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LITHIUM-7 AND PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF METHYLLITHIUM/DIMETHYLMAGNESIUM (ZINC, CADMIUM) IN TETRAHYDROFURAN AND METHYLLITHIUM/DIMETHYLCADMIUM IN ETHER*

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SUMMARY

Lithium-7 and proton nuclear magnetic resonance spectra of ether solutions of methyllithium with dimethylcadmium have been examined over a range of temperatures. The spectra show that, like the magnesium and zinc systems, complexes of the form $Li_2Cd(CH_3)_4$ and $Li_3Cd(CH_3)_5$ are formed. No evidence was obtained for or against the formation of 1/1 complex. In contrast to the magnesium and zinc systems, methyl group exchange between methyllithium and complex appears to be faster than lithium exchange; both are more rapid than in the zinc system. Lithium exchange is apparently rate-determined by the dissociation of methyllithium tetramer to dimers. The mechanism of methyl exchange is uncertain. Evidence for rapid exchange of methyl groups between molecules of $Li_2Cd(CH_3)_4$ is discussed.

Proton and lithium-7 nuclear magnetic resonance spectra of tetrahydrofuran (THF) solutions of methyllithium with dimethylmagnesium, dimethylzinc, and dimethylcadmium have been obtained over a wide temperature range. In contrast to ether solutions, no 3/1 complex is observed. The 2/1 complex predominates in the magnesium system, whereas spectra of the zinc system are consistent with an approximately equal molar mixture of 2/1 and 1/1 complexes. Finally, 1/1 complex predominates in the cadmium system. Lithium and methyl group exchange between methyllithium and complex in each system occur at comparable rates and activation energies; the rates increase in the order Mg< Zn< Cd. For magnesium and zinc, the exchange rates in THF and ether are similar, but for cadmium they are slower in THF. Exchange of methyl groups between $(CH_3)_2M$ ($M=Mg$, Zn, Cd) and complex is very rapid. Evidence is presented for facile methyl group exchange between molecules of 1/1 complex in the cadmium system and between 2/1 and 1/1 complexes in the zinc system.

INTRODUCTION

In a preceding paper[1], the results of a lithium-7 and proton NMR study of the methyllithium/dimethylmagnesium and methyllithium/dimethylzinc systems in

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* Part of this work was presented at the third Midwest Regional American Chemical Society Meeting, Columbia, Mo., Nov. 1967.

diethyl ether have been described. The present paper includes the results of a similar study of the methyllithium/dimethylcadmium system in diethyl ether. The results reported herein show that, except for relative lithium and methyl group exchange rates, the cadmium system is quite analogous to the magnesium and zinc systems.

In order to ascertain the importance of solvent basicity in determining the general behavior of these systems, we have obtained proton and lithium-7 spectra of $CH_3Li/(CH_3)_2M$ ($M = Mg$, Zn, Cd) in tetrahydrofuran (THF). The spectra were recorded over a large temperature range and with solutions of various Li/M ratios*. The results, when compared with corresponding systems in diethyl ether, clearly demonstrate that the donor strength of the solvent is an important factor, especially in determining the stoichiometry of the complex species in solution. Exchange reactions which occur in THF solutions are discussed and compared with corresponding or similar exchange reactions in ether.

EXPERIMENTAL SECTION

Most of the experimental procedures such as the handling of solutions in an inert atmosphere glove box, the determination of concentrations of CH_3Li and $(CH_3)_2M$, and the preparation of NMR samples of $CH_3Li/(CH_3)_2M$ mixtures have been described previously[1].

Diethyl ether and tetrahydrofuran were dried with sodium, distilled from lithium aluminum hydride, and stored in the glove box.

Solutions of methyllithium in ether were prepared from lithium metal and dimethylmercury as described previously[1]. Low temperature ^7Li and ^1H spectra of these solutions consisted of only a single resonance line.

Dimethylmagnesium was prepared from magnesium metal and dimethylmercury. Dimethylzinc and dimethylcadmium were prepared by reaction of CH_3MgI or $(CH_3)_2Mg$ with the respective metal chlorides and then distillation from the reaction mixture. The purity of these solutions were checked by PMR; each exhibited only a single resonance line at low temperature in either solvent.

The concentrations of methyllithium solutions were determined by decomposing aliquot samples with water and titrating to a phenolphthalein end point with standard 0.1 *N* hydrochloric acid or 0.1 *N* potassium hydrogen phthalate. Concentrations of dimethylmagnesium, dimethylzinc, and dimethylcadmium were determined by decomposing aliquot samples with water and titration with standard EDTA solution (NH_4Cl/NH_4OH buffer, pH 10) using Erichrome black T as indicator[2].

After the concentrations (usually about 1.0 to 1.4 *M* for methyllithium and 0.5 to 0.85 *M* for $(CH_3)_2M$ of the separate solutions were determined, they were mixed in the appropriate volume proportions, using delivery pipets, to form the $CH_3Li/(CH_3)_2M$ mixtures. The solutions were sealed under vacuum in standard 5 mm NMR tubes and stored in dry ice.

Solutions of methyllithium in THF were prepared by first preparing methyllithium in diethyl ether, from lithium metal and dimethylmercury, and the pumping off the ether and redissolving in THF. This procedure was followed to minimize the

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* Li/M will represent the mole ratio $CH_3Li/(CH_3)_2M$; $M = Mg$, Zn, Cd.

reaction of methyllithium with THF*. Once the methyllithium was dissolved in THF, the $CH_3Li/(CH_3)_2M$ mixtures were prepared, placed in NMR tubes, sealed off and placed in dry ice as rapidly as possible.

