

complexes are similar. Furthermore, the ^7Li resonances of Li_2MR_4 complexes are further upfield when R is phenyl than when R is methyl. The trend seems to be that, in more ionic organolithium species in ether, the ^7Li resonance is further upfield, presumably as a result of increased solvation. Thus, the chemical shift and exchange rate data indicate that the phenyl complexes of magnesium and zinc are more ionic than their methyl counterparts. This is reasonable in light of the greater electron withdrawal of the phenyl group relative to methyl.

The only kinetic evidence relating to the systems that arise when $\text{Li}:\text{M} < 2$ derives from the downfield (*ortho*-proton) multiplet in the proton spectra. In the samples

$\text{Li}:\text{Zn} = 1.15$ and $\text{Li}:\text{Mg} = 1.05$, only one *ortho*-proton multiplet was evident at all the temperatures investigated, from $+34$ to -66° . However, in a sample of $\text{Li}:\text{Mg} = 0.705$, two *ortho*-proton multiplets did appear; the one furthest downfield presumably represents a 1:1 complex while the other represents free diphenylmagnesium. The temperature dependence of the spectrum is shown in Figure 6. It appears that phenyl group exchange between diphenylmagnesium and the 1:1 complex, whatever its nature, is slower than methyl group exchange between dimethylmagnesium and the 2:1 complex, $\text{Li}_2\text{Mg}(\text{CH}_3)_4$.⁵

Lithium-7 spectra of the samples mentioned above when $\text{Li}:\text{M} < 2$ consist of only one resonance at -72° .

Organometallic Exchange Reactions. VII. Distribution of Phenyl and Alkyl Groups on Lithium and Lithium-Magnesium Species in Ether¹

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Abstract: Low-temperature lithium-7 and proton nuclear magnetic resonance spectra have been employed to observe equilibria in ether solutions of the following systems: methyl lithium-phenyllithium, methyl lithium-diphenylmagnesium, and phenyllithium-dimethylmagnesium. In the first, mixed species $[\text{Li}_2(\text{CH}_3)(\text{C}_6\text{H}_5)]_n$ and $\text{Li}_4(\text{CH}_3)_3(\text{C}_6\text{H}_5)$ are observed. In the lithium-magnesium systems, mixed 2:1 complexes, $\text{Li}_2\text{Mg}(\text{CH}_3)_4-n(\text{C}_6\text{H}_5)_n$, are observed. Phenyl exhibits a strong tendency to reside on the complex in preference to the more highly bridge-bonded $\text{Li}_4(\text{CH}_3)_3(\text{C}_6\text{H}_5)$. The systems observed here may serve as prototypes for benzylic or allylic lithium species in equilibria with excess saturated alkyl lithium, as in initiation of anionic polymerizations.

Results reported in this series of papers have served to demonstrate a striking difference between methyl and phenyl groups in lithium and group II organometallic compounds.^{2,3} Most of the differences observed can be accounted for by the statement that methyl is a stronger bridge-bonding group than phenyl. Nuclear magnetic resonance spectra of ether solutions containing methyl lithium are most readily interpreted in terms of a methyl lithium tetramer in solution.^{2,4} Phenyllithium, on the other hand, is dimeric in ether solution.⁵ In the tetramer the organic group is directly bonded to three metal atoms, in the dimer to two. In the mixed systems only the 2:1 phenyl complex, $\text{Li}_2\text{M}(\text{C}_6\text{H}_5)_4$ ($\text{M} = \text{Mg}$ or Zn), is observed, whereas in the methyl series a 3:1 complex is also formed.² The latter is presumably a tetramer with four bridging methyl groups and one terminal $\text{M}-\text{CH}_3$ group. Also, in hydrocarbon solvents triphenylaluminum is apparently less strongly bonded in the dimer than trimethylaluminum.⁶ The weaker

bridge-bonding tendency of phenyl is understandable, since the phenyl group is more electron-withdrawing than a saturated alkyl group and has a larger steric requirement than methyl.

The purpose of the present study is to evaluate the different propensities of phenyl and alkyl groups for bridge bonding and complex formation.

