e.g., $[Re\{P(C_6H_5)(C_2H_5)_2\}_2Cl_3(NC_6H_5)]$ and $[Ir\{P(C_6H_5)_3\}_2Cl(NC_6H_5)]$. These Re complexes, unlike $[Ir(NH_3)_5NH]^{3+}$, do not show the electrophilic behavior of singlet nitrene and appear to be quite stable to nucleophilic attack. Hence, the electron distribution in these complexes may be more correctly indicated by formulating them as Re(V) alkyl- and arylimido complexes after Chatt.[38]

Treatment of $[Re\{P(C_6H_5)_2CH_3\}_2CH_3]$ with NaN_3 yields $[Re\{P(C_6H_5)_2CH_3\}_3Cl_2N]$,[40] which can also be prepared by a different method.[40] This complex has been formulated as a nitrido complex of Re(V) but could also be viewed as a complex of Re(III) with a deprotonated nitrene ligand. This complex, like the alkyl- and arylimido compounds discussed above, is unreactive toward nucleophilic attack reacting only with Lewis acids, *e.g.*, BF_3.[41] It therefore should not be considered as a complex of singlet nitrene.

Hence, although some $d\pi \rightarrow p\pi$ donation appears to be necessary for the formation of $[Ir(NH_3)_5NH]^{3+}$ from $[Ir(NH_3)_5N_3]^{2+}$, extensive electron transfer leads to loss of nitrene-like properties of the resulting ligand. We propose the name "coordinated nitrene" to describe the NH ligand in $[Ir(NH_3)_5NH]^{3+}$ as a means of distinguishing compounds of this type from the formally similar alkyl- and arylimido and nitrido ligands of $[Re\{P(CH_3)_2C_6H_5\}_2Cl_3NR)$ and $[Re\{P(CH_3)_2C_6H_5\}_3Cl_2N]$ which show very different chemical behavior.

Acknowledgment. The authors would like to thank Dr. V. G. Myers, whose doctoral thesis provided the basis for this work, and Mr. T. R. Weaver for useful discussion. The iridium trichloride was generously loaned to us by the Matthey Bishop Co. This research was supported by a National Institutes of Health Predoctoral Research Fellowship to J. W. M. and by a National Science Foundation grant.

[40] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc. A*, 2288 (1969).

[41] J. Chatt and B. T. Heaton, *ibid.*, 705 (1971).

Mixed Complex Formation between Methyllithium and Lithium Bromide or Iodide in Diethyl Ether[1]

David P. Novak[2] and Theodore L. Brown*

Contribution from Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received September 15, 1971*

Abstract: Methyllithium forms mixed complexes with both LiBr and LiI in ether. The association of LiBr in ether at 0° varies from 2.8 at 0.025 *F* to 3.2 at 0.25 *F*, whereas LiI association varies from 1.24 at 0.024 *F* to 1.97 at 0.24 *F*. On the basis of ^7Li and 220-MHz ^1H spectra in the range -50 to $-90°$ for solutions of $LiCH_3$ and LiBr in various ratios, the species present in solution are assigned as $Li_4(CH_3)_4$, $Li_4(CH_3)_3Br$, $Li_4(CH_3)_2Br_2$, and $(LiBr)_n$. Analogous studies on the iodide system show that only $Li_4(CH_3)_4$, $Li_4(CH_3)_3I$, and $(LiI)_n$ are present. Intermolecular exchanges between the various species present are most rapid for the species richest in halide.

It has been reported on several occasions that the reactivity of an organolithium reagent[3–7] is influenced by the presence of lithium halide. Ternary organolithium–lithium halide–etherate complexes have been isolated by Talalaeva and coworkers.[8] Glaze and West have also reported the isolation of butyllithium–lithium bromide complexes of variable composition from hydrocarbon solution.[9] On the basis of this earlier work it is reasonable to suppose that organolithium compounds enter into mixed complex formation with lithium halides in solution, especially in those solvents in which the lithium halides possess considerable solubility. The existence of such mixed complex formation between methyllithium and lithium bromide or iodide in diethyl ether was revealed through ^7Li nmr studies by Brown and Wells.[10] Waack and coworkers reported low temperature ^7Li spectra of THF solutions of $LiCH_3$ and LiBr which showed a limited degree of mixed complex formation.[11]

We report here the results of extensive ^7Li and proton nmr studies of mixed complex formation between methyllithium and lithium bromide or lithium iodide in diethyl ether.

Experimental Section

All operations were performed in a glove box under an argon atmosphere. Removal of traces of oxygen and water was effected by continuous circulation of the box atmosphere through molecular sieve (4A and 13X) and manganese(II) oxide columns as described previously.[12] The water content of this atmosphere was always

---

[1] This research was supported in part by the National Science Foundation through Grant GP 6396X.

