{}_e$ = 7.3 kcal and $\Delta S^{\ddagger}{}_e$ = −3.4 eu. The latter entropy of activation implies that the slow step for specie interconversion is accompanied by little change in solvation of lithium. The actual exchange rate at 155 K, $\tau_{X\rightarrow Y}$ of 0.14 s is still fast enough to obscure a possible $^{13}C,^{6}Li$ coupling (if it exists) of as much as 5 Hz.

$$\begin{bmatrix} 0 & k_r & \tau(X\rightarrow Y)^{-1} & 0 \\ k_r & 0 & 0 & \tau(X\rightarrow Y)^{-1} \\ \tau(Y\rightarrow X)^{-1} & 0 & 0 & k_r \\ 0 & \tau(Y\rightarrow X)^{-1} & k_r & 0 \end{bmatrix} \tag{4}$$

We have observed similar effects to those reported for **1**, implicating slow interconversion of species, in the proton NMR of allyllithium in diethyl-d_{10} ether. These results clearly show a selective broadening of one of the methylene proton resonances by 155 K (Figure 3). Apparently exchange is still too fast to permit ^{1}H NMR resolution of different species at 500 MHz. Thus previous reports in the literature, of excessively broadened proton NMR of allylic lithium compounds,[3a,7-9,16] which were ascribed to viscosity and precipitation effects, may well have been due to a slowing of interaggregate exchange. Most of these studies were not conducted below 200 K. Hence NMR resolution of species would not have been possible. Clearly, both bond rotation and specie interconversion dynamics influence the appearance of NMR spectra of allyllithium compounds, and neither one can be mea-

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Table III. ^{6}Li NOE of **1** in Diethyl Ether: % ^{6}Li NMR Enhancement

proton irrad	CH_3	H(syn)	H(anti) less assoc	H(anti) more assoc
3 s	12	25	29.5	29.5
10 s		28	39	39

sured unless the line-shape calculation takes account of both processes. Further, NMR studies of allyllithium compounds must be carried out as a function of RLi concentration, ligand, concentration, and temperature, the latter as low as is consistent with good NMR resolution.

This work emphasizes the utility of NOE measurements to determine the relative positions of hydrogens relative to lithium. Further, we establish the necessity of obtaining NMR data at as low a temperature as is practical in order to minimize the effects of exchange processes.

Experimental Section

NMR spectroscopy was carried out using Bruker equipment, AM-500 for protons and MSL 300 for ^{6}Li and ^{13}C. Relevant instrumental parameters are listed in Table II.

NOE effects were measured for ^{6}Li NMR spectra by selectively irradiating hydrogen resonances. In these experiments, first both proton and lithium NMR spectra were recorded. A proton frequency list was then created including the following resonances: methyl, CH(syn), CH(anti) both species, and a frequency approximately 10 ppm removed from all resonances, selected as null.

In a typical accumulation the proton resonance was irradiated for 3 s, then the decoupler turned off and the ^{6}Li spectrum recorded (see Table III). These results establish the relative proximities of ^{6}Li and different protons. Because of a slow but significant interspecie exchange rate, the above results are probably somewhat attenuated.

Tetrakis(2-methylallyl)tin. The general procedure follows that of Fishwich and Wallbridge.[17] A 2-L three-neck flask fitted with an overhead stirrer, a reflux condenser, and an addition funnel was flame-dried while flushing with argon. Magnesium (25 g) was added along with a crystal of iodine and 25 mL of THF. Methallyl chloride (10 g) was added and the solution stirred without further addition until the yellow/brown color of the iodine solution was dissipated. Once this occurred the solution was cooled with ice, and a solution of allyl chloride (85 g) and tin tetrachloride (25 mL, 55.7 g, 0.21 M) in hexane (200 mL) was added dropwise. After approximately 15 mL an additional liter of THF was added to dissolve the Grignard reagent. After complete addition the mixture was stirred at room temperature overnight and then heated to reflux for 0.5 h. After cooling to room temperature this reaction mixture was poured into an ice/ammonium chloride slurry and the organic layer extracted with hexane. The combined organic layers were dried over $MgSO_4$ and filtered; then the solvent was removed in vacuo, yielding 36 g of the title compound, bp 134 °C (4 Torr), 50% yield; proton NMR (250 MHz, $CDCl_3$) δ 1.71 (s, 3 H), 1.91 (s, 2 H), 4.54, 5.24.

2-Methylallyllithium.[18] All of the following procedures were performed in a Vacuum-Atmospheres inert atmosphere box, with argon. Glassware was oven-dried at 130 °C and cooled in vacuo.

Freshly distilled and degassed tetrakis(2-methylallyl)tin (1.7 g) was weighed into a 150-mL Schlenk flask. Diethyl ether (25 mL, freshly vacuum transferred from Na/K benzophenone ketyl) was added and stirring begun. *n*-Butyllithium-^{6}*Li* (4 mL, 2.6 M in hexane) was added via syringe over 15 min. The yellow solution was stirred 1 h. The diethyl ether was removed in vacuo (in the glove box). A yellow paste formed together with a layer of dibutyldiallyltin. Three times pentane (10 mL) was added; the phases were mixed for 30 min and the pentane was poured off. The viscous allyllithium etherate was evacuated for a short period to remove pentane and then dissolved in ether (5 mL). This reaction is essentially quantitative. An NMR sample of this solution showed no impurities.

Acknowledgment. This research was partly supported by the National Science Foundation, Grant No. CHE 8304636, which also helped finance the high-field NMR equipment used in this work. We thank Dr. Charles Cottrell, Chemical Instrumentation Center, The Ohio State University, for assistance with the NMR technology.

Registry No. 2-Methylallyllithium, 61777-16-0; tetrakis(2-methylallyl)tin, 39482-35-4; methallyl chloride, 563-47-3; tin tetrachloride, 7646-78-8; *n*-butyllithium-^{6}*Li*, 20535-67-5.

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Multicomponent Quantitative Analysis Using Second-Order Nonbilinear Data: Theory and Simulations

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Contribution from the Laboratory for Chemometrics, Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195. Received July 22, 1988

Abstract: The application of rank annihilation to a class of instruments generating data which can be classified as second-order nonbilinear is described. This method permits determining the concentration of an analyte of interest even in the presence of spectral interferents unknown and unaccounted for during calibration. The primary difficulty in applying rank annihilation to nonbilinear data is that multiple, different concentration estimates are obtained; it is shown that, for two-dimensional mass spectrometry and absolute value mode two-dimensional nuclear magnetic resonance spectroscopy, the correct concentration estimate should be the smallest of those obtained. The method provides a back-estimate of the calibration matrix, which can be used as an indication of the accuracy of the resulting concentration estimate, as well as a diagnostic for the presence of matrix effects between the calibration and unknown samples. In this paper, the theory and motivation for rank annihilation is presented, and the application to nonbilinear data is presented using computer simulations and a test system consisting of 2D *J*-coupled NMR spectra (COSY) of six sugars in D_2O.

In modern analytical chemistry, one of the fastest growing areas for practical applications is the use of multivariate calibration for multicomponent quantitative analysis.[1] Multivariate methods are necessary in order to utilize the tremendous amounts of data that can be collected with modern analytical instruments and laboratory computers, and because fast, inexpensive calibration methods can largely replace slower, more expensive direct determination methods. A good example of this is the use of near-infrared reflectance spectroscopy to routinely measure the protein content of wheat, while the Kjeldahl nitrogen analysis is

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