Nuclear Magnetic Resonance Studies of Organometallic Exchange Processes

THEODORE L. BROWN

Noyes Chemical Laboratory, University of Illinois,
Urbana, Illinois 61801

Nuclear magnetic resonance techniques are useful in the study of rapid intermolecular exchange processes in organometallic systems. It is possible to deduce the form of the rate expression by observing the effect of varying concentrations and concentration ratios on line shape. In this manner it is possible, for example, to deduce that the exchange of methyl groups bonded to the metal in the system $Ga(CH_3)_3 \cdot N(CH_3)_3$ + $Ga(CH_3)_3$ is rate determined by dissociation of the acid–base adduct. By contrast, the analogous exchange in the system $Ga(CH_3)_3 \cdot$pyridine + $Ga(CH_3)_3$ is rate determined by a bimolecular process. It has been shown that bridge–terminal exchange in $Al_2(CH_3)_6$ in hydrocarbon solvent occurs *via* a dissociative step, rather than by a nondissociative intramolecular process. Exchange of methyl groups between $Al_2(CH_3)_6$ and $Ga(CH_3)_3$ or $In(CH_3)_3$ in cyclopentane has been shown to involve a cage effect, operative also in exchanges involving organolithium compounds in hydrocarbon solvents. Using ^7Li magnetic resonance spectra, the kinetics of dissociation of the *t*-butyllithium tetramer in cyclopentane and toluene have been evaluated. Both ^7Li and proton magnetic resonance spectra provide information regarding equilibria and exchange processes in solutions containing more than one organolithium compound. The stoichiometries of mixed complexes with organometallic compounds of groups II and III have been determined from low-temperature ^7Li and ^1H spectra.

Since the pioneering work of Gutowsky and co-workers, nuclear magnetic resonance techniques have proven to be of great value in studies of numerous rapid exchange processes.[1] Although the techniques have been very effective in studies of intramolecular exchanges, they have not been widely applied until recently to systems involving intermolecular processes. Where applicable, however, nuclear magnetic resonance is an extremely effective tool in observing the kinetics of intermolecular exchange. The method can be used to study exchange reactions which are too rapid to be followed by conventional kinetics techniques. A major advantage of the technique is that it permits the study of systems which are in a state of chemical equilibrium. Furthermore, because the system can be studied while enclosed in a sealed sample tube, and at low temperatures, systems which are thermally unstable and/or reactive toward oxygen and water can be studied.
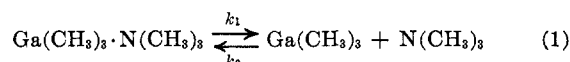
The nuclear magnetic resonance experiment provides access to τ_i, the mean lifetime of an absorbing nucleus at the site giving rise to the *i*th resonance absorption. The inverse mean lifetime, $1/\tau_i$, is the first-order rate constant for transfer out of the *i*th site. The quantity $1/\tau_i$ may be determined from the experimental line-shape data in a number of ways.[1] Measurement of the half-intensity line width of the *i*th absorption, Δ_i (in Hz), in the exchanging system and the analogous quantity in the absence of exchange, Δ_i^0, yields $1/\tau_i$ *via* the expression $1/\tau_i = \pi(\Delta_i - \Delta_i^0)$. This relationship applies to the slow exchange region, well below the coalescence temperature. It is most effectively employed when Δ_i^0 is available experimentally.

Matching of a calculated over-all line shape with experimental results is most effective when the populations of the exchanging sites are not grossly different.[2] The calculation is quite simple in the limiting case of an uncoupled, two-site system. The quantity evaluated is an exchange parameter, τ, related to the mean lifetimes on sites A and B: $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$.