[2] National Institutes of Health Predoctoral Fellow, 1969–1971.

[3] D. Y. Curtin and E. W. Flynn, *J. Amer. Chem. Soc.*, 81, 4714 (1959).

[4] R. Huisgen and W. Mack, *Chem. Ber.*, **93**, 332 (1960).

[5] R. Waack and M. A. Doran, *Chem. Ind. (London)*, 496 (1964).

[6] T. Holm, *Acta Chem. Scand.*, 23, 1829 (1969).

[7] L. Charbonneau, D. P. Novak, S. G. Smith, and T. L. Brown, unpublished kinetic studies.

[8] T. V. Talalaeva, A. N. Rodinov, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **140**, 847 (1961); **154**, 174 (1964).

[9] W. G. Glaze and R. West, *J. Amer. Chem. Soc.*, 82, 4437 (1960).

[10] T. L. Brown and W. L. Wells, paper presented at The 3rd International Symposium on Organometallic Chemistry, Munich, Aug 1967; W. L. Wells, Ph.D. Thesis, University of Illinois, 1967.

[11] R. Waack, M. A. Doran, and E. B. Baker, *Chem. Commun.*, 1291 (1967).

[12] (a) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, 33, 491 (1962); (b) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, pp 179–182.

well below 1 ppm as measured by a Panametrics Model 1000 hygrometer with calibrated probe.

Cold nitrogen gas coming from the boil-off of a liquid nitrogen dewar was used to cool different apparatus (a cold well, jacketed flasks, condensers, etc.) inside the glove box. The cold gas passes in an isolated line first through the glove box wall, then through the apparatus, and finally back out through the box wall into the laboratory. Valves and T's in the line control the flow of cold gas. The apparent molecular weights of lithium bromide and lithium iodide at 0° were determined by direct differential vapor pressure measurements[13] using an MKS Model 90 Baratron electronic pressure meter, MKS Instruments, Inc., Burlington, Mass. The results are presented in Table I.

Table I. Association of Lithium Halides in Diethyl Ether at 0°

Molarity (as monomer)	Degree of association
LiBr	
0.0210	2.50
0.0389	3.33
0.0747	3.00
0.136	2.96
0.276	3.16
LiI	
0.024	1.24
0.052	1.55
0.120	1.83
0.240	1.97

All ^{7}Li nmr spectra were obtained with a Varian Associates Model HA-100 spectrometer at 38.863 MHz in a 23,490-G field while operating in the HR mode. Low probe temperatures were achieved with standard Varian variable temperature accessories. Chemical shifts were measured relative to a 3 *M* aqueous LiBr solution inserted as a capillary.[14,15] Proton spectra were obtained using a Varian Model 220 HR spectrometer.

Lithium metal was obtained as a dispersion in mineral oil from Lithium Corp. of America, Inc. The fine lithium particles were washed free of oil with portions of dry pentane and ether, filtered free of these solvents, and then dried under vacuum.

"Baker Analyzed" reagent grade anhydrous diethyl ether was dried over sodium wire and then distilled from ethyllithium inside the glove box. The distilled ether was stored in amber bottles until use, usually within a few days.

Anhydrous, high purity lithium bromide and lithium iodide were purchased from the Anderson Physical Laboratory, Inc., Urbana, Ill. Matheson Coleman and Bell now supply these salts as their Polaroquality Grade reagent.

Dimethylmercury was obtained from Eastman Organic Chemicals in sealed glass vials which were opened inside the glove box immediately before using.

Methyllithium solutions in ether, usually about 1 *M*, were prepared by dropwise addition of dimethylmercury to a stirred suspension of lithium particles (twofold molar excess) in dry diethyl ether cooled to approximately −20°. After addition the mixture was stirred for 1–2 hr at −20°. Filtration of the reaction mixture through a medium porosity glass fritted filter yielded a clear, colorless solution of methyllithium in ether. This was stored in the glove box cold well at −45° until use. Aliquots of this stock solution were removed from the glove box, hydrolyzed, and titrated to a phenolphthalein end point with standard 0.1 *N* HCl to determine their concentration.

Saturated solutions of lithium bromide (1 *M*) and lithium iodide (*ca.* 3 *M*) were prepared from freshly distilled anhydrous diethyl ether. These were later diluted to the concentrations needed for preparing nmr samples.

The concentrations of the various lithium halide solutions were determined by hydrolyzing aliquot samples and titrating with standard mercuric nitrate solution.[16]

Samples of varying ratios (10:1 through 1:10) of methyllithium to lithium halide were prepared in the nmr tubes by the volumetric addition (using 1-ml Hamilton gas tight syringes) of stock methyllithium and lithium halide solutions, and anhydrous diethyl ether.

