

¹H AND ⁷Li NMR OBSERVATIONS OF EXCHANGE PROCESSES IN ALKYL LITHIUM-ATE COMPLEXES

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Summary

The kinetics of ⁷Li exchange between LiR and LiAlR₄, where R = CH₃, C₂H₅ and CH₂Si(CH₃)₃, have been observed in diethyl ether solutions. In agreement with earlier conclusions, the exchange is found to be rate-determined by dissociation of alkyl lithium tetramer, with rate constant *k*₁. Line shape analysis of the NMR spectra over a wide range of temperature yields an Arrhenius activation energy of 12.4 ± 1.5 kcal/mole (99% confidence level) and pre-exponential term of 1.43 × 10¹³ sec⁻¹ for R = CH₃; 11.3 ± 1.7 kcal/mole and 2.12 × 10¹² sec⁻¹ for R = C₂H₅. For R = Me₃SiCH₂, ⁷Li exchange is rapid on the NMR time scale (i.e., *k*₁ > ~10³ sec⁻¹) at -90°C. It thus appears that dissociation of the alkyl lithium tetramer is promoted by increased electron release and/or increased steric requirement of the alkyl group. Alkyl group exchange is slow at room temperature in mixtures of Me₃SiCH₂Li—LiAl(CH₂SiMe₃)₄ and Me₃SiCH₂Li—LiCr(CH₂SiMe₃)₄. ⁷Li exchange is rapid at -95°C in mixtures of Me₃SiCH₂Li and Me₃SiCH₂Cu at various ratios. In the ¹H spectrum distinct resonances corresponding to a 1/1 Li/Cu species and Me₃SiCH₂Li are seen for Li/Cu ratios > 1, at -50°C and below. The NMR results show that the only significant mixed species in the solutions is the 1/1, probably a dimeric species (Me₃SiCH₂)₄Li₂Cu₂.

Introduction

The natures of several lithium "ate" complexes in solution have been clarified as a result of work performed during the past several years [1,2]. In particular, it has been quite securely established that LiMR₄ compounds, where M is a Group III metal and R is an alkyl group, are largely ionic in ethers, and that an equilibrium occurs between contact and solvent-separated ion pairs [3,4]. Williams and Brown observed that exchange of ⁷Li between methyllithium and

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lithium tetramethylaluminate or tetramethylboronate in diethyl ether is first order in methyllithium and zero order in the ate complex [5]. Furthermore, it proved to be independent of the particular choice of ate complex. The rate-determining process was postulated to be dissociation of the alkyllithium tetramer.

We have undertaken an enlarged investigation of LiR-LiAlR_4 systems, with the intention of observing the effect of change in the alkyl group on the rate and energetics of the exchange. A reinvestigation of the methyl system originally studied is also advisable in light of improved NMR instrumentation and line shape analysis capability, which makes it possible now to obtain considerably more reliable data on these important equilibria.

We report in this paper also on the formation of lithium ate complexes with various metals involving the trimethylsilylmethyl group (Me_3SiCH_2).

Results

^7Li lineshape studies in LiR-LiMR_4 solutions

Methyllithium, ethyllithium and trimethylsilylmethylmethyllithium all exhibit single symmetrical lines in the ^7Li NMR spectrum in the temperature interval $+30$ to -90°C . The chemical shifts relative to an external aqueous lithium bromide standard at 30° are -51 , -23 and -63 Hz, respectively. The ^7Li linewidth of methyllithium increases markedly in the temperature range from 0 to -50° . Similar broadening is observed for ethyllithium in a slightly lower temperature interval, -10 to -65°C . This broadening is due to scalar coupling between ^7Li and the protons of the α -carbon of the alkyl groups [6]. The broadening occurs in the region of transition from fast to slow intermolecular exchange among the lithium tetramers. If the coupling were large enough, methyllithium would have a ten line ^7Li spectrum at low temperature, due to interaction of a given Li with three equivalent methyl groups. However, since the coupling constant is of the order of perhaps 0.2 or 0.3 Hz, only a broadening is seen [6]. Intermolecular exchange of ^7Li between LiR and LiMR_4 species occurs in the temperature interval in which the scalar interaction just described becomes operative. To carry out reasonably accurate line shape analyses it is necessary to decouple the ^7Li from protons via heteronuclear spin-spin decoupling. This was not done in the earlier work [5].