Experimental Section

The instrumental methods and details of sample preparation have been discussed in previous papers.^{2,3}

Results and Discussion

Ethyllithium-Phenyllithium. Ethyllithium-phenyllithium mixtures were examined to take advantage of the ^7Li chemical shift difference for the two substances in ether (-0.70 and -1.25 ppm, for $\text{C}_2\text{H}_5\text{Li}$ and $\text{C}_6\text{H}_5\text{Li}$, respectively). With this chemical shift difference (13 cps), it is feasible to look for the ^7Li resonances of mixed species. The ^7Li spectra of three typical mixtures at -80° are shown in Figure 1. By examining a number of spectra spanning a wide range of phenyl:ethyl ratios, it was possible to ascertain that there are but four distinguishable resonances. The end members of the set of four are separated by 13 cps and can be assigned with confidence to phenyllithium and ethyllithium. In the sample with a 2.44 phenyl:ethyl ratio,

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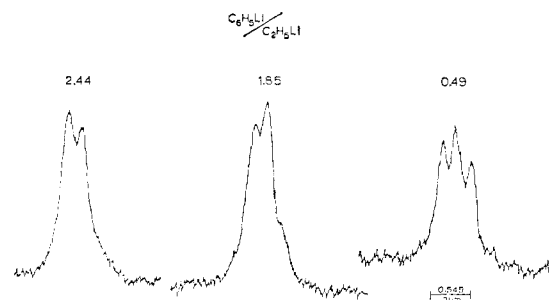


Figure 1. Lithium-7 spectra of ethyllithium-phenyllithium mixtures in ether at -80° .

there are only two distinguishable lines, indicating that all the ethyllithium is involved in formation of some mixed species. Furthermore, there is probably only one such mixed species, since one of the lines is due to phenyllithium. If it is assumed that all the ethyllithium has been consumed in the formation of a 1:1 mixed species, $[\text{Li}_2(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)]_n$, the ratio of the phenyllithium absorption to that of the mixed species should be about 1.4. This is in reasonable agreement with the observed spectra, although the lines are too extensively overlapped to permit an adequate quantitative comparison of areas. It is quite clear, however, that the mixed species cannot be due to the mixed tetramer $\text{Li}_4(\text{C}_6\text{H}_5)_3(\text{C}_2\text{H}_5)$ since this would require that the ^7Li resonance due to the mixed species have a much higher intensity than that due to phenyllithium. With increasing relative concentration of ethyllithium, the second intermediate absorption increases in relative importance, as shown in Figure 1. Assuming that the assignment discussed above is correct, the three absorptions shown in Figure 1 for the 0.49 phenyl:ethyl ratio are, from left to right, $\text{Li}_2(\text{C}_6\text{H}_5)_2$, $[\text{Li}_2(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)]_n$, and a second mixed species. It is difficult to make a clear assignment of the second mixed species from the ^7Li ratios, even when the phenyl:ethyl ratio is much lower than that shown. Fortunately, methyllithium-phenyllithium mixtures exhibit multiple methyl resonances and provide useful information on this point.

Methyllithium-Phenyllithium. Lithium-7 nuclear magnetic resonance spectra of methyllithium-phenyllithium mixtures are not useful, since the ^7Li chemical shifts of the compounds in ether are very nearly the same. It is possible, however, to employ the methyl group proton magnetic resonance spectra, since mixed species containing different numbers of methyl and phenyl groups give rise to different methyl resonances. This behavior is in contrast to methyllithium-ethyl-lithium mixtures, in which the mixed species all give rise to a single methyl resonance.⁴ Since the phenyl group is a considerably larger perturbation than ethyl in electron-withdrawing ability, some chemical shift in the methyl resonance due to an inductive effect is plausible. In addition, the diamagnetic ring current in the phenyl groups no doubt occasions chemical shifts in the methyl groups. Typical proton spectra at -62° are shown in Figure 2 for three different methyl:phenyl ratios.

Assuming that methyllithium is tetrameric and phenyllithium is dimeric, a number of possibilities exist for the mixed species, $\text{Li}_4(\text{CH}_3)_{4-n}(\text{C}_6\text{H}_5)_n$ and $\text{Li}_2(\text{CH}_3)(\text{C}_6\text{H}_5)$. It is not likely that the dis-

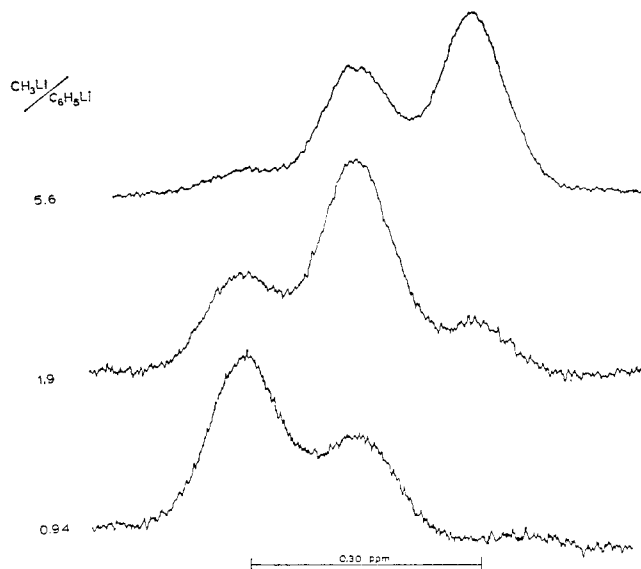


Figure 2. Methyl group proton spectra of methyllithium-phenyllithium mixtures in ether at -62° .