All solutions containing methyllithium were kept below 0° while they were being handled in the glove box. At other times they were stored in the cold well at −45°. Solutions prepared for nmr studies were degassed, sealed under vacuum in standard-size nmr tubes, and stored at Dry Ice temperatures. None of the samples studied contained white precipitate or other visible evidence of decomposition.

Lithium-7 nmr spectra were recorded in a frequency sweep, nonlock mode while observing the upfield sideband produced from the imposition of an "internal" 2.5-kHz audiofrequency on the 38.863-MHz resonance frequency. A 250-sec sweep time was used for recording all spectra, but the sweep rate was varied from spectrum to spectrum when looking for different spectral characteristics. Several spectra were usually recorded for each sample. Some of these were calibrated by using the sideband technique. The rf power levels used were always tested to ensure that they were directly proportional to the intensity of the most intense resonance.

Results and Discussion

Colligative property[17] and nmr studies[15,18] both indicate that methyllithium is tetrameric in diethyl ether. Both LiBr and LiI were reported as dimeric in ether by Talalaeva and coworkers.[8] The data from our differential vapor pressure experiments (Table I) are too limited to accurately define equilibria, but it is evident that LiBr is more highly associated than LiI. We speculate that LiBr may be involved in a tetramer–dimer equilibrium and LiI in a dimer–monomer equilibrium.

Methyllithium in ether exhibits a single resonance in the ^{7}Li nmr spectrum at −1.32 ppm. The line shape and chemical shift of this resonance relative to the external standard do not change significantly as a function of concentration or temperature in the range −90 to +25°. Lithium bromide (0.25 *F*) in ether exhibits a single sharp ^{7}Li absorption at a chemical shift of 0.44 ppm. Lithium iodide (0.25 *F*) in ether exhibits a similarly sharp singlet at a chemical shift of 0.56 ppm. The fact that single sharp resonances are observed indicates that equilibria are rapid on the nmr time scale at the lowest temperature studied, −90°.

The formation of cross-associated species $Li_4R_nR'_{4-n}$ in mixtures of two different organolithium compounds is well documented.[19] It is reasonable to expect that mixtures of an organolithium compound and a lithium halide might also contain mixed associated species, and this has been found to be the case. However, because of the great difference in properties between bromide or iodide and an organic moiety, formation of such mixed species does not occur in accord solely with simple entropy considerations. The ^{7}Li spectra of mixtures of methyllithium with lithium bromide in THF show that mixed complexes do not form to a great extent.[11] Earlier work carried out in our laboratories with diethyl ether solutions containing a high methyllithium/lithium halide ratio showed formation of Li_4R_3X but did not reveal the overall outlines of the mixed complex formation.[10]

Low temperature ^{7}Li nmr spectra of mixtures of $LiCH_3$ and LiBr are shown in Figure 1. The spectra at −90° show the presence of four distinguishable reso-

---

[13] (a) A. L. Myers, W. J. McDowell, and C. F. Coleman, *J. Inorg. Nucl. Chem.*, **26**, 2005 (1964); (b) J. W. Roddy and C. F. Coleman, *ibid.*, **32**, 3891 (1970).

[14] T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

[15] L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 2174 (1966).

[16] F. W. Cheng, *Microchem. J.*, **3**, 537 (1959).

[17] P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967).

[18] L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *ibid.*, **91**, 1057 (1969).

[19] T. L. Brown, *Pure Appl. Chem.*, **23**, 447 (1970).