The ^7Li resonance absorptions of lithium tetraalkylaluminates are also single, symmetrical lines. At 30°C , ethereal lithium tetramethylaluminate, lithium tetraethylaluminate and lithium tetrakis(trimethylsilylmethyl)aluminate have respective chemical shifts of $+50$, $+57$ and $+56$ Hz relative to aqueous lithium bromide external standard. There is a large temperature dependence of the ^7Li chemical shift of both $\text{LiAl}(\text{CH}_3)_4$ and $\text{LiAl}(\text{C}_2\text{H}_5)_4$. At -50°C the chemical shift relative to the external aqueous LiBr reference is around 11 Hz upfield from the $+30^\circ\text{C}$ value.

Solutions of CH_3Li and $\text{LiAl}(\text{CH}_3)_4$ in diethyl ether at room temperature exhibit a single ^7Li NMR signal, as a result of rapid ^7Li exchange. Lowering the temperature slows the exchange until the stopped exchange region is reached around -50°C . Figure 1 shows representative ^7Li NMR spectra for the proton decoupled $\text{CH}_3\text{Li-LiAl}(\text{CH}_3)_4$ system.

Detailed lineshape analysis was carried out on the $\text{CH}_3\text{Li-LiAl}(\text{CH}_3)_4$ system by comparison of observed and calculated lineshapes. The calculated

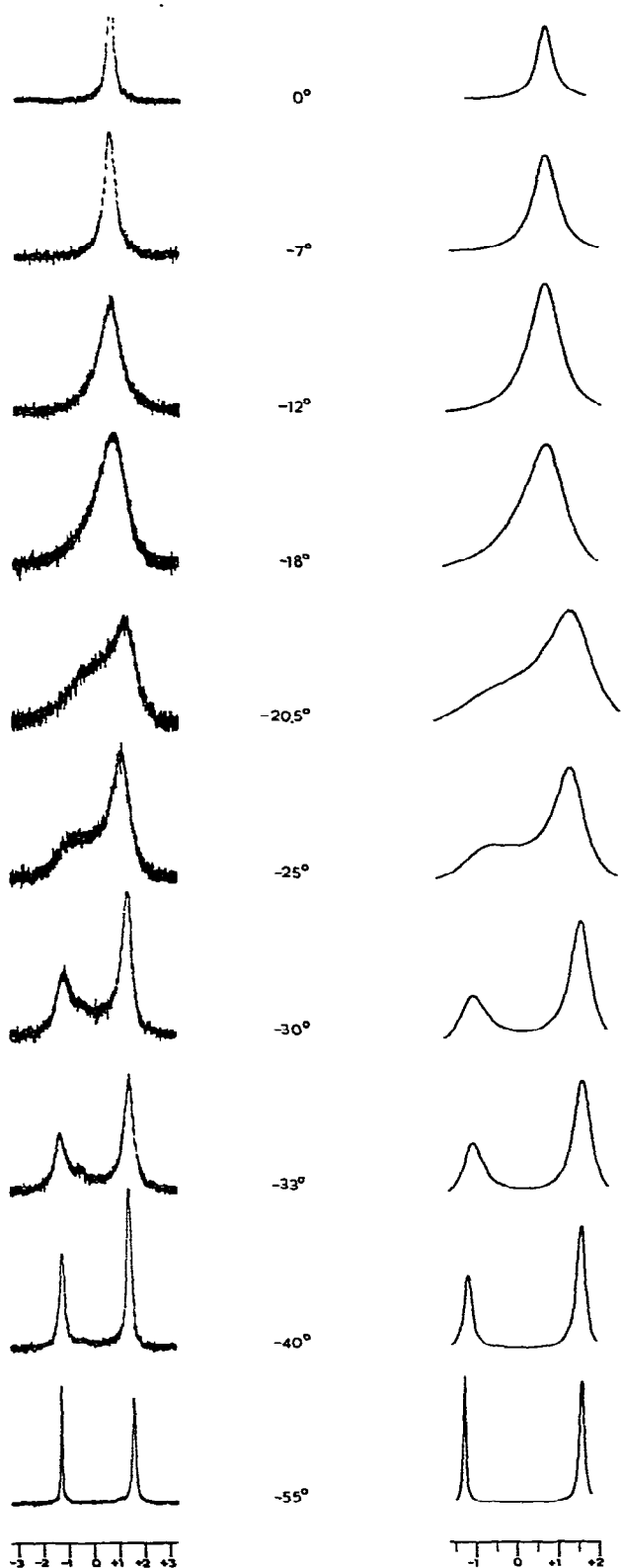
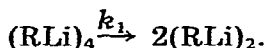