tribution among these species will be statistical. The methyl resonance spectra can be assigned by noting that there are but three distinct resonances for samples extending over a wide range of methyl:phenyl ratio (Figure 2). The absorption at highest field is assignable to methyllithium on the basis of its chemical shift. In the sample corresponding to a methyl:phenyl ratio of 0.94, the most intense resonance can be assigned to the methyl group in $[\text{Li}_2(\text{C}_6\text{H}_5)(\text{CH}_3)]_n$, by analogy with the ethyl-phenyl system. This is the furthest downfield methyl resonance seen in methyl-phenyl mixtures, even at lower ratios than those shown. With this assignment in mind, the absorption just below that due to the methyllithium tetramer can be assigned. In the solution corresponding to a methyl:phenyl ratio of 5.6, there is only a slight quantity of the 1:1 mixed species, as evidenced by the methyl resonance due to this species. Allowing for the fact that some phenyl is present in this form, it is clear that the ratio of methyl to phenyl in the species which gives rise to the intermediate absorption is much larger than 1. If it is assumed that the intermediate species is $\text{Li}_4(\text{CH}_3)_3(\text{C}_6\text{H}_5)$, the calculated ratio of the methyllithium resonance to the mixed species in the spectrum labeled 5.6 is about 1.5. This is only a rough estimate, because the quantity of phenyllithium in the form of 1:1 mixed species can be estimated only poorly from the areas, but the agreement with the observed ratio is quite good. Assuming that the mixed species is $\text{Li}_3(\text{CH}_3)_2(\text{C}_6\text{H}_5)$, the calculated ratio is on the order of 3.3, in rather poor agreement with the data. Similarly, if the relative area due to the 1:1 species is estimated for the spectrum corresponding to the ratio 1.9, the relative areas due to methyl absorptions in methyllithium tetramer as compared with the $\text{Li}_4(\text{CH}_3)_3(\text{C}_6\text{H}_5)$ species is calculated to be from 1:2.5 to 1:3.5. This again is in good agreement with experiment, with due regard for the roughness of the estimation.

In summary, the proton and ^7Li data together indicate that in solutions of methyllithium or ethyllithium with phenyllithium just two mixed species occur. It is evident from the relative intensities of the absorptions

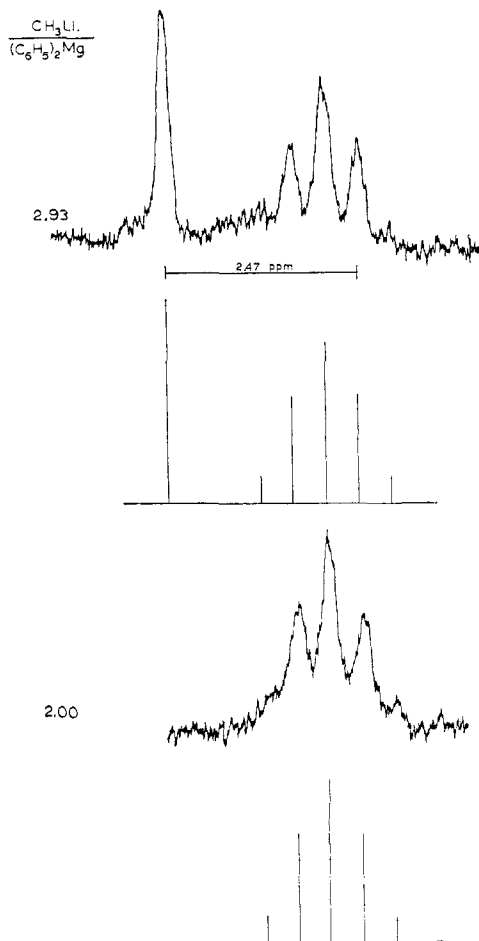


Figure 3. Lithium-7 spectra of methyllithium-diphenylmagnesium mixtures in ether at -70° .

that they are quite abundant in the mixtures and predominate when the alkyl:phenyl ratio is near 1.⁷ Given that methyllithium or ethyllithium is present in ether solution as a tetramer, an assumption for which there is considerable evidence, and that phenyllithium is present as dimer, the most reasonable molecular formulas for the two mixed species are $\text{Li}_2(\text{C}_6\text{H}_5)(\text{R})$ and $\text{Li}_4(\text{C}_6\text{H}_5)(\text{R})_3$ ($\text{R} = \text{alkyl}$). The latter conclusion follows directly from the assumption that the alkyl species are tetrameric. There is no reason whatever to expect formation of an Li_3 species. Assignment of the 1:1 species as a dimer seems more reasonable than the most plausible alternative, $\text{Li}_4(\text{C}_6\text{H}_5)_2(\text{R})_2$, but there is no relevant test of this point at present.