Nuclear magnetic resonance spectra

Lithium-7 spectra were obtained at 23.3 MHz using a Varian DP60 Spectrometer and at 32.1 MHz using a Varian HA-100 spectrometer. Aqueous lithium bromide solution (7 g of commercial grade LiBr/10 ml of solution) was employed as an external standard for the room temperature chemical shift measurements. Proton spectra were obtained at 60 MHz using Varian DP60, A56/60, and A60 spectrometers and at 100 MHz using a Varian HA-100 spectrometer.

The low temperatures were obtained using the standard low-temperature accessories supplied by Varian Associates. A number of spectra were recorded at each temperature with temperature measurements before and after. A copper/constantan thermocouple was employed for the temperature measurements, which are accurate to ±1°.

RESULTS AND DISCUSSION

I. $CH_3Li/(CH_3)_2Cd$ system in ether

At room temperature mixtures of methyllithium and dimethylcadmium in ether exhibit only a single proton resonance line whose chemical shift is intermediate

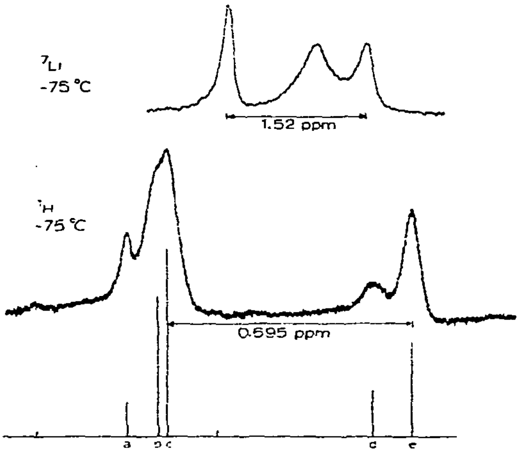

Fig. 1. Low temperature 100 MHz proton and 32.1 MHz lithium-7 spectra of $CH_3Li/(CH_3)_2Cd$, Li/Cd = 3.51. Calculated intensities are shown below the experimental proton spectrum; see text for explanation of alphabetical labels.

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* A sample of methyllithium in THF was allowed to stand at room temperature for 2 to 3 h before a low temperature ^{7}Li spectrum was recorded. A resonance upfield from methyllithium at the position indicated by the arrow in Fig. 2 was observed in the spectrum. The "impurity" resonance grows in rather rapidly during the first 2-h period. For example, the methyllithium THF solution employed to prepare the $CH_3Li/(CH_3)_2Zn$ mixtures had stood at room temperature no more than 1 h. The form of the impurity is uncertain; however it could be $Li_4(CH_3)_3OR$. Thus a small amount of LiOR could produce a sizable "impurity" resonance in the ^{7}Li spectrum. The area in this peak was taken into account in the mixed complex stoichiometry determinations.

between the chemical shift for pure dimethylcadmium and pure methyllithium in ether, 1.62 ppm and 3.08 ppm, respectively, upfield from the ether triplet. Since the position of the resonance also depends on Li/Cd*, rapid methyl group exchange between species in solution is apparent. Very low temperatures are required to slow the exchange sufficiently to allow observation of the various types of methyl groups (Fig. 1).

Likewise, rapid lithium exchange is apparent because room temperature lithium-7 spectra consist of only a single resonance line whose chemical shift moves upfield as Li/Cd is decreased, as shown in Table 1. Separate resonances are observed only at very low temperature when Li/Cd >2 (Fig. 1).

TABLE 1

^{7}Li CHEMICAL SHIFT IN METHYLLITHIUM/DIMETHYLCADMIUM SOLUTIONS AT ABOUT 30°

$CH_3Li/(CH_3)_2Cd$	^{7}Li shift (ppm)
∞	-1.32[a]
2.5	-0.485
0.98	-0.0423
0.65	-0.0880

[a] The concentration dependence for pure methyllithium in ether is negligible.

Stoichiometry and structures of complexes. The cadmium system, like the magnesium and zinc systems[1], displays the following properties: (1) both 2/1 and 3/1 complexes are observed, (2) the 2/1 complex is the one more readily formed such that the reaction proceeds essentially to completion, and (3) the 3/1 complex forms

$$\tfrac{1}{2}(CH_3Li)_4 + (CH_3)_2Cd \rightarrow Li_2Cd(CH_3)_4 \qquad (1)$$

only when Li/Cd >2, with the following equilibrium being established. Evidence for equilibrium (2) is provided by the fact that lithium-7 and/or proton resonance

$$\tfrac{1}{4}(CH_3Li)_4 + Li_2Cd(CH_3)_4 \rightleftarrows Li_3Cd(CH_3)_5 \qquad (2)$$

ascribeable to free methyllithium or 3/1 complex are seen only when Li/Cd >2 (refer to Fig. 2).

When Li/Cd< 2, however, a proton resonance line representing dimethylcadmium was not observed even at −85°, apparently due to very rapid methyl group exchange between dimethylcadmium and $Li_2Cd(CH_3)_4$. As a result, the existence of a 1/1 complex when Li/Cd< 2 cannot be ruled out, although its concentration is believed to be small, especially at low temperature. A similar situation prevails in the zinc system.