Fig. 1. Experimental and calculated ${}^7\text{Li}$ NMR spectra for a $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$ mixture in ether at various temperatures.

lineshapes were obtained by using values of T_{2A} , T_{2B} and peak separation from spectra of pure methyl lithium and pure lithium tetramethylaluminate. These values were then varied slightly at each temperature in order to give the best fit. The calculated spectra for the $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$ system are also shown in Fig. 1

In order to calculate values for the rate constant and activation energy from the values obtained in the lineshape analysis, it is necessary to devise a mechanism consistent with the NMR data and determine the relationship between τ and the rate constant. The mechanism originally developed by Williams and Brown [5] was found to agree with the NMR data. In this mechanism it is assumed that the exchange is rate-determined by dissociation of the alkyllithium tetramer. The process is envisaged as a dissociation to dimers:



The data do not show that it is dimers and not monomers that undergo exchange with LiAlR_4 . It seems reasonable, however, as argued previously [5], that dimers are the kinetically active species. The reciprocal mean lifetimes, τ_i , for ^7Li nuclei at the $(\text{CH}_3\text{Li})_4$ and $\text{LiAl}(\text{CH}_3)_4$ sites are given in eqns. 1 and 2 [5].

$$\frac{1}{\tau(\text{LiAlR}_4)} = 4k_1 \frac{[\text{Li}_4\text{R}_4]}{[\text{LiAlR}_4]} \quad (1)$$

$$\frac{1}{\tau(\text{Li}_4\text{R}_4)} = k_1 \quad (2)$$

The weighted average time between exchanges obtained from the line shape analysis is thus [5]:

$$\frac{1}{\tau} = k_1 \left[1 + 4 \frac{[\text{Li}_4\text{R}_4]}{[\text{LiAlR}_4]} \right] \quad (3)$$

$[\text{Li}_4\text{R}_4]$ represents the concentration of methyl lithium computed as tetramer.

The reciprocal exchange rate $1/\tau$ depends only on the dissociation rate constant, k_1 , and the ratio $[\text{Li}_4\text{R}_4]/[\text{LiAlR}_4]$. The validity of eqns. 1 and 2 was tested by observing the linewidths at the two sites in the slow exchange region as a function of the ratio $[\text{LiR}]/[\text{LiAlR}_4]$. The quantity $1/\tau(\text{LiAlR}_4)$ was observed to increase linearly with increasing ratio. The slope of the line each case yielded a value for k_1 in good agreement with the value obtained from the Arrhenius plot. The quantity $1/\tau(\text{Li}_4\text{R}_4)$ was found to be invariant to changes in the $[\text{LiR}]/[\text{LiAlR}_4]$ ratio.

For the $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$ system, values of k_1 were calculated using eqn. 3 and the τ values obtained from the lineshape analysis. Figure 2 shows a graph of $\ln k_1$ vs. $1/T$ for the $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$ system. From a least squares fit of the data an Arrhenius energy of $12.4 \text{ kcal mole}^{-1}$ and a value of $A = 1.43 \times 10^{13} \text{ sec}^{-1}$ are obtained. The uncertainty in the activation energy is $\pm 1.5 \text{ kcal mole}^{-1}$ at the 99% confidence level.