With these results in hand, we turn now to a consideration of mixtures of methyl and phenyl groups and mixtures of lithium and magnesium. It is convenient to consider these in two groups.

Methyllithium-Diphenylmagnesium. The ^7Li and proton spectra of two mixtures of methyllithium and diphenylmagnesium are shown in Figures 3 and 4, respectively.

Since the ^7Li resonances of methyllithium and phenyllithium occur at the same chemical shift, it can-

(7) These solutions exemplify what is, to our knowledge, a new type of redistribution system. Other systems are known in which two different groups, R and R' , are distributed between different metal atoms which have different numbers of groups attached, e.g., $\text{HgR}_n\text{R}'_{2-n} + \text{PbR}_m\text{R}'_{4-m}$. In the present case, however, the relative quantity of n -mer vs. m -mer is determined solely by the relative concentrations of R and R' .

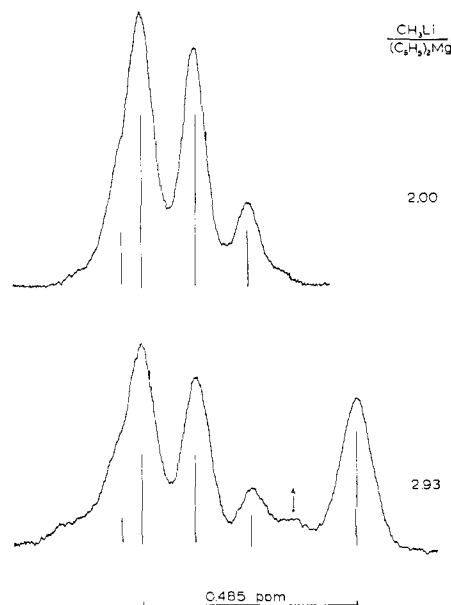


Figure 4. Methyl group proton spectra of methyllithium-diphenylmagnesium mixtures in ether at -62° .

not be ascertained from the ^7Li spectra alone whether the lowest field resonance is in fact due to methyllithium. The presence of methyllithium is quite evident, however, from the methyl group proton spectrum (Figure 4). The highest upfield resonance is due to methyllithium; the remaining four are due to the mixed 2:1 complexes. It is remarkable that so little phenyl group is displaced from the 2:1 complexes by excess methyllithium. The general shape of the spectrum in the region of the complexes is essentially unchanged in the two solutions, which differ considerably in the methyllithium:diphenylmagnesium ratio. The distribution of methyl and phenyl groups between 2:1 complex and excess methyllithium tetramer is thus quite nonrandom. This result again points out the tendency of phenyl groups to remain in the more ionic species, as opposed to associated species involving bridge bonding. The ^7Li resonance furthest downfield in Figure 3 represents methyllithium. The complexes $\text{Li}_2\text{Mg}(\text{C}_6\text{H}_5)_n(\text{CH}_3)_{4-n}$ are five in number and should give rise to five distinct ^7Li resonances. A 3:1 complex is not observed in phenyllithium-diphenylmagnesium mixtures.³ Formation of 3:1 complexes, $\text{Li}_3\text{Mg}(\text{C}_6\text{H}_5)_{5-n}(\text{CH}_3)_n$, in the present systems can therefore be ignored, even though such a 3:1 species is observed in methyllithium-dimethylmagnesium mixtures² when the $\text{Li}:\text{Mg}$ ratio exceeds 2. Assuming that only 2:1 complexes are formed, the relative intensities of the ^7Li lines based on an assumed random distribution of methyl and phenyl within the 2:1 complexes are shown in Figure 3. The distribution is calculated for a methyl:phenyl ratio which has been corrected for the fraction of methyl group present as methyllithium. Correspondence with the observed spectra is reasonably good; there does appear to be some favoring of the mixed species. It is significant that each lithium resonance can be associated with a distinct complex, $\text{Li}_2\text{Mg}(\text{C}_6\text{H}_5)_{4-n}(\text{CH}_3)_n$. This means that the two lithiums in the mixed species are equivalent by symmetry or, more probably, that a rapid intramolecular exchange occurs. The agreement between calculated