That the stoichiometry of the second complex is indeed 3/1 was established from measured ^{7}Li resonance areas and the known Li/Cd ratio in the same manner as described previously for the magnesium and zinc systems[2]. The middle absorption is assigned to the 3/1 complex since its area increases as Li/Cd increases, as required by eqn. (2). This behavior is shown in Fig. 2. The equilibrium constant at −84° calculated on the basis of eqn. (2) is 1.89, which compares with 0.76 and 0.28 for the

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* Li/Cd represents the mole ratio methyllithium/dimethylcadmium.

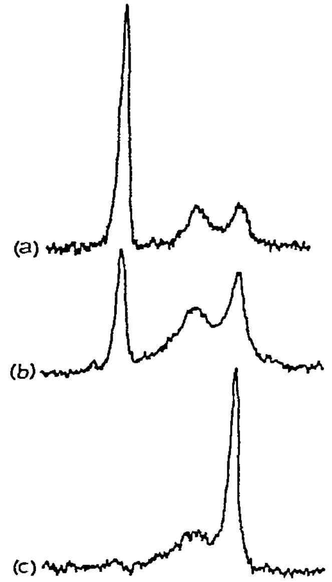

Fig. 2. Lithium-7 spectra recorded at −84°. The Li/Cd ratios are: (a), 5.02; (b), 3.17; (c), 2.48.

zinc and magnesium systems, respectively. It is clear, therefore, that the relative amount of the 3/1 complex increases in the order $Mg < Zn < Cd$. Although the temperature dependance of K was not determined quantitatively due to the difficulty of measuring areas at temperatures much above −75°, the appearance of the spectra suggest that the concentration of the 3/1 complex increases slightly with an increase in the temperature. Since ΔH for eqn. (2) must be positive and about the same magnitude as in the zinc and magnesium systems, it appears that the entropy change is the major factor contributing to the observed trend.

The low temperature proton spectra can be interpreted by assuming the same structure for the 3/1 complex as assumed in the magnesium and zinc systems, which involves the replacement of one of the lithium atoms of methyllithium tetramer with a cadmium atom (see Fig. 3 of ref. 1). The vertical lines below the 100 MHz proton spectrum in Fig. 1 represent positions of the various types of methyl groups observed, and their heights represent the calculated relative intensities as determined from the lithium-7 spectrum (Fig. 1). The agreement between observed and calculated intensities is quite satisfactory. The resonance at position (a) is assigned to the terminal methyl group of the 3/1 complex, and the very weak absorptions symmetrically arranged about resonance (a) arise from ^{111}Cd–H and ^{113}Cd–H coupling. The average coupling constant is 51 Hz as compared to 51.0 Hz and 53.0 Hz for the ^{111}Cd–H and ^{113}Cd–H coupling constants, respectively, for dimethylcadmium in ether. The values of these coupling constants being similar is consistent with the terminal group assignment since this methyl group is considered to be bonded directly to cadmium via a normal two-center bond. The resonance at position (b) is assigned to the three equivalent methyl groups of the 3/1 complex which are bonded to two lithium atoms and one cadmium atom via a four-center bond. No Cd–H coupling is detected for these protons; it is expected to be quite small and undetectable due to the close proximity of resonances (a) and (c). Position (c) results from the four equivalent methyl groups on the 2/1 complex. Again no Cd–H coupling is observed, but in this case it seems that it should be observable if it were present (see next paragraph). The rather broad resonance at (d) represents the single methyl group which is bonded to three lithium atoms via a four-center bond. Finally, free methyllithium is indicated by position (e).

The lack of Cd–H coupling in the 2/1 complex requires further comment. Three explanations could be advanced. One is that the coupling is very small and undetected. Any coupling constant below 5 Hz would probably not be detected, but it should not be this small. Secondly, there is a chance that the electric quadrupole moment of lithium could cause rapid relaxation of the cadmium nucleus and thereby eliminate the coupling. This possibility can be ruled out by the observation of reasonably sharp ^{7}Li lines, indicating the quadrupolar relaxation is not extremely rapid. A third and most plausible possibility is the occurrence of rapid intermolecular methyl group exchange between molecules of $Li_2Cd(CH_3)_4$, even at −85°.

Exchange reactions. Like the magnesium and zinc systems, it is possible to distinguish between two general types of exchange systems. One arises when Li/Cd < 2 and involves methyl group exchange between dimethylcadmium and 2/1 complex*, whereas the second arises when Li/Cd > 2 and involves methyl and lithium exchange between methyllithium and the 2/1 and 3/1 complexes. The former exchange type is very rapid; only a single rather sharp resonance is observed at −85°. The discussion which follows refers to the second exchange type. It should be noted at the outset that all of the exchange reactions are significantly more rapid than in either the magnesium or zinc systems.