Determination of the Rate Expression

Whereas the relative populations of the sites between which exchanges occur are usually fixed in intramolecular processes, it is possible to vary relative and absolute concentrations as an aid in deducing the form of the rate expression for intermolecular exchanges. For example, in the system $Ga(CH_3)_3 \cdot N(CH_3)_3$ + $Ga(CH_3)_3$ in CCl_3F as solvent,[3] all of the methyl groups bonded to gallium give rise to but one line in the proton magnetic resonance spectrum at room temperature. At lower temperatures, two lines are observed. In the slow exchange region, the lines due to $Ga(CH_3)_3 \cdot N(CH_3)_3$ and $Ga(CH_3)_3$ are well separated, but broadened as a result of exchange. Measurement of the line width at half-height provides a measure of exchange broadening which can be related to mean lifetime of a proton at each of the two chemical sites. In the mechanism proposed for this system, the exchange rate is determined by the dissociation of the adduct (eq 1).

$$Ga(CH_3)_3 \cdot N(CH_3)_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ga(CH_3)_3 + N(CH_3)_3 \qquad (1)$$

(1) Three reviews of this area have recently appeared: (a) L. W. Reeves, *Advan. Phys. Org. Chem.*, **3**, 187 (1965); (b) C. S. Johnson, Jr., *Advan. Magnetic Resonance*, **1**, 33 (1965); (c) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).
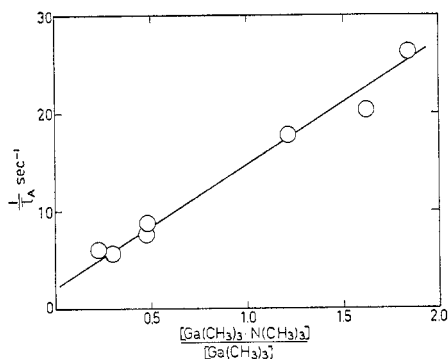
(2) K. C. Williams and T. L. Brown, *ibid.*, **88**, 4134 (1966).

(3) J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, **4**, 1741 (1965).

Figure 1. Variation of inverse mean lifetime of a proton on $Ga(CH_3)_3$, $1/\tau_A$, with concentration ratio, $[Ga(CH_3)_3 \cdot N(CH_3)_3]$: $[Ga(CH_3)_3]$. $1/\tau_A$ is obtained from the relation $1/\tau_A = \pi(\Delta - \Delta^0)$, where Δ is the width (in Hertz) at half-height of the line due to $Ga(CH_3)_3$ in the exchanging system and Δ^0 is the width when $Ga(CH_3)_3$ is present alone under the same temperature and solvent conditions.

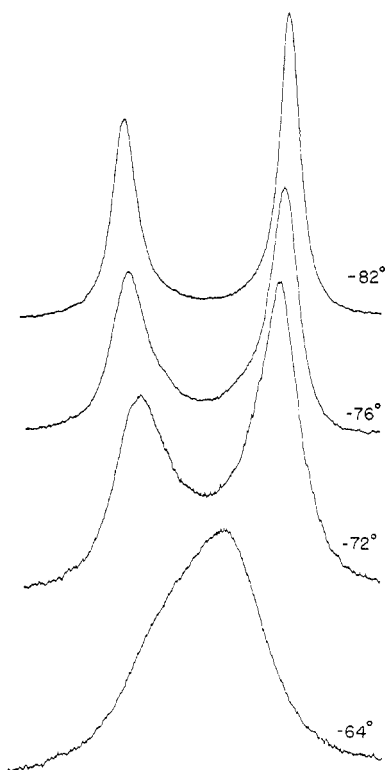The inverse mean lifetime of a methyl group on the adduct, $1/\tau_{AB}$, is independent of the concentrations of either the adduct or free $Ga(CH_3)_3$. The inverse mean lifetime of the methyl group on the free $Ga(CH_3)_3$, $1/\tau_A$, is given by the expression

$$\frac{1}{\tau_A} = k_2 K_e \frac{[Ga(CH_3)_3 \cdot N(CH_3)_3]}{[Ga(CH_3)_3]} \qquad (2)$$

where

$$K_e = \frac{[Ga(CH_3)_3][N(CH_3)_3]}{[Ga(CH_3)_3 \cdot N(CH_3)_3]}$$

Thus the proposed mechanism allows a clear prediction regarding the effect of concentrations upon the line widths of the two resonances in the slow-exchange region. The manner in which $1/\tau_A$ varies with the adduct–Lewis acid ratio is depicted in Figure 1. $1/\tau_{AB}$ is found to be independent of concentration, as predicted. From the line shapes at various temperatures, the activation energy for the exchange process may be computed. In the system just cited, the Arrhenius activation energy was found[3] to be about 24 kcal/mole, slightly larger than the reported dissociation energy for the adduct (21 kcal/mole), as expected.