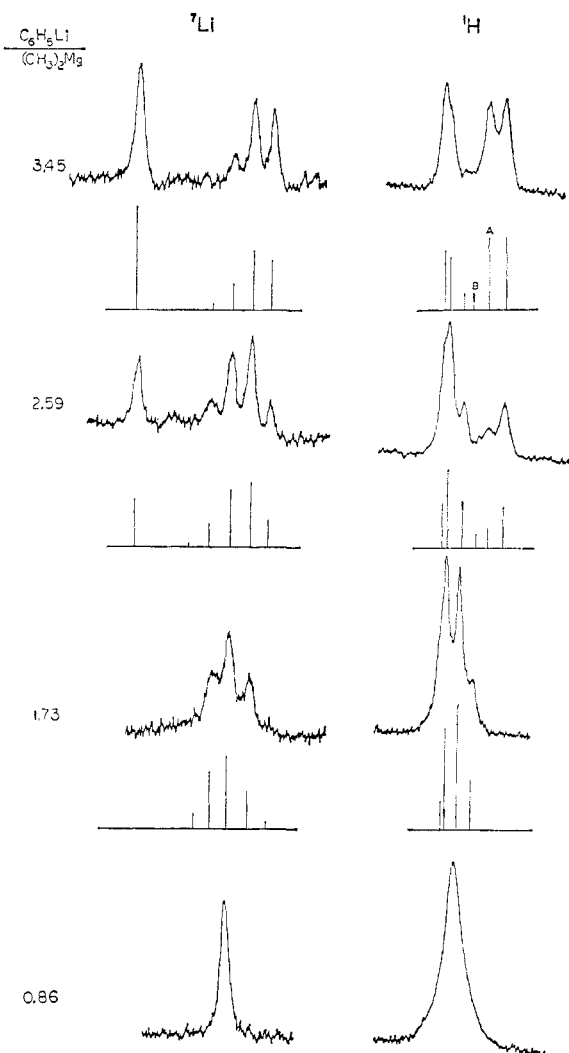


Figure 5. Lithium-7 spectra (at -70°) and methyl group proton spectra (at -62°) of phenyllithium-dimethylmagnesium mixtures in ether.

and observed proton spectra for distribution of methyl and phenyl groups within the 2:1 complexes is also quite reasonable, again showing some favoring of the mixed species. The small absorption marked A on the lower spectrum of Figure 4 is apparently due to Li_4 -

$(\text{CH}_3)_3(\text{C}_6\text{H}_5)$, which might be expected to occur to at least a slight extent.

Phenyllithium-Dimethylmagnesium Mixtures. These mixtures differ from those just discussed in that the phenyl:methyl ratio on the complex can be altered, whereas in the methyllithium-diphenylmagnesium mixtures it is necessarily 1:1 because of the strong tendency of phenyl groups to reside in the complexes. Low-temperature proton and ^7Li spectra of four mixtures are shown in Figure 5. The assignment of four resonances is as before, with the following additions. The relatively large absorption at A in the proton resonance (Figure 5) is due to $\text{Li}_4(\text{CH}_3)_3(\text{C}_6\text{H}_5)$. A small amount of $[\text{Li}_2(\text{CH}_3)_2(\text{C}_6\text{H}_5)]_n$ is observed at B in Figure 5. From the observed relative intensities of the absorptions, the quantity of phenyl groups which must exist as phenyllithium dimer can be estimated. Thus a correct over-all methyl:phenyl ratio in the complexes can be estimated and used in calculating an assumed random distribution within the five complexes. The calculated relative abundances are shown in Figure 5. The agreement between calculated and observed distributions within the 2:1 complexes is quite satisfactory.

The effect of an excess of dimethylmagnesium is shown in the bottom spectrum of Figure 5. Only one resonance is observed in the methyl group proton spectrum and in the ^7Li spectrum. This is a consequence of rapid exchange of methyl groups between dimethylmagnesium and the complexes.

The results obtained here have served to confirm that phenyl group is found on less associated species, and in relatively ionic species, in preference to more associated species requiring a greater degree of bridge bonding. The phenyllithium-methyllithium system may be a prototype for others involving saturated alkyl groups with allylic or benzylic groups.^{8,9} The present data should be of relevance in interpreting studies of cross-association between alkyllithium and polyisoprenyllithium or polystyryllithium, and in developing a model for the mechanism of initiation of anionic polymerization. Efforts along these lines are underway in our laboratory at present.

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