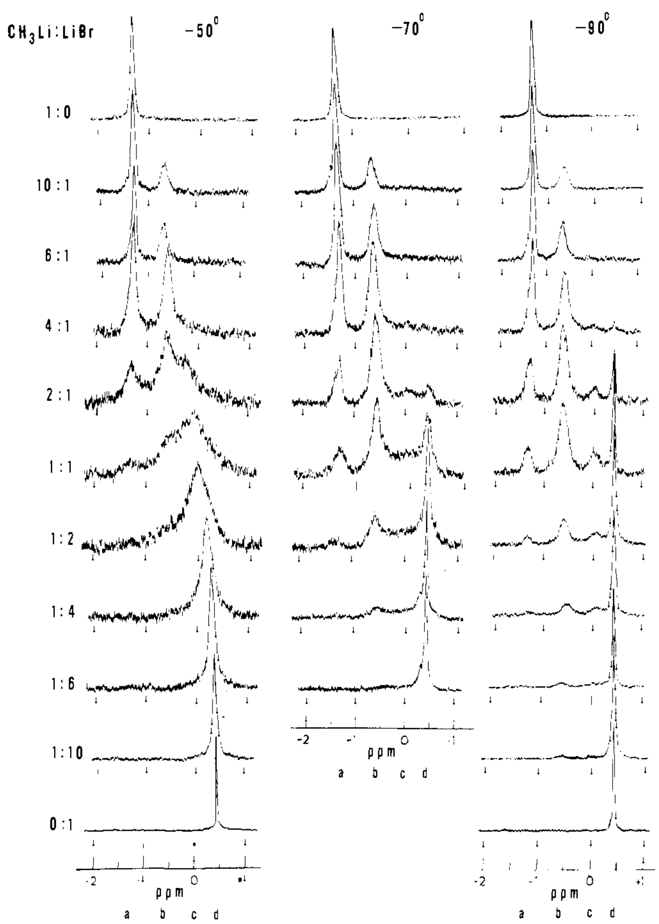


Figure 1. Low temperature ^{7}Li nmr spectra of methyllithium–lithium bromide mixtures in diethyl ether. The chemical shift scale varies slightly among the spectra due to variations in sweep rate.

nances. The extreme low and high field absorptions occur at the same chemical shifts as seen in solutions containing pure LiCH$_3$ and pure LiBr, respectively. The number and relative intensities of the absorptions in the various solutions suggest that the lines can be associated with lithium "local environments."[15] Although we recognize that LiBr may not be present to a large extent as tetramer, it is convenient to take as a point of departure an assumed statistical distribution of mixed tetramers of the form $\mathrm{Li_4(CH_3)_{4-n}Br_n}$.

If the two components formed all the various possible mixed complexes, $\mathrm{Li_4R_{4-n}Br_n}$, n = 0–4 (where R = CH$_3$), five distinct associated species would prevail in solution, at relative concentrations determined in part by the R/Br ratio. Although there are eight distinct chemical environments for lithium in these five species, there are but four possible local environments, determined by the three bridging groups (CH$_3$ or Br) which are bonded to the faces adjacent to an individual lithium. If it is assumed that the ^{7}Li chemical shift is determined solely by the identity of the three adjacent bridging groups, *i.e.*, that it is independent of the fourth bridging group on the opposite face of the tetramer, a total of four ^{7}Li resonances is to be expected for the various mixed species. This situation also requires that intramolecular exchange (within each tetramer), and of course all intermolecular exchanges between tetramers, be slow.

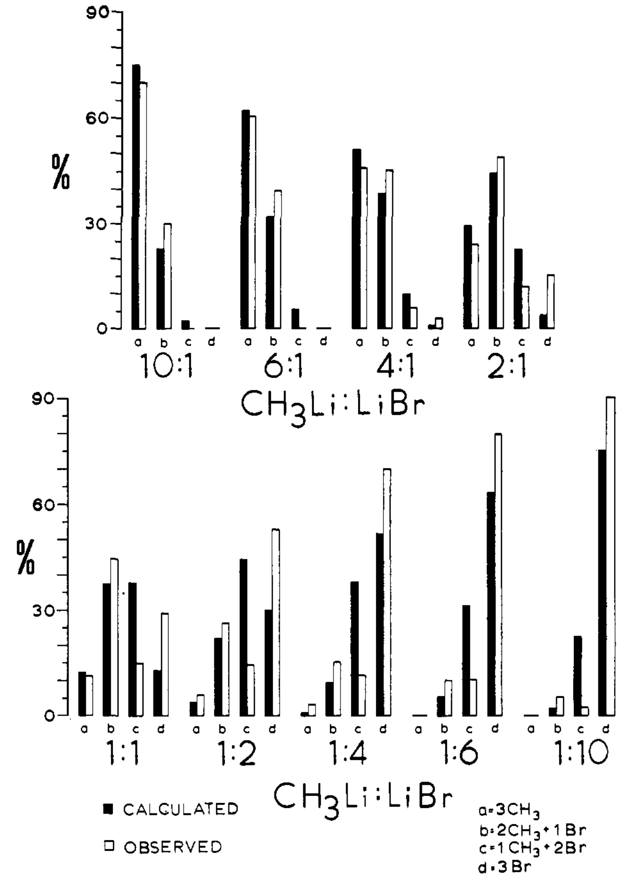


Figure 2. Relative amounts of observed and calculated local environments in the ^{7}Li spectra for LiCH$_3$–LiBr mixtures.

If the free-energy differences between tetramers were zero except for the statistical factors involved in forming the mixed tetramers the fractional quantities of each would be given by

$$F(\mathrm{Li_4R_{4-n}Br_n}) = f_{\mathrm{LiR}}^{\;4-n} f_{\mathrm{LiBr}}^{\;n} \frac{4!}{n!(4-n)!} \qquad (1)$$

where f_{LiR} and f_{LiBr} represent the fractional concentrations of the initial components, *i.e.*, $f_{\mathrm{LiR}} + f_{\mathrm{LiBr}} = 1$. Similarly, the fractional concentrations of the four local environments distinguishable in the nmr are given by

$$F(\mathrm{R_{3-n}Br_n}) = f_{\mathrm{LiR}}^{\;3-n} f_{\mathrm{LiBr}}^{\;n} \frac{3!}{n!(3-n)!} \qquad (2)$$

The fractional populations for the idealized system can be compared with the observed spectra if the four resonances observed are associated with local environments consisting of 3R, 2R + Br, R + 2Br, and 3Br, in the order of increasing upfield chemical shift. The bar graphs in Figure 2 show the comparison between the purely idealized and observed relative populations. The observed populations were obtained by graphical resolution and integration of the ^{7}Li spectra taken at −90°.