The trimethylgallium–pyridine system is formally similar, but exchange proceeds via a different mechanism. Studies of concentration effects on line shapes in the $Ga(CH_3)_3 \cdot NC_5H_5 + Ga(CH_3)_3$ system reveal that the line widths at both sites are affected by concentration.[4] Some representative spectra are shown in Figure 2. Table I shows typical data obtained for this system.

A bimolecular rate-determining process should yield expressions for the inverse mean lifetimes of methyl groups on the two sites as given in eq 3 and 4. From

$$\frac{1}{\tau_A} = k_1[AB] \qquad (3)$$

$$\frac{1}{\tau_{AB}} = k_1[A] \qquad (4)$$

the results, it is clear that the mechanism is not a dissociative process, but is most probably a bimolecular reaction of the form of eq 5. Again, from observation

$$Ga(CH_3)_3 \cdot NC_5H_5 + Ga(CH_3)_3 \xrightarrow{k_1}$$
$$\text{AB} \qquad + \quad \text{A}$$
$$[Ga(CH_3)_3 \cdot \cdot NC_5H_5 \cdot \cdot Ga(CH_3)_3] \quad (5)$$
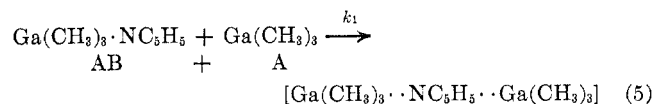
of the manner in which the line shape changes as a function of temperature, it is possible to ascertain the activation energy for the process. In this case, it is 8.5 kcal/mole. The different mechanisms operative in the two examples just cited are reflected not only in the activation energies but in the entropies of activation, as shown in Table II. In the absence of strong solvent participation, the entropy of activation is expected to be positive for a dissociative rate-determining step and negative for an associative step.

Figure 2. Proton magnetic resonance spectra of a toluene solution containing 0.21 M $Ga(CH_3)_3 \cdot NC_5H_5$ and 0.29 M $Ga(CH_3)_3$. The upfield resonance is due to free $Ga(CH_3)_3$.

Table I

Dependence of $1/\tau_A$ and $1/\tau_{AB}$ on Concentrations in the System $Ga(CH_3)_3 \cdot NC_5H_5 + Ga(CH_3)_3$ in Toluene Solvent

$[Ga(CH_3)_3 \cdot NC_5H_5]$	$[Ga(CH_3)_3]$	$1/\tau_{AB}$	$1/\tau_A$	$1/\tau_e{}^a$	Temp,°C
0.28	0.22	23[b]	34[b]	56.5	−72
0.21	0.29	35[b]	23[b]	57.2	−72
0.105	0.145	13.0	10.5	23.5	−72
0.053	0.073	6.7	5.7	12.3	−72
0.035	0.048	3.1	3.02	6.1	−72
0.105	0.145	5.8	4.65	10.45	−64
0.053	0.073	2.65	2.14	4.79	−64
0.035	0.048	1.57	1.42	2.99	−64

^{a} $\tau_e = \tau_A \tau_{AB}/(\tau_A + \tau_{AB})$. ^{b} Slow exchange condition not met.

(4) L. L. Murrell and T. L. Brown, unpublished results.

<div align="center">

Table II

Thermodynamic Parameters of Some Organometallic Exchange Systems

</div>

Assumed rate-determining step	Solvent	$\Delta H^{\ddagger},^a$ kcal/mole	$\Delta S^{\ddagger},^b$ cal/deg mole	Temp,^{c} °K
$Tl(CH_3)_3 + Tl(CH_3)_3 \rightarrow$ $[Tl_2(CH_3)_6]$	Toluene	6	−22	256
$Al_2(CH_3)_6 \rightarrow \{2Al(CH_3)_3\}$	Toluene or cyclopentane	15	+15	223
$Ga(CH_3)_3 \cdot N(CH_3)_3 \rightarrow$ $Ga(CH_3)_3 + N(CH_3)_3$	CCl$_3$F	24	+31	284
$Ga(CH_3)_3 \cdot NC_5H_5 + Ga(CH_3)_3 \rightarrow$ $[Ga(CH_3)_3 \cdot \cdot NC_5H_5 \cdot \cdot Ga(CH_3)_3]$	Toluene	8	−8	196
$[(CH_3)_3CLi]_4 \rightarrow 2[(CH_3)_3CLi]_2$	Cyclopentane	24	−1	302
$[CH_3Li]_4 \rightarrow 2[CH_3Li]_2$	$(C_5H_5)_2O$	10	−6	238