Detailed lineshape analysis was carried out on the $\text{C}_2\text{H}_5\text{Li}-\text{LiAl}(\text{C}_2\text{H}_5)_4$ system via the same procedures used for $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$. The two systems are

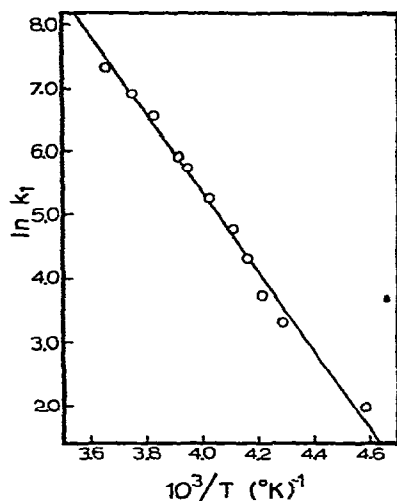


Fig. 2. Arrhenius plot for ^7Li exchange in $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$ in ether, based on eqn. 3. $[\text{CH}_3\text{Li}]$ 0.430M, $[\text{LiAl}(\text{CH}_3)_4]$ 0.795M.

entirely comparable in terms of procedures employed and quality of the data. Studies of samples containing various ratios of $\text{C}_2\text{H}_5\text{Li}$ to $\text{LiAl}(\text{C}_2\text{H}_5)_4$ yielded results similar to those obtained from the $\text{CH}_3\text{Li}-\text{LiAl}(\text{CH}_3)_4$ mixtures.

A least squares fit of the $\ln k_1$ vs. $1/T$ data yields an Arrhenius energy of $11.3 \text{ kcal mole}^{-1}$ and a value of $A = 2.12 \times 10^{12} \text{ sec}^{-1}$. The uncertainty in the activation energy is $1.7 \text{ kcal mole}^{-1}$ at the 99% confidence level. Mixtures of $\text{Me}_3\text{SiCH}_2\text{Li}$ and $\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ in ether exhibit fast ^7Li exchange even at -90°C . This would indicate that the dissociation rate constant, k_1 , for $(\text{Me}_3\text{SiCH}_2\text{Li})_4$ is much larger than that found for $(\text{CH}_3\text{Li})_4$ and $(\text{C}_2\text{H}_5\text{Li})_4$.

Attempts were made to study the $\text{Me}_3\text{SiCH}_2\text{Li}-\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ system in several other solvents in an effort to find a solvent in which it was possible to slow down the ^7Li exchange. Table 1 lists the results for different solvents, none of which exhibited slow ^7Li exchange.

^7Li and ^1H NMR spectra of $\text{Me}_3\text{SiCH}_2\text{Li}$ -ate complexes with Cu and Cr

Alkyl lithium and alkyl copper(I) compounds are known to form mixed com-

TABLE 1
RESULTS OF THE $\text{Me}_3\text{SiCH}_2\text{Li}-\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ SYSTEM IN VARIOUS SOLVENTS

Solvent	Result
Tetrahydrofuran	Fast exchange at -90°C
Dimethoxyethane	Fast exchange at -90°C
Triethylamine	Fast exchange at -90°C
Pentane	$\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ insoluble
Toluene	$\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ insoluble
Hexamethylphosphoramide	Decomposed
2,6-Lutidine	Decomposed
2-Picoline	Decomposed
Tetrahydrothiophene	Some decomposition; exchange appears fast at -90°C

plexes in solution [7-10]. Very little is known about the structure and extent of aggregation of these ate complexes [7-11]. $\text{Me}_3\text{SiCH}_2\text{Cu}$ has recently been reported on the basis of an X-ray crystallographic study to be a square-planar, tetranuclear cluster [12].