While the correspondence is surprisingly close, certain systematic discrepancies between the idealized and observed distributions are evident. The absorption ascribed to an all-bromide local environment is characteristically more intense than calculated. This absorption, of course, includes all associated forms of

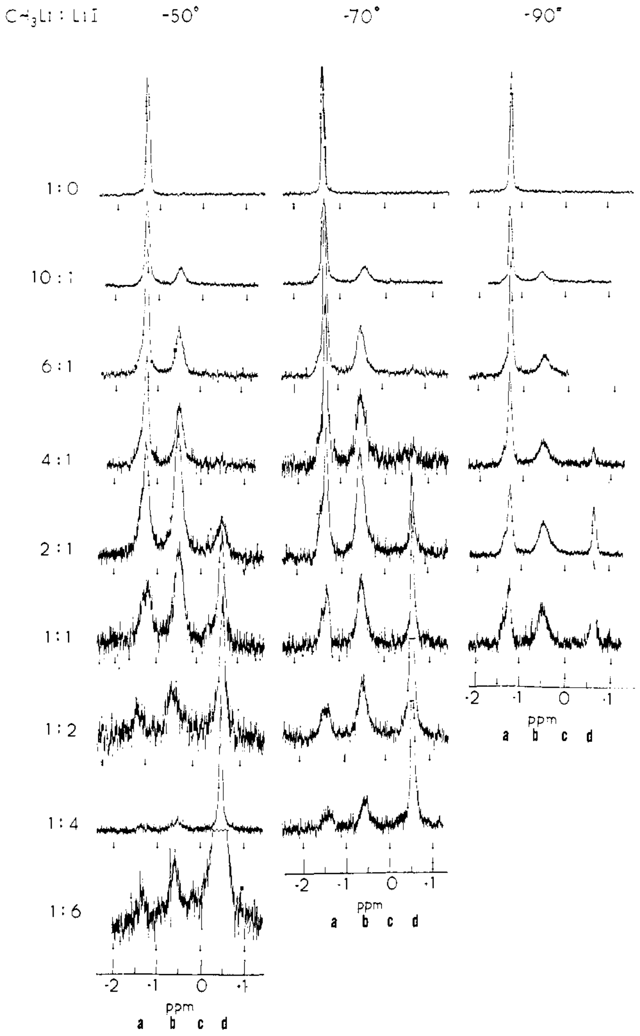


Figure 3. Low temperature ^7Li nmr spectra of methyllithium–lithium iodide mixtures in diethyl ether.

LiBr. The local environment ascribed to R + 2Br is always low and never attains an intensity greater than that due to 2R + Br. We conclude that the species Li_4RBr_3 is not present to a significant extent, even at low CH_3/Br ratios. This conclusion is substantiated by the results of 220-MHz proton spectra (*vide infra*).

The association data for LiBr raises the question of whether there might not also be a mixed dimer of the form $Li_2(CH_3)Br$. Dimeric species of this form probably do not exist to an appreciable extent in ether. Methyllithium itself does not exist as dimer to any observable degree. Although lithium bromide is less than fourfold associated at 0°, tetramers are probably an important component at 0° in the concentration range employed. If we assume that the tendency of the tetramer to dissociate decreases regularly with the replacement of bromine by methyl groups, then $Li_4(CH_3)_2Br_2$ should show much less tendency to form dimers than does LiBr. There is the further point that neither the ^7Li or ^1H spectra show an absorption in addition to that ascribed to $Li_4(CH_3)_2Br_2$, which might be assigned to a dimer. We conclude, therefore, that the $LiCH_3$–LiBr spectra can be satisfactorily interpreted by assuming that the only species present are $Li_4(CH_3)_4$, $Li_4(CH_3)_3Br$, $Li_4(CH_3)_2Br_2$, and $Li_4Br_4 \rightleftarrows Li_2Br_2$.[20]

The ^7Li nmr spectra at −70 and −50°, Figure 1, reveal the beginning of exchange between the local environments upon an increase in temperature. The local environments richer in bromide undergo exchange at a lower temperature than those containing more alkyl. Little or no temperature dependence of the relative concentrations of local environments is apparent.