$^a \Delta H^{\ddagger} = E_a - RT.$ $^b k_t = kT/h \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT).$ ^{c} The temperature at which expression b is evaluated.

The exchange of methyl groups between two chemically different sites might conceivably occur, in the two examples cited above, without rupture of a metal–carbon bond. Exchange might be effected simply by formation of the acid–base adduct. However, methyl groups are probably rapidly exchanged between metal atoms in these systems. $Ga(CH_3)_3$ and $In(CH_3)_3$ exhibit rapid exchange of methyl groups in hydrocarbon solvent, even at −100°.[5] Methyl group exchange in the $Tl(CH_3)_3$ system is also rapid[6] and proceeds with a low activation energy (Table II).

The Cage Effect in Dissociative Processes

Exchanges in which the rate-determining step is a dissociative process generally proceed through a solvent-caged species. In a noninteracting solvent, the solvent-caged species is actually an intermediate. The free-energy diagram for a dissociative process of the form of eq 6, in which { } denotes solvent-caged species, is depicted in Figure 3.

$$A_{2n} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \{2A_n\} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_n + A_n \qquad (6)$$
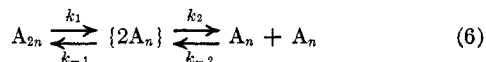
When dissociation within the solvent cage is essentially complete, the barrier to solvent separation is largely entropic in character and is related to the diffusion coefficient for the dissociated solute species.[7,8] Thus, k_{-1} might be expected to be on the order of 10–100 times larger than k_2. If dissociation within the cage is not complete, recombination may be expected to predominate much more heavily over solvent separation.

The exchange of bridge and terminal methyl groups in trimethylaluminum dimer, as compared with methyl group exchange between trimethylaluminum and trimethylgallium, affords an interesting illustration of the cage effect.[5] It has generally been assumed that
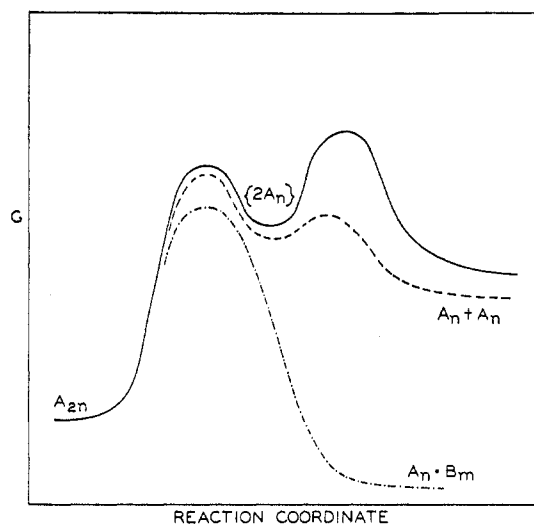
(5) K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 5460 (1966).

(6) J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 5534 (1963).

(7) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 544.

(8) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p 61.

Figure 3. Free-energy profile for a dissociative process under varying degrees of solvent interaction: (————), noninteracting; (— — —), weakly interacting; (·······), strongly interacting solvent.
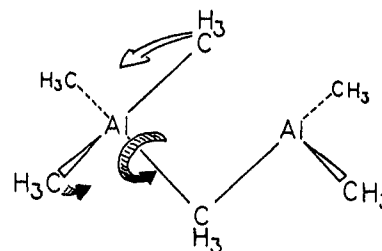