The temperature dependence of the ^{7}Li spectrum when Li/Cd > 2, shown in Fig. 3, is analogous to that observed for the magnesium and zinc systems. The resonances due to the 2/1 and 3/1 complexes coalesce well before the methyllithium absorption is significantly broadened, indicating a facile exchange between the 2/1 and 3/1 complexes which does not involve free methyllithium. Although less pronounced, the temperature dependence of the proton spectrum suggests similar

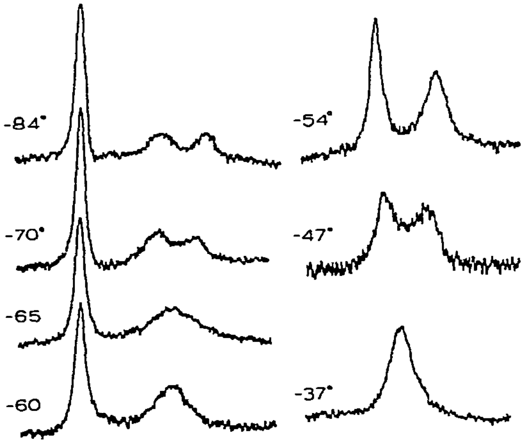

Fig. 3. Temperature dependence of lithium-7 spectra, Li/Cd = 5.02.

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* When Li/Cd < 2, the possibility of some 1/1 complex being present cannot be ruled out.

behavior for methyl group exchange. Therefore, like the magnesium and zinc systems, it appears that a methyllithium molecule is rapidly exchanged between the 2/1 and 3/1 complexes via a bimolecular mechanism.

With reference to Fig. 3, one can see that methyllithium eventually becomes involved in exchange with 2/1 and/or 3/1 complex as the temperature is increased. The analysis of the lithium-7 spectra to obtain the data plotted in Fig. 4 was performed with the aid of a line shape computer program[3] in the same manner as described previously for the magnesium and zinc systems[1]. Due to the assumptions necessary in order to complete the analysis, the activation energy obtained from the slope is subject to substantial uncertainty*. However it appears that, at least within experimental error, the activation energy for lithium exchange is the same as in the magnesium and zinc systems, 12±3 kcal/mole. On the other hand, it is quite certain that lithium exchange in the cadmium system is 7 to 8 times more rapid than in the zinc systems.

The methyl group exchange data presented in Fig. 4 were obtained from proton

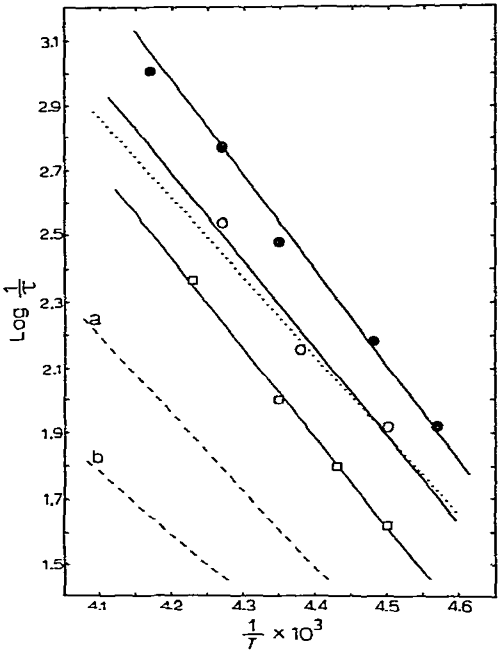

Fig. 4. $1/\tau$ as a function of temperature for solution with Li/Cd >2. For Li/Cd = 5.02: □, ^{7}Li data [$-2770(1/T)+14.0$]; ○, proton data [$-2670(1/T)+13.9$]. For Li/Cd = 3.51: ●, proton data [$-2890(1/T)+15.1$]. The solid lines through data points were drawn according to least squares analysis; the temperature dependences of log $1/\tau$ are given by the expressions in parentheses. Approximate concentration of species for Li/Cd = 5.02 are: $(CH_3Li)_4 = 0.12$ *M*; $Li_2Cd(CH_3)_4 = 0.094$ *M*; $Li_3Cd(CH_3)_5 = 0.10$ *M*; for Li/Cd = 3.51: $(CH_3Li)_4 = 0.062$ *M*; $Li_2Cd(CH_3)_4 = 0.12$ *M*; $Li_3Cd(CH_3)_5 = 0.12$ *M*. The dotted line represents ^{7}Li data for the $CH_3Li/LiB(CH_3)_4$ system from footnote at p. 234. The dashed lines represent ^{7}Li (a) and proton (b) data for the zinc system from ref. 1.

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* It was necessary to assume that the separation of the two resonances in the limit of no exchange was insensitive to temperature changes, and to estimate the $1/T_2$ for the resonance representing complex. These assumptions and estimates could lead to systematic error which mainly affect the slope of the line, *i.e.* $1/\tau$ *vs.* $1/T$ (°K), and the activation energy obtained therefrom[4].

spectra with the aid of the line shape program. The data were obtained in the temperature region in which the shape of spectrum was quite temperature sensitive, *i.e.*, near the coalescence point of the methyllithium and complex resonances (same is true for the lithium-7 analysis). Due to the rather short temperature range and the necessary assumptions*, the activation energy obtained from the slope of the line could be in error. However it seems that the activation energy for methyl group exchange is not grossly different from that for lithium exchange. There is no doubt that methyl group exchange is much faster in the cadmium system than in either the zinc or magnesium systems; it is 10 to 12 times and 17 to 19 times faster than in the zinc and magnesium systems, respectively.