From the manner in which the absorptions due to local environments merge with increasing temperature, to give a single sharp resonance in the fast exchange limit well above −50°, exchange between the various tetramers obviously occurs, presumably *via* dissociation of the tetramers to give dimers and then possible monomers, *e.g.*

$$\begin{tikzcd} Li_4R_3X \arrow[r, shift left] & Li_2RX \arrow[l, shift left] \arrow[d, shift left] & + & Li_2R_2 \arrow[d, shift left] \\ & LiR + LiX \arrow[u, shift left] & & 2LiR \arrow[u, shift left] \end{tikzcd} \tag{3}$$

On the basis of the temperature dependence of the spectra we deduce that the equilibria leading to exchange are more rapid for the species richer in bromide. More detailed considerations of the exchange between Li_4R_4 and Li_4R_3Br are presented below.

The ^7Li spectra of $LiCH_3$–LiI mixtures, Figure 3, reveal a much different tendency toward mixed complex formation. Only a single absorption of intermediate chemical shift is visible as evidence of mixed complex formation. The spectra show no evidence of exchange collapse at −50°. The major effect of temperature variation in the −50 to −90° interval is an increase in relative intensity of the intermediate absorption with increasing temperature. There is essentially no absorption attributable to a local environment of R + 2I. The $Li_4R_2I_2$ and Li_4RI_3 tetramers cannot therefore be present to a significant extent. The one intermediate absorption seen is assigned to the Li_4R_3I tetramer. Fortunately, it is possible to establish this assignment unambiguously.

If the local environment approximation is to fail, one might expect that it would do so for iodide as a bridging group. In the spectra of $LiCH_3$/LiI mixtures containing comparable concentrations of the two components the absorption at −1.3 ppm is seen to consist of two lines. The second, barely resolvable line is assigned to the lithium in the Li_4R_3I tetramer which possesses a local environment of three methyl groups but which is shifted from the resonance due to the Li_4R_4 tetramer because of the presence of iodide on the opposite face. This effect is shown very clearly in the two expanded scale spectra shown in Figure 4. The area under the downfield shoulder should be $^1/_3$ that of the absorption due to the local environment of 2R + I. Integration of several spectra with the aid of a DuPont Model 310 curve resolver established that this is indeed the case.

The spectra of Figure 4 serve not only to establish the existence of the Li_4R_3I tetramer but also to demonstrate that intramolecular exchange within the Li_4R_3I tetramer is slow at −70°. A fast intramolecular ex-

---

(20) In contrast to the present results, $LiCH_3$–LiBr mixtures in THF exhibit almost no tendency toward mixed tetramer formation.[11] Colligative property data for lithium halides in THF are not yet available. It seems likely, however, that the absence of substantial mixed complex formation is related to the fact that lithium bromide is strongly stabilized by solvation in THF.

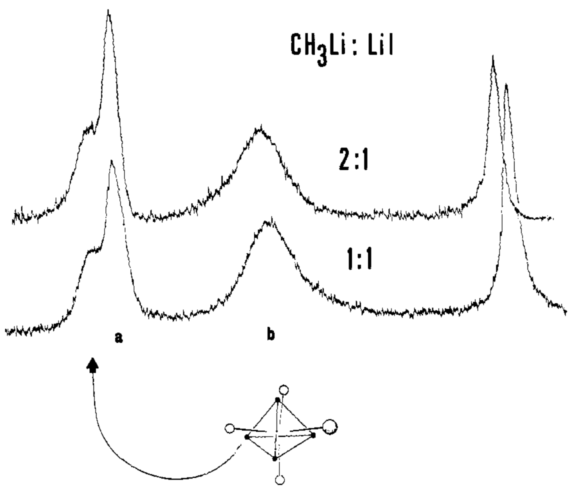


Figure 4. ^{7}Li spectra of LiCH$_3$–LiI mixtures at −70° in diethyl ether. The absorption at a is due to Li$_4$(CH$_3$)$_4$. The shoulder indicated by the arrow is due to the Li in Li$_4$(CH$_3$)$_3$I with a local environment of 3CH$_3$. The absorption at b is due to the three Li of Li$_4$(CH$_3$)$_3$I with a local environment of 2CH$_3$ + I.