Figure 4. Schematic illustration of a possible pathway for intramolecular exchange of bridge and terminal methyl groups. In the process depicted, one side of a bridge bond is momentarily opened; rotation about the Al–C bond as shown results in exchange of the bridge methyl group for one of the two terminal groups. The process might occur at any one of the four Al–C bonds. The experimental results indicate, however, that a nondissociative path is not rate determining in bridge–terminal exchange.
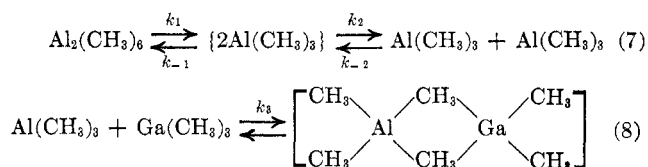
bridge–terminal exchange in the dimer occurs in an intramolecular process such as is illustrated in Figure 4. A nondissociative path for the bridge–terminal exchange is ruled out, however, by the comparative kinetics of bridge–terminal exchange and exchange with Ga(CH₃)₃, which is monomeric in solution. In cyclopentane, an essentially noninteracting solvent, the rate constant for bridge–terminal exchange in $Al_2(CH_3)_6$ is about ten times larger than the rate constant for exchange of methyl groups between $Al_2(CH_3)_6$ and Ga(CH₃)₃.[9] In toluene, on the other hand, the rate constant for bridge–terminal exchange is essentially the same as the rate constant for exchange between $Al_2(CH_3)_6$ and Ga(CH₃)₃. The exchange system may be described in terms of eq 7 and 8.

$$Al_2(CH_3)_6 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \{2Al(CH_3)_3\} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Al(CH_3)_3 + Al(CH_3)_3 \quad (7)$$

$$Al(CH_3)_3 + Ga(CH_3)_3 \overset{k_3}{\rightleftarrows} \begin{bmatrix} CH_3 & CH_3 & CH_3 \\ & Al & Ga & \\ CH_3 & CH_3 & CH_3 \end{bmatrix} \quad (8)$$

The exchange of methyl groups between the monomeric trimethyl moieties, as in eq 8, proceeds very rapidly. According to this mechanistic scheme, assuming $k_3 \gg k_1$, the following characteristics are predicted: (1) The inverse mean lifetime of a methyl group on trimethylgallium, $1/\tau_{Ga}$, should be proportional to the concentration ratio $[Al_2(CH_3)_6]:[Ga(CH_3)_3]$. It should not, however, vary with dilution of the sample provided that the ratio remains constant. (2) Upon substitution of In(CH₃)₃ for Ga(CH₃)₃, $1/\tau_{In}$ should show behavior identical with that of $1/\tau_{Ga}$. (3) The activation energy for exchange of a methyl group from Ga(CH₃)₃ or In(CH₃)₃ with a methyl group on $Al_2(CH_3)_6$ should be identical with the activation energy for bridge–terminal exchange.

All of these observations have been verified for cyclopentane and toluene solutions. Taken together, they rule out other plausible pathways, e.g., a bimolecular rate-determining step involving Ga(CH₃)₃ and $Al_2(CH_3)_6$. Although the activation energies for bridge–terminal exchange in $Al_2(CH_3)_6$ and for methyl group exchange between Ga(CH₃)₃ or In(CH₃)₃ and $Al_2(CH_3)_6$ are the same in toluene and cyclopentane, about 16 kcal/mole in all cases, the rates for the latter processes differ markedly in the two solvent systems. Bridge–terminal exchange has essentially the same kinetic parameters in cyclopentane and toluene. This is just what one expects from the model; bridge–terminal exchange is rate determined by k_1. Once the monomeric species have been formed inside a solvent cage and are free to tumble with respect to one another, they may recombine to form the dimer (k_{-1}) or dissociate further to form solvent-separated monomers with a rate constant k_2. In either case, bridge–terminal exchange is effected. The rate of bridge–terminal exchange is thus determined by the rate at which the dimers dissociate to form the solvent-caged monomers. This process should be largely independent of the nature of the solvent.