The lithium exchange results can be explained in terms of the same mechanistic approach employed for the zinc system[1,**].

$$\underset{(T)}{(CH_3Li^*)_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(D)}{2\,(CH_3Li^*)_2} \qquad (3)$$

$$(CH_3Li^*)_2 + Li_2Cd(CH_3)_4 \xrightarrow{k_2} LiLi^*Cd(CH_3)_4 + LiLi^*(CH_3)_2 \qquad (4)$$

$$\underset{(D)}{(CH_3Li^*)_2} + \underset{(C)}{Li_3Cd(CH_3)_5} \xrightarrow{k_2} \underset{(C^*)}{Li^*Li_2Cd(CH_3)_5} + \underset{(D^*)}{LiLi^*(CH_3)_2} \qquad (5)$$

Again, it is not possible to determine whether both (4) and (5) are operative. The rate constant k_1 is known from a study of the $CH_3Li/LiAl(CH_3)_4$ system and its corresponding boron analog[3]. It was stated previously[1] that lithium and methyl group exchange in the magnesium and zinc systems is lower than that predicted from considering (3) to be the rate-determing step, presumably because the condition $k_{-1} \ll k_2' \cdot [(C)]$ is not strictly met. However, for the cadmium system it appears that this condition is very nearly satisfied and that dissociation of methyllithium tetramer into dimers is indeed the rate-limiting step for lithium exchange. If this is true and if statistical factors and concentrations are taken into account the line in Fig. 4 representing lithium-7 exchange should be about 0.38 log unit lower than for the $CH_3Li/LiB(CH_3)_4$ system, which is in reasonable agreement with experiment.

A different mechanistic approach is necessary in order to explain the methyl group exchange results. At this point the behavior exhibited by the cadmium system deviates significantly from the magnesium and zinc systems. Contrary to the latter systems, methyl group exchange in the cadmium system is significantly more rapid than lithium exchange. This can be seen by reference to Fig. 4. If lithium and methyl group exchange were concurrent, the log $1/\tau$ *vs.* $1/T$ (°K) line for methyl group exchange (represented by ○) should lie about 0.12 log unit below the line for lithium

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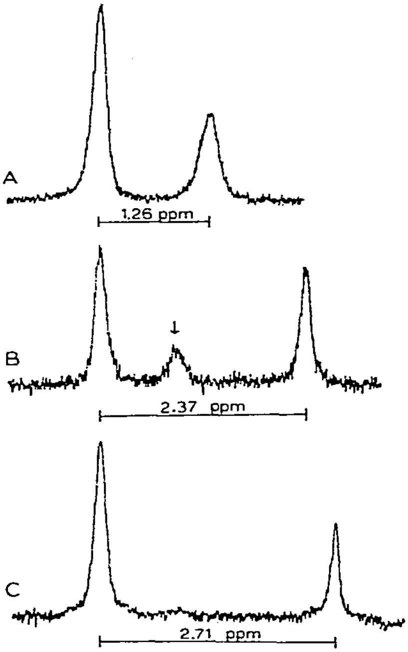
* See footnote at preceding page.

** Due to confusion of concentration of species present with the concentration of the nucleus at the chemical site in question, the $1/\tau$'s in ref. 1 (eqns. 6–9) are incorrect by the factor 1/2. For example, [(D)] should have represented the concentration of *Li nuclei* in the dimer form instead of the actual dimer concentration. Making this change, $d(D)/dt$ becomes equal to $4k_1 \cdot [(T)] - k_{-1} \cdot [(D)]^2 - k_2 \cdot [(D)] \cdot [(C)]$; [(T)] and [(C)] equal tetramer and complex concentrations. Thus $1/\tau(T)$ should be equal to k_1 instead of $k_1/2$ given in ref. 1. The ratio $[1/\tau(Li)]/[1/\tau(H)]$ remains unaltered, however. These alterations also apply to ref. 3, but the comparison of $1/\tau(Li)$ for $CH_3Li/(CH_3)_2Cd$ with $1/\tau(Li)$ for $CH_3Li/LiB(CH_3)_4$ is not affected.

exchange; instead it is about 0.27 log unit above the lithium line. Steps (4) and (5) of the lithium exchange mechanism quite probably involve methyl group exchange also (this was presumed to be the case in the magnesium and zinc systems), but in view of the results given above, it appears that an additional pathway which allows methyl group exchange without lithium exchange is operative.

II. $CH_3Li/(CH_3)_2Mg(Zn, Cd)$ *systems in tetrahydrofuran*

Representative low temperature proton and lithium-7 spectra are presented in Fig. 5 and 6, respectively. Only two resonances appear in the proton spectrum of each system; the upfield resonance represents methyllithium while the low field resonance represents complex. Likewise the lithium-7 spectrum of each system contains only two resonances which can be assigned to methyllithium and complex, the low field and high field resonances, respectively. The third resonance in the lithium-7 spectrum (marked by the arrow in Fig. 6) and the slight shoulder on the upfield side of the methyllithium peak in the proton spectrum of the zinc system are due to an impurity which results from the reaction of methyllithium with solvent (see footnote* at p. 229). The stoichiometry of the mixed complex in each system was obtained from the known Li/M ratio and the measured ^{7}Li and proton peak areas.