A copper-lithium ate complex has been prepared using trimethylsilylmethyl as the alkyl group [11]. In the present work solutions in diethyl ether with varying Li/Cu ratios were prepared and their ^7Li NMR spectra recorded. ^7Li exchange is fast in all samples; only one ^7Li resonance is found, even at -95°C . The signal is broad at -95°C , but this is partially due to the fact that part of the sample, especially excess $\text{Me}_3\text{SiCH}_2\text{Cu}$, precipitates from solution. For samples containing a lithium to copper ratio of 1/1 in ether, a single CH_2 absorption appears in the ^1H NMR spectrum over the entire temperature range of $+30$ to -90°C . A -50°C spectrum for the $\text{Me}_3\text{SiCH}_2\text{Li}-\text{Me}_3\text{SiCH}_2\text{Cu}$ system with ratio of 1/1 is shown in Fig. 3. When excess $\text{Me}_3\text{SiCH}_2\text{Cu}$ is present, the slow exchange limit is not attained; only one resonance for the CH_2 protons is observed even at -95°C . When excess $\text{Me}_3\text{SiCH}_2\text{Li}$ is present, slow exchange is reached at -50°C . Figure 3 shows a -50°C spectrum for a Li/Cu ratio of 3/1. The CH_2 protons exhibit two resonances, one with a chemical shift for $\text{LiCu}(\text{CH}_2\text{SiMe}_3)_2$ (as found in the spectra with Li/Cu ratio of 1/1) and one with a chemical shift for $\text{Me}_3\text{SiCH}_2\text{Li}$. These results strongly suggest that the only ate complex in solution is the 1/1 complex $\text{LiCu}(\text{CH}_2\text{SiMe}_3)_2$. If complexes with other Li/Cu ratios were present, they would have to undergo fast intermolecular exchange with the 1/1 complex below -50°C without exchanging with the excess $\text{Me}_3\text{SiCH}_2\text{Li}$ and must exhibit the same proton chemical shift as the 1/1 complex. This is unlikely because plausible processes for intermolecular exchange. (dissociation, association or ionic pathways) would also lead to exchange with excess $\text{Me}_3\text{SiCH}_2\text{Li}$.

$\text{LiCr}(\text{CH}_2\text{SiMe}_3)_4$ has been reported by Wilkinson and co-workers [13]. This complex is paramagnetic and its NMR spectrum in diethyl ether gives broad singlets at $\delta +2.2$ ppm for the CH_2 resonance and $\delta +0.4$ ppm for the CH_3 resonance.

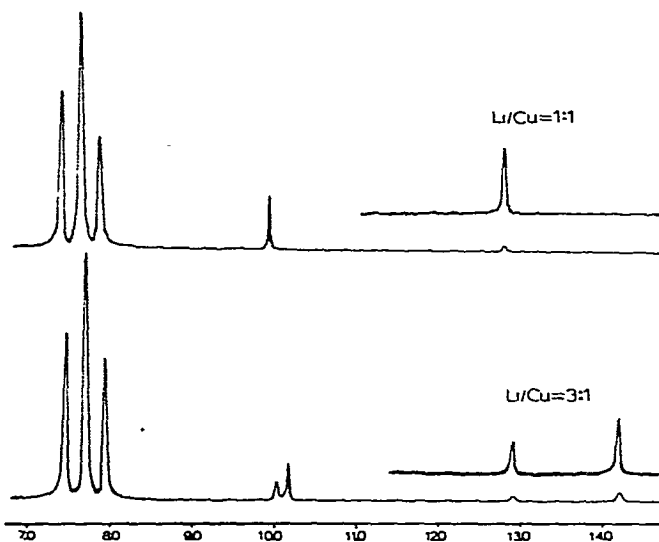


Fig. 3. ^1H NMR spectra at -50°C of $\text{Me}_3\text{SiCH}_2\text{Li}-\text{Me}_3\text{SiCH}_2\text{Cu}$ mixtures in ether.