The exchange represented by eq 8, however, requires the formation of solvent-separated Al(CH₃)₃ monomers. The kinetic results show that recombination prevails over solvent separation in cyclopentane solution, i.e., $k_{-1} \gg k_2$. In toluene, the weakly basic character of the aromatic solvent molecules apparently is sufficient for the development of a weak interaction between the Al(CH₃)₃ monomers and solvent which promotes solvent separation over recombination, i.e., $k_2 \gg k_{-1}$. One might think of the solvent-caged species as undergoing "sticky" collisions with the solvent walls, with formation of a weak complex which survives long enough for a rotational motion to separate the monomers. In any event, if $k_2 \gg k_{-1}$, the rate constants for bridge–terminal exchange and for exchange of methyl groups between the aluminum and gallium sites become essentially equal. This is just the result observed.

The free-energy profile for the dissociative process in a solvent system in which there is a weak interaction is shown as a dashed line in Figure 3. Within the limits of the experimental uncertainties associated with the nmr measurements, there is no difference in the Arrhenius energy for either bridge–terminal or aluminum–gallium (–indium) exchanges in either solvent. This implies that the same amount of energy is required to form the solvent-caged species in either solvent. In a solvent of more strongly basic character, there might be some lowering of the activation energy for dissociation of $Al_2(CH_3)_6$. Of course, if the solvent is strongly basic, the free energy of the Lewis acid–base adduct is lower than that of the associated species plus free base, so that the situation indicated as a dotted line in Figure 3 prevails. Under these conditions the predominant species present in solution is the acid-base adduct, and exchange of methyl groups, if it occurs at all, must occur via a quite different rate-determining step.

It is clear that a cage effect might operate as a limiting factor in intermolecular exchange processes whenever a dissociative step is involved. We have found the notion to be particularly fruitful in dealing with exchange processes of organolithium compounds in various solvent systems and in the presence of bases.

Structures of Organolithium Compounds

Before considering the application of nmr techniques to the study of exchange processes in solutions of organolithium compounds, it is well to review briefly the current picture with respect to bonding and associations.[10] The organolithium compounds are nearly always observed as polyhedral aggregates, held together by multicenter bonds involving bridging organic groups. Figure 5 shows a schematic illustration of the

(9) These remarks apply to rate constants which have been corrected by statistical factors arising from the number of equivalent methyl groups in each case.[5]

(10) T. L. Brown, Advan. Organometal. Chem., 3, 365 (1966).

Table III
Freezing Point Lowering Results on the Degree of Association, $\bar{n}$, of Organolithium Compounds in Hydrocarbon Solvents[a]

Compound	Benzene		Cyclohexane	
	Concn range studied, m	n	Concn range studied, m	$\bar{n}$
C_2H_5Li	0.006–0.19	6.1 ± 0.18	0.006–0.08	6.0 ± 0.12
n-C_4H_9Li			0.002–0.6	6.0 ± 0.12
i-C_3H_7Li			0.004–0.02	4.0 ± 0.08
				(>4.0 above 0.02 m)
$(CH_3)_3CLi$	0.26–0.66	4.0 ± 0.04	0.0005–0.3	4.0 ± 0.05
$(CH_3)_3SiCH_2Li$	0.03–1.1	4.0 ± 0.03	0.002–0.05	6.0 ± 0.18
$C_6H_5CH_2Li$	0.0072–0.036	2.2 ± 0.3		

[a] Other data are cited in ref 10.

geometry of the hexamer, tetramer, and dimer species.

The bonding in the associated species may be viewed in terms of delocalized molecular orbitals extending over the framework. It is simpler, however, and probably a reasonably good approximation, to think of the bonding in terms of a localized multicenter bond involving one alkyl (or aryl) group and a group of lithium atoms. In the hexamer and tetramer, the localized bond is a four-center type, *i.e.*, it involves an orbital from the carbon atom of the organic group and orbitals from three equivalent lithium atoms. One electron pair is found within this grouping, and there is one such grouping for each alkyl group.

On the basis of indirect experimental indications, carbon–lithium bonds appear to have considerable polarity. Apparently the repulsive forces in the electropositive core of lithiums are more than counterbalanced by interactions with the bridging alkyl groups. The bonding in the hexamer and tetramer species is quite strong; the mass spectra of organolithium vapor species, at fairly high temperatures (60–120°) and at low vapor pressures (~10⁻⁵ torr), do not reveal the presence of any parent species less associated than tetrameric. The hexamer and tetramer species do not appear to differ a great deal in energy.