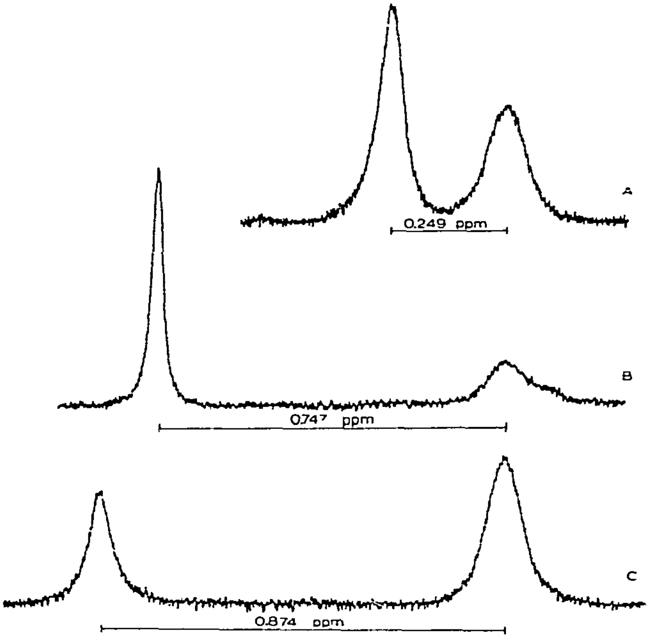


Fig. 5. Proton spectra: (A) methyllithium–dimethylmagnesium, Li/Mg = 5.50, −58°; (B) methyllithium–dimethylzinc, Li/Zn = 3.66, −50°; (C) methyllithium–dimethylcadmium, Li/Cd = 5.27, −53°.

Fig. 6. Lithium-7 spectra recorded at −66°: (A) methyllithium–dimethylmagnesium, Li/Mg = 5.50; (B) methyllithium–dimethylzinc, Li/Zn = 3.66; (C) methyllithium–dimethylcadmium, Li/Cd = 3.83.

One major difference between ether and THF solutions of the magnesium, zinc, and cadmium systems is immediately apparent from the proton and lithium-7 spectra; the 3/1 complex is not present in the more strongly donating solvent THF.

Resonances assigned to this complex in ether solutions are absent from the spectra of THF solutions*. Another difference is apparent from the peak areas and the known Li/M. In ether the stoichiometery of the mixed complex remains the same in each case, *i.e.* 2/1 and 3/1, but in THF it is clear that even the tendency to form the 2/1 complex diminishes in the order Mg > Zn > Cd. With magnesium the 2/1 complex predominates, whereas spectra of the zinc system are consistent with a mixture of 2/1 and 1/1 complexes which are undergoing rapid exchange**. Finally, only 1/1 complex is observed in the cadmium system.

Lithium-7 chemical shifts also indicate a change in the nature of the complex species as the solvent is changed from ether to THF. This can be seen by reference to Table 1. The chemical shifts of the magnesium system in ether and THF, in which the complex is mainly 2/1 in each of these solvents, are quite similar. In the cadmium system, where the stoichiometry of the complex differs in these solvents, the chemical shifts are very different. The ^{7}Li chemical shift of the 1/1 complex appears at much higher field than 2/1 complex; this conclusion is corroborated by the chemical shift data given in Fig. 6.

TABLE 2

SOME REPRESENTATIVE LITHIUM-7 CHEMICAL SHIFTS IN ETHER AND THF

System	Solvent	^{7}Li shift (ppm)
CH_3Li only	THF	−1.47
CH_3Li only	Ether	−1.32 (ref. 1)
Li/Cd 0.50	THF	+1.20
Li/Cd 0.66	Ether	+0.0872
Li/Mg 0.66	THF	0
Li/Mg 0.80	Ether	+0.214 (ref. 1)

It is also of interest to note from Table 1 the similarity in the methyllithium chemical shift in ether and THF. This could be taken as an indication that the associated methyllithium species in THF and ether are similar, and therefore lend support to recent observations which indicate methyllithium is tetrameric in THF as well as in ether[5].

The absence of the 3/1 complex in THF can be rationalized by considering expected relative degrees of solvation of the 3/1, 2/1, and 1/1 complex species. From their presumed structures, the 2/1 and 1/1 complexes would appear to be more highly solvated than the 3/1 complex. Since an increase in solvent basicity would likely tend to favor those species with higher degrees of solvation it is understandable that the 2/1 or 1/1 complexes are favored in THF. In any case the results presented here indicate that the 3/1 complex will only be present in solvents of relatively weak basicity, *i.e.* similar to ether or weaker.

The nature of the complexes present when $(CH_3)_2M$ is in excess (or that is when Li/M is such that excess methyllithium is no longer present) remains uncertain due

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* Support for the expectation that the 3/1 complex might be present is provided by recent vapor-phase osmometry and ^{7}Li NMR results which indicate methyllithium is tetrameric in THF[5].

** Although it seems less likely, the existance of a single species of stoichiometry $Li_3Zn_2(CH_3)_7$ cannot be ruled out at the present time.

to very rapid exchange reactions. In such cases, it is possible the solutions may contain several species, all undergoing rapid methyl group exchange.

Exchange reactions. As in ether solutions, two types of exchange reactions arise depending on Li/M. One type involves lithium and methyl group exchange between methyllithium and complex, whereas the other involves $(CH_3)_2M$–complex and/or complex–complex methyl group exchanges. The latter exchange is much faster, which again is the same behavior observed in ether solution. At about −70°, only a single sharp line appears in the proton spectrum of each of these systems when Li/M is such that no excess methyllithium is present. On the other hand, separate resonances are observed when Li/M is such that methyllithium and complex are present, as evidenced by Figs. 5 and 6. Therefore, the discussion which follows will mainly deal with exchange between methyllithium and complex, although some mention of complex–complex exchange in the cadmium system is made at the end of the paper. No attempt was made to study the very facile $(CH_3)_2M$–complex and/or complex–complex exchanges.