Mixtures of this complex with $\text{Me}_3\text{SiCH}_2\text{Li}$ were examined in diethyl ether to determine whether exchange occurs. The NMR spectra of the mixtures revealed four broad peaks, two due to $\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ and two due to excess $\text{Me}_3\text{SiCH}_2\text{Li}$. There is no evidence of alkyl group exchange at room temperature. NMR samples were prepared which contained several drops of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) added to the mixtures. The NMR spectra of the mixtures containing added TMEDA, however, also reveal no evidence of alkyl group exchange.

Discussion

Assuming our model for the exchange process, the results obtained for the RLi-LiAlR_4 systems, where $\text{R} = \text{CH}_3$ or C_2H_5 , provide accurate values for the rate constant and activation energy of the dissociation of methyl lithium and ethyllithium tetramers. Table 2 gives values for k_1 at various temperatures for the two systems. The Arrhenius energy obtained in this study for the $\text{CH}_3\text{Li-LiAl}(\text{CH}_3)_4$ system is only about 1 kcal mole⁻¹ larger than the previously reported value [5], but the newer value is considerably more reliable.

The results of the present study indicate that both increased electron release and increased steric requirement of the alkyl group promote dissociation of the alkyllithium tetramer. Since the exchange was not stopped in the $\text{Me}_3\text{SiCH}_2\text{Li-LiAl}(\text{CH}_2\text{SiMe}_3)_4$ system, it was not possible to show that the rate law for exchange follows the form of eqns. 1 and 2. However, it seems very likely that $\text{Me}_3\text{SiCH}_2\text{Li}$ is tetrameric in ether, as the *n*-alkyllithium compounds have been shown to be [6,14,15]. Assuming that $\text{Me}_3\text{SiCH}_2\text{Li}$ is tetrameric in ether, it would appear that dissociation of the tetramer to give a less associated species which might undergo exchange with $\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$, is considerably more facile for $(\text{Me}_2\text{SiCH}_2\text{Li})_4$ than for either $(\text{CH}_3\text{Li})_4$ or $(\text{C}_2\text{H}_5\text{Li})_4$.

It is also possible that dissociation of the $\text{Me}_3\text{SiCH}_2\text{Li}$ tetramer to form solvated dimers in ethers occurs to a considerable extent, and that the rate-determining process in the exchange is a relatively facile interaction of a dimeric species, $(\text{Me}_3\text{SiCH}_2\text{Li})_2$, with $\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$. The apparently low degree of interaction of $\text{Me}_3\text{SiCH}_2\text{Li}$ with triethylamine in hydrocarbon solvent [16] might be ascribed to the existence of an equilibrium involving tetramers and dimers. Some of the driving force for such an equilibrium would come from the greater possible degree of interaction of base with the dimers as compared with the more sterically hindered tetramers. Evidence for or against such an equilibrium must await detailed and accurate colligative property measurements on $\text{Me}_3\text{SiCH}_2\text{Li}$ in basic solvents.

TABLE 2

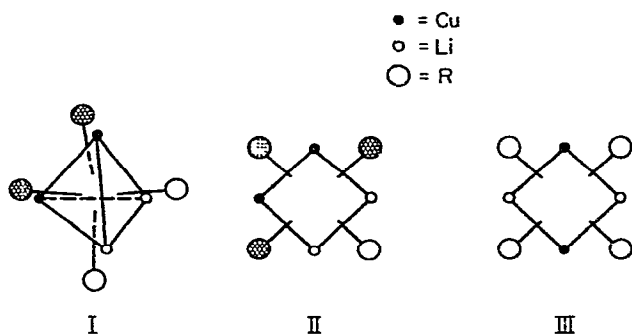
VALUES FOR k_1 (sec⁻¹) AT VARIOUS TEMPERATURES FOR THE $\text{CH}_3\text{Li-LiAl}(\text{CH}_3)_4$ AND $\text{C}_2\text{H}_5\text{Li-LiAl}(\text{C}_2\text{H}_5)_4$ SYSTEMS IN ETHER