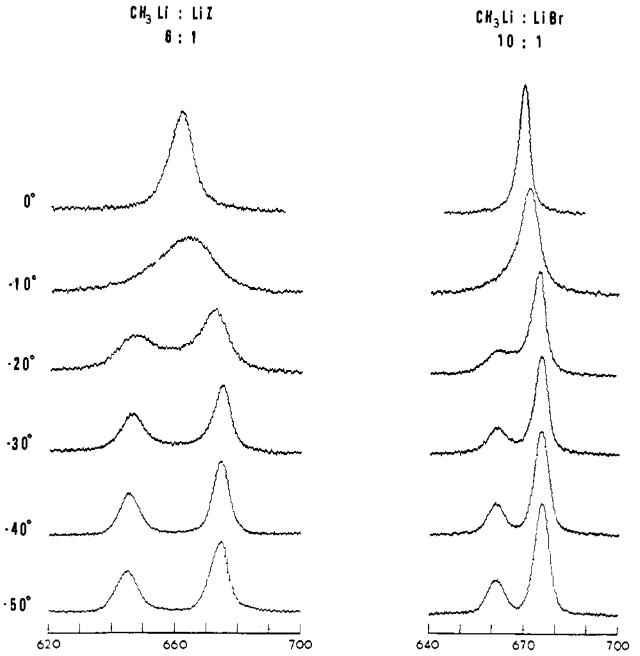


Figure 5. Temperature dependence of the 220-MHz proton nmr spectra of LiCH$_3$–LiBr and LiCH$_3$–LiI mixtures. The chemical shift scale denotes the upfield shift in hertz from the center of the solvent ether methyl group triplet.

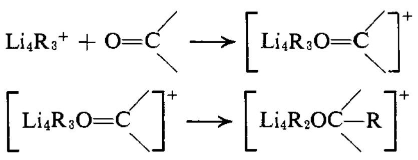
change within the Li$_4$R$_3$I tetramer would result in a collapse of the downfield shoulder with the line due to the 2R + I local environment. At −50° some evidence of the onset of such an exchange is seen in the broadening of the lines. However, the intramolecular exchange within Li$_4$R$_3$I cannot be much faster than the intermolecular exchange between Li$_4$R$_3$I and Li$_4$R$_4$. The latter is probably rate determined by the rate of dissociation of Li$_4$R$_4$.[21]

The fact that intramolecular exchange in Li$_4$R$_3$I is not considerably faster than intermolecular exchange with Li$_4$R$_4$ is of interest, because it helps to rule out the importance of an ionic equilibrium which might have been accorded considerable *a priori* credibility.

$$\mathrm{Li_4R_3X} \rightleftharpoons \mathrm{Li_4R_3^+ + X^-} \tag{4}$$

Such a heterolytic dissociation could be an important step preceding reaction with a nucleophile such as a carbonyl.

$$\mathrm{Li_4R_3X} \longrightarrow \mathrm{Li_4R_3^+ + X^-}$$



$$\mathrm{Li_4R_3^+ + O{=}C\langle} \longrightarrow \left[\mathrm{Li_4R_3O{=}C\langle}\right]^+$$

$$\left[\mathrm{Li_4R_3O{=}C\langle}\right]^+ \longrightarrow \left[\mathrm{Li_4R_2OC{\langle}{-}R}\right]^+$$

The three alkyl groups in Li$_4$R$_3^+$ would be expected to undergo facile intraionic exchange, in that movement of an alkyl group to the vacant face should be a low energy process. The fact that intramolecular exchange is not extremely rapid in Li$_4$R$_3$I therefore suggests that nonionic dissociation as shown in eq 3 provides the pathway by which this species undergoes ^{7}Li exchange. Ionic dissociation could still, of course, play a role in certain organolithium reactions, especially in more polar media.

Because the local environment approximation is not so clearly violated in the case of LiCH$_3$/LiBr mixtures, it is not possible to be as clear about the temperature dependence of the spectra with respect to the Li$_4$R$_3$Br species. It does appear that intramolecular exchange may be more rapid in the bromide than in the iodide system. On the other hand, intermolecular exchange between the Li$_4$R$_4$ and Li$_4$R$_3$X species is probably rate determined by dissociation of Li$_4$R$_4$ tetramer and so occurs at about the same rate for both halide systems, as evidenced in the 220-MHz ^{1}H spectra.

Figure 5 shows the 220-MHz proton spectra at various temperatures for solutions containing high LiR/LiX ratios. The only two species expected to be present in significant concentrations at high ratios are Li$_4$R$_4$ and Li$_4$R$_3$X. The higher field resonance occurs at the same chemical shift as that for methyllithium alone in ether. The second resonance is assigned to the methyl groups of the Li$_4$R$_3$X tetramer. The relative areas of the two absorptions are in agreement with this assignment, assuming that the two tetramers are present in relative amounts predicted from a statistical distribution. This is a valid assumption at high R/X ratios, judging from the previously presented ^{7}Li spectra for these systems.

At temperatures above −50° exchange of methyl groups between the two chemical sites causes a broadening and then collapse of the separate resonances to a single sharp line. The spectra have not been subjected to a detailed line shape analysis, but it would appear that exchange is occurring at about the same rate for the bromide- and iodide-containing mixtures. Because the chemical shift separation is smaller for the bromide system, the coalescence temperature is somewhat lower, but the reciprocal exchange times are approximately the same in the two systems. This suggests that the exchange between the Li$_4$R$_4$ and Li$_4$R$_3$X systems is rate determined primarily by dissociation of Li$_4$R$_4$. As further indication of this, the exchange rates observed here are about the same as observed for ^{7}Li exchange in mixtures of LiCH$_3$ and LiAl(CH$_3$)$_4$ in ether,[21] in which

---

(21) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4134 (1966).