Lithium-7 and proton spectra were analyzed with the aid of a line shape computer program described previously[3], to obtain the data shown in Fig. 7. Since only two resonances were present at low temperature, as opposed to three or more in ether solutions, it was possible to complete the analyses in a more conventional

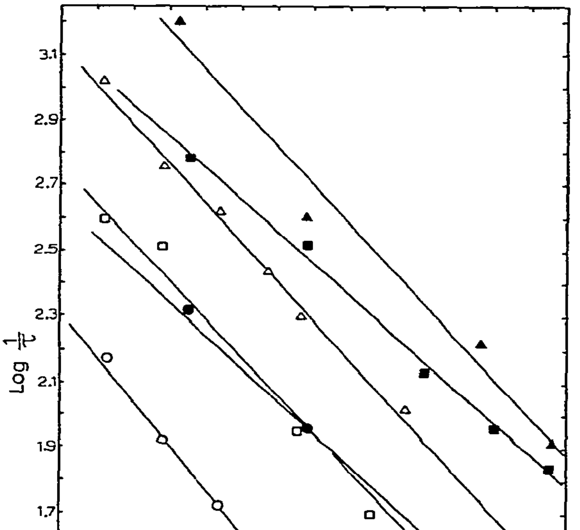

Fig. 7. Plot of Log $1/\tau$ *vs.* $1/T$ (°K) for lithium and methyl group exchange between methyllithium and complex in THF solutions. For Li/Mg = 7.15: ○, proton data [$-2700(1/T)+12.0$]; ●, ^{7}Li data [$-2010(1/T)+9.89$]; for Li/Zn = 3.66: □, proton data [$-2330(1/T)+11.0$]; ■, ^{7}Li data [$-1950(1/T)+10.2$]; for Li/Cd = 3.83: △, proton data [$-2400(1/T)+11.8$]; ▲, ^{7}Li data [$-2360(1/T)+12.0$]. The solid lines through data points were drawn according to least squares analysis; the temperature dependence of log $1/\tau$ are given by the expressions in parentheses above. See text for concentration of species.

manner than that required for ether solutions, although the usual sources of error still exist (see footnote* at p. 233).

The Arrhenius activation energies from the slopes of the lines in Fig. 7 are: 9.2, 9.0, 10.8 for ^{7}Li exchange; and 12.4, 10.7, 11.0 kcal/mole for methyl group exchange in the magnesium, zinc, and cadmium systems, respectively. Within the estimated experimental uncertainty, ±2 kcal/mole, these activation energies are essentially the same.

Fig. 7 also shows that methyl group and lithium exchange rates increase in the order $Mg < Zn < Cd$, which is the same order observed with ether solutions. Considering statistical factors, the difference between the zinc and cadmium systems is quite small.

A comparison of exchange rate data from ether solutions with the THF data shows the following. In the magnesium system, it is apparent that methyl group exchange takes place at very nearly the same rate in the two solvents; lithium exchange, however, appears to be somewhat faster in THF. Methyl group and lithium exchange rates in the zinc system are quite similar in the two solvents. In contrast, the cadmium system exhibits two rather marked changes: (1) methyl group and lithium exhanges are slower in THF than ether, and (2) methyl group and lithium exchange appears to be concurrent in THF (see below) whereas such is not the case in ether. These changes are no doubt due to differences in the nature of the complex species in these two solvents.

At this stage there is insufficient information available to determine exchange mechanisms. For example, rates of methyl and lithium exchange in THF solutions of methyllithium alone are not known, nor is it known whether the exchange occurs thru a dissociative step similar to ether, *i.e.*

$$(CH_3Li)_4 \rightleftharpoons 2\,(CH_3Li)_2 \tag{6}$$

However, it seems quite reasonable to expect that such a step could be important, especially since Waack's observations[5] together with ^{7}Li chemical shift information (Table 1) seem to indicate that methyllithium is tetrameric in THF*. Also preliminary proton linewidth *vs.* temperature data for methyllithium in THF indicate that intermolecular methyl group exchange is only slightly more rapid than in ether. Thus, a general similarity between the exchange pathways in THF and ether seem possible, *i.e.*:

$$\underset{(T)}{(CH_3Li)_4} \rightleftharpoons \underset{(D)}{2\,(CH_3Li)_2} \tag{7}$$

$$(D)+(C^*) \rightarrow (C)+(D^*) \tag{8}$$

For THF, (C) would be $Li_2Mg(CH_3)_4$ in the magnesium system, $Li_2Zn(CH_3)_4$ and/or $LiZn(CH_3)_3$ in the zinc system, and $LiCd(CH_3)_3$ in the cadmium system.