	0°C	-25°C	-50°C
$\text{CH}_3\text{Li-LiAl}(\text{CH}_3)_4$	1720	173	10.3
$\text{C}_2\text{H}_5\text{Li-LiAl}(\text{C}_2\text{H}_5)_4$	2080	257	19.9

It was noted in the previous study of $\text{LiR}-\text{LiMR}_4$ systems that the ^1H spectrum shows slow exchange of alkyl groups between LiAlR_4 and excess LiR [5]. The same observations were made in the present study, including slow exchange of Me_3SiCH_2 between $\text{LiAl}(\text{CH}_2\text{SiMe}_3)_4$ and excess $\text{Me}_3\text{SiCH}_2\text{Li}$. An analogous result is seen also in the mixtures of $\text{Me}_3\text{SiCH}_2\text{Li}$ and $\text{LiCr}(\text{CH}_2\text{SiMe}_3)_4$.

The ^1H NMR spectra for $\text{Me}_3\text{SiCH}_2\text{Li}-\text{Me}_3\text{SiCH}_2\text{Cu}$ mixtures establish quite unambiguously that the 1/1 ate complex is the only species of significant concentration formed. The variation in ^7Li chemical shift in the mixtures as a function of ratio is also in agreement with this result. The ^7Li chemical shift was observed to lie downfield from the aqueous LiBr standard in solutions containing a 1/1 $\text{Me}_3\text{SiCH}_2\text{Li}-\text{Me}_3\text{SiCH}_2\text{Cu}$ ratio. Since this is considerably downfield from the range characteristic of the more ionic LiMR_4 compounds (vide supra) we conclude that the ate complex is probably not ionic, i.e., $\text{Li}^+\text{Cu}(\text{CH}_2\text{SiMe}_3)_2^-$.

The results do not indicate the extent of association for the 1/1 complex. Since both organocopper(I) [11,12,17-19] and alkyllithium compounds [16] are associated in solution it is reasonable to expect that the 1/1 complex LiCuR_2 will be associated. Noltes has reported [20] that $\{2-[(\text{CH}_3)_2\text{NCH}_2]\text{C}_6\text{H}_4\}_2\text{CuLi}$ exists as the dimer $(\text{R}_4\text{Cu}_2\text{Li}_2)$ in benzene. A dimeric species could exist as a tetrahedral structure with two lithium atoms and two copper atoms at the corners of a tetrahedron. Since the solid state structure of $(\text{Me}_3\text{SiCH}_2\text{Cu})_4$ has been shown to consist of a square planar array of copper atoms bridged by alkyl groups [12], alternative structures for the ate complex involving this geometry may be proposed. The most reasonable structures for $(\text{Me}_3\text{SiCH}_2)_4\text{Cu}_2\text{Li}_2$ are shown as I-III. Note that only in structure III are all the alkyl groups equivalent.



Given the large CH_2 chemical shift difference between $\text{Me}_3\text{SiCH}_2\text{Li}$ and $\text{Me}_3\text{SiCH}_2\text{Cu}$, it is reasonable to expect that the CH_2 groups of non-equivalent alkyl groups in structures I and II would exhibit significantly different shifts. But only one CH_2 resonance ascribable to a mixed complex appears in the NMR spectra, as is evident from Fig. 3. This requires either that structure III is the correct structure for the 1/1 species or that a rapid exchange process is occurring which mixes the two kinds of alkyl groups in one of the other structures. It seems very unlikely that the mixed species, whatever its structure, is undergoing rapid dissociation on the NMR time scale, since the dissociation products would then be expected to undergo rapid exchange with the excess $\text{Me}_3\text{SiCH}_2\text{Li}$. A rapid intramolecular exchange within the $(\text{Me}_3\text{SiCH}_2)_4\text{Cu}_2\text{Li}_2$ species would lead to equivalence of the four alkyl groups. At present it is not possible to tell which of these

alternatives is correct. The question might be answered by observing the NMR spectra of mixtures of appropriate R_2CuLi and R'_2CuLi pairs.