Table III shows the results of recent freezing point lowering measurements of the associations of organolithium compounds in hydrocarbon solutions.[10,11] From these results, it is apparent that the alkyl groups of lower steric requirement, *i.e.*, *n*-alkyl groups, favor hexamers, whereas the more highly branched alkyl groups lead to tetramer association. There are intermediate cases, *e.g.*, trimethylsilylmethyllithium, in which merely a change in solvent from cyclohexane to benzene is sufficient to alter the equilibrium from hexamer to tetramer. The dimeric species, which involves only a three-center bond (*i.e.*, one in which an alkyl group bridges two rather than three lithium atoms), is clearly less stable than either the hexamer or tetramer.

Relatively electron-withdrawing groups such as phenyl or benzyl apparently give rise to dimeric as-
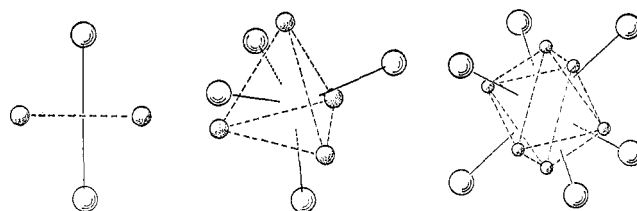

Figure 5. Schematic illustrations of the structures of dimeric, tetrameric, and hexameric organolithium compounds. The lithium atoms are denoted by the smaller, stipled spheres. The larger sphere represents the carbon atom of the organic group. The other groups bonded to the carbons are omitted for clarity.

sociation, although the comparisons are rather obscured by lack of data in a common solvent. Phenyllithium is not appreciably soluble in hydrocarbon solvents; it is found to be dimeric in ether.[12] Benzyllithium is approximately dimeric in benzene solution[13] and monomeric in ether.[14] In general, organolithium compounds with saturated alkyl groups exist as hexamers or tetramers, the dimer being significantly less stable. This is illustrated by the recent findings[14] that methyllithium and *n*-butyllithium are tetrameric in ether and that methyllithium is tetrameric even in a solvent as basic as THF.

Incidentally, it appears that those organolithium species which are hexameric in a noninteracting or weakly interacting solvent are tetramers in more basic solvents such as ether, triethylamine, or THF. Where the hexamer is only slightly more stable than the tetramer, as in trimethylsilylmethyllithium, benzene is sufficiently basic to displace the equilibrium toward tetramer (Table III).

⁷Li Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra of ⁷Li have proven of great value in the study of organolithium compounds in solution. Table IV lists the relevant

(11) H. L. Lewis, University of Illinois, unpublished results.

(12) (a) G. Wittig, F. J. Meyer, and G. Lange, *Ann.*, **57**, 1967 (1951); (b) T. V. Tallalaeva, A. N. Rodinov, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **154**, 174 (1964).
(13) M. York, Ph.D. Thesis, University of Illinois, 1967.
(14) P. West and R. Waack, *J. Am. Chem. Soc.*, **89**, 4395 (1967).

properties of the two naturally occurring nuclides of Li along with those of ^{1}H for comparison. Although the ^{7}Li nucleus has a substantial quadrupole moment, the line shapes observed for the organolithium species in solution are reasonably narrow (from 1 to 4 Hz) and amenable to study. The chief limitations encountered in the technique revolve about the relatively small range of chemical shifts encountered and rather poor signal:noise ratios. The dangers of saturation render quantitative assessment of intensities rather difficult. Chemical shifts are measured relative to a 3 M aqueous LiBr solution inserted as a capillary. Table V lists chemical shift values relative to this standard for a number of organolithium compounds.

In a solution containing two different organolithium compounds, LiR and LiR', mixed associated species of the form $Li_nR_xR'_{n-x}$ will be formed. This cross-association phenomenon can be observed in the ^{7}Li magnetic resonance spectrum if the two organolithium compounds possess distinctly different ^{7}Li chemical shifts.

If LiR and LiR' are associated to the same degree, it may be assumed as a first approximation that the groups R and R' are randomly distributed among the