A more complete test of mechanism must await a detailed evaluation of concentration dependence. The data presented in Fig. 7, however, provide some indication

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* Preliminary exchange results from the $CH_3Li/(CH_3)_2Be$ system in ether and THF, and the $CH_3Li/(CH_3)_2Hg$ system in THF also appear to be interpretable in terms of methyllithium tetramer/dimer dissociation.

of whether or not lithium and methyl exchange is concurrent. Assuming the pathway to be as given by eqns. (7) and (8), and adopting a steady state assumption for (D), eqn. (9) can be derived[1,**]. The relative magnitudes of $k_{-1}\cdot[(D)]$ and $k_2\cdot[(C)]$ are

$$\frac{d[(C)]}{dt}=\frac{4k_1\cdot k_2\cdot[(T)]\cdot[(C)]}{k_{-1}\cdot[(D)]+k_2\cdot[(C)]} \qquad (9)$$

not known, but it happens that this is not critical since both extreme assumptions, *i.e.* $k_{-1}\cdot[(D)] \ll k_2\cdot[(C)]$ and *vice versa*, lead to the same calculated difference between the methyl and lithium exchange lines for a given system when concurrent exchange is assumed. Following the general approach given in ref. 1 and taking into account the appropriate statistical factors, one can calculate that $[1/\tau(Li)]/[1/\tau(H)]$ would be $\{2[(T)]+[(C)]\}/\{[(T)]+[(C)]\}$ for the magnesium system and $\{12[(T)]+3[(C)]\}/\{4[(T)]+3[(C)]\}$ for the cadmium system.

In the sample Li/Mg 7.15 employed to obtain the data in Fig. 7, $[(T)]=0.175$ and $[(C)]=0.134$; thus the ratio $[1/\tau(Li)]/[1/\tau(H)]$ is 1.57. Then the log $1/\tau$ *vs.* $1/T$ (°K) line representing lithium should be 0.20 log unit above the line for methyl group data, whereas the observed difference is 0.40 to 0.60. The observed difference being somewhat larger than expected could be constructed to mean that lithium exchange is faster than methyl exchange, but the rates could only differ by about a factor of 2. Such could be the case if eqn. (8) in the mechanism given above actually represents two separate exchange pathways in the case of magnesium; one which involves lithium exchange without methyl exchange and another which involves concurrent exchange.

In the sample Li/Cd 3.83 employed to obtain the cadmium data in Fig. 7, $[(T)]=0.158$ and $[(C)]=0.22$; thus the ratio $[1/\tau(Li)]/[1/\tau(H)]$ is 1.92. Then the line representing lithium exchange should be 0.28 above the methyl group line. The observed value is 0.40 which is in reasonable agreement with concurrent exchange.

The apparent presence of two complexes makes the zinc system more complicated, but even here methyl group and lithium exchange rates appear to be comparable. It has already been mentioned that the solutions of the zinc system contained a small but observable quantity of impurity. The form of this impurity is unknown; however, it could be $Li_4(CH_3)_3OR$, where OR is an alkoxide of unknown type. We believe this impurity has not seriously affected the exchange rate results shown in Fig. 7. From a close examination of the temperature dependence of the ^{7}Li spectra, shown in Fig. 4, it is seen that exchange between methyllithium and complex (1/1 and/or 2/1) is much faster than between methyllithium and impurity or between complex and impurity. Note that the observed line shape appears to be what one would obtain if the impurity resonance (at the position marked by the arrow in Fig. 8) were superimposed on the line shape resulting from exchange between methyllithium and complex.

Complex–complex exchanges. Since cadmium has two isotopes with nuclear spin one-half, ^{111}Cd and ^{113}Cd, there exists the possibility of observing Cd–H coupling in the complex $LiCd(CH_3)_3$ at low temperature. However, all attempts to observe this coupling at temperatures as low as −75° failed, which we take as evidence for rapid exchange of methyl groups between molecules of $LiCd(CH_3)_3$. It is reasonable to expect that this exchange should be rapid since the expected transition state, as

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[*] [(D)] represents the concentration of lithium nuclei in the dimer form see footnote* at p.

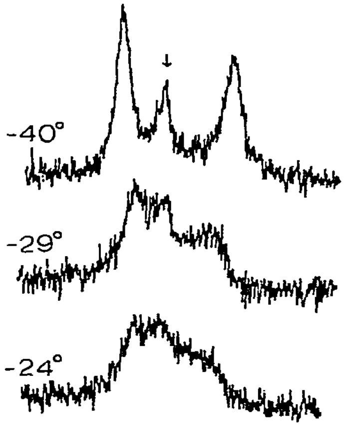
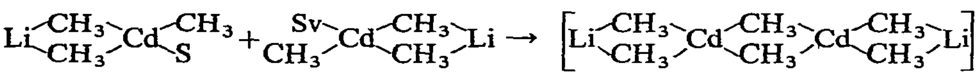


Fig. 8. Temperature dependence of ^{7}Li spectra of $CH_3Li/(CH_3)_2Zn$ solution in THF which contains impurity; see text.

shown below, is very similar to what one would write for exchange between $(CH_3)_2Cd$ and $LiCd(CH_3)_3$ or between $(CH_3)_2Mg$ and $Li_2Mg(CH_3)_4$, exchanges which are known to be very rapid.



Evidence for rapid complex–complex exchange in the cadmium system lends support to the conclusion that there must be rapid exchange between 2/1 and 1/1 complexes in the zinc system. Further support for this facile exchange is contained in the low temperature proton and lithium-7 spectra of the zinc system shown in Figs. 1 and 2; the resonances representing complex are quite sharp, being as sharp or sharper than resonances representing complex in either the magnesium or cadmium systems. Finally, to expel any notion that such facile exchanges are unusual, we mention again that evidence has been obtained for rapid methyl group between molecules of $Li_2Cd(CH_3)_4$ in ether (*vide supra*).

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