Finally, it should be noted that exchange of alkyl groups is rapid on the NMR time scale to -90° when $Li/Cu < 1$. We may speculate that the exchange in this instance is between the 1/1 ate complex and excess copper reagent. The mechanism of the exchange process is not clear. The behaviour is, however, similar to that observed with ate complexes of Group II metals [21].

Experimental

Proton NMR spectra were obtained using Varian Associates A-60A and A-56/60 spectrometers equipped with standard Varian temperature controllers. The temperature was measured with an accuracy of $\pm 1^\circ C$ by measuring the chemical shift of methanol [22].

Lithium-7 spectra were obtained at 38.862 MHz in a field of 23487 gauss using a Varian Associates model HA-100 spectrometer equipped with standard Varian temperature accessories. The temperature was measured with an accuracy of $\pm 1^\circ C$ with a copper constantan thermocouple. Spectra were obtained by observing the upfield sideband produced from the imposition of an "internal" 2500 Hz audio frequency on the 38.862 MHz resonance frequency. Spectra were recorded in a frequency sweep, non-lock mode.

Aqueous lithium bromide (7 g commercial grade lithium bromide in 10 ml of solution) was used as an external standard for all 7Li chemical shifts. In some spectra, the $^7Li-^1H$ scalar coupling was eliminated by proton decoupling over a two KHz frequency range.

NMR spectra were analyzed using a general two site computer program [5,23].

All synthetic work was performed in the absence of oxygen and water, in a Vacuum Atmospheres Corporation glove box with a continuously recirculated argon atmosphere [24].

Air sensitive samples were prepared in the glove box, and then removed to the vacuum line where they were degassed and sealed off. After the samples were prepared, they were kept at dry ice temperatures until the appropriate spectra were obtained.

Mixed solutions containing various ratios were prepared from stock solutions previously standardized. All solvents employed were carefully purified by standard techniques.

The concentration of alkyllithium solutions were determined by decomposing aliquot samples with water and immediately titrating to a phenolphthalein end point with standard acid. The concentrations of lithium tetraalkylaluminate and lithium dialkylcuprate solutions were determined using standard EDTA titrations.

Alkylaluminums were obtained from the Ethyl Corporation and used without further purification.

Ethyllithium in benzene was purchased from Lithium Corporation of America. It was recrystallized from cyclohexane until white crystals were obtained.

The following compounds were prepared as reported in the chemical literature: methyllithium [6], lithium tetramethylaluminate [25], lithium tetraethylaluminate [25], trimethylsilylmethylcopper(I) [11], lithium bis(trimethyl-

silylmethyl)cuprate(I) [11], and lithium tetrakis(trimethylsilylmethyl)chromate (III) [13], trimethylsilylmethyl lithium [26], and bis(trimethylsilylmethyl)mercury [27].

*Tris(trimethylsilylmethyl)aluminum**

One gram of $(\text{Me}_3\text{SiCH}_2)_2\text{Hg}$ and 0.5 g of aluminum turnings were sealed under vacuum in a Carius combustion tube. The tube was heated to 110°C for 12 h. The tube was then broken open inside the glove box to yield a clear liquid of $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ (Anal. found: C, 49.29; H, 11.10. $\text{C}_{12}\text{H}_{33}\text{Si}_3\text{Al}$ calcd.: C, 49.94; H, 11.52%.)

Lithium tetrakis(trimethylsilylmethyl)aluminate

A solution containing 0.30 g of $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ in 200 ml of pentane was prepared inside the glove box. A second solution containing 0.90 g of $\text{Me}_3\text{SiCH}_2\text{-Li}$ dissolved in 25 ml of pentane was then added to the $(\text{Me}_3\text{SiCH}_2)_3\text{Al}$ solution, resulting in the formation of a thick white precipitate. The solution was stirred for one hour and then filtered under vacuum. The precipitate was dried under vacuum. (Anal. C/H ratio, found, 2.73. calcd.: 2.75.)

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