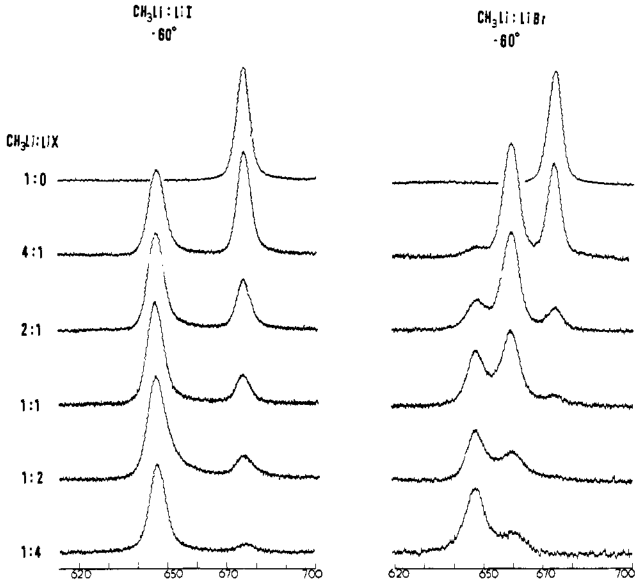


Figure 6. Low temperature 220-MHz proton nmr spectra of LiCH$_3$–LiBr and LiCH$_3$–LiI mixtures in diethyl ether.

it was shown that the rate-determining process involved just the methyllithium tetramer. The rate-limiting process was postulated to consist of dissociation of the methyllithium tetramer.

The 220-MHz proton spectra of various LiR/LiX mixtures at −60° are shown in Figure 6. The LiR/LiI spectra show the presence of only two distinguishable methyl resonances, even at high iodide concentration. Because the chemical shift separation between the methyl resonances of Li_4R_4 and Li_4R_3I is substantial, it is reasonable to expect that tetramers containing more than one iodide would produce resonances still further downfield. The fact that none are seen is therefore strong support for the conclusion drawn from the ^7Li spectra, that the sole mixed species present in the mixtures with lithium iodide is Li_4R_3I. The $LiCH_3$–LiBr spectra show the formation of three distinct methyl-containing species with changing CH_3/Br ratio. Based on their relative areas and chemical shifts these are assigned to $Li_4(CH_3)_4$, $Li_4(CH_3)_3Br$, and $Li_4(CH_3)_2Br_2$, in the order of increasing downfield shift. There is no evidence in the spectra for a fourth species, $Li_4(CH_3)Br_3$, at about 635 Hz, where it might be expected to appear. The ^1H data thus completely confirm the conclusions drawn from the ^7Li data.

The Schlenk equilibrium (which in elaborated form describes a multiplicity of possible equilibria[22]) is a special case of the general equilibria which can occur between a light metal organometallic compound and corresponding metal halide compounds. It has been clear for a long time that the ratio of organic moiety to halide in Grignard solutions is important in determining the reactivity of the reagent.[23] Further, the extent to which the Schlenk equilibrium occurs and the rate at which equilibrium is established have been known to be functions of the organic group, the halide, and the solvent. The organolithium systems are considerably more tractable than the Grignard, because of the closed polyhedral character of the associated species. Thus, it may be expected that for most simple organic groups, and most basic solvents such as ether and amines, the predominant alkyl-containing species will be tetramers, and the equilibria will be of the type which we have described here. In most instances the use of both ^7Li and ^1H nmr is feasible, thus providing a body of data not readily obtained for the Grignard solutions. From a knowledge of the equilibria which prevail in solution, and with knowledge of the rates at which exchanges occur between the prevalent species, it should be possible for the first time to proceed with meaningful kinetic and mechanistic studies of organolithium reactions, as modified by the presence of other lithium-containing compounds. Where solubility conditions permit, complex formation of the type we have seen here is to be expected also between organolithium compounds and LiX compounds where X = –OR, –NR_2, etc.

Acknowledgment. Initial investigations on methyllithium–lithium halide mixtures were carried out by Dr. W. L. Wells. We are indebted to the staff of the Molecular Spectroscopy Laboratory and R. L. Kieft for assistance in carrying out the nmr experiments and to L. Charbonneau for assistance with the differential vapor pressure studies.

---

[22] F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969).

[23] J. Billet and S. G. Smith, *Tetrahedron Lett.*, 4467 (1969), and references cited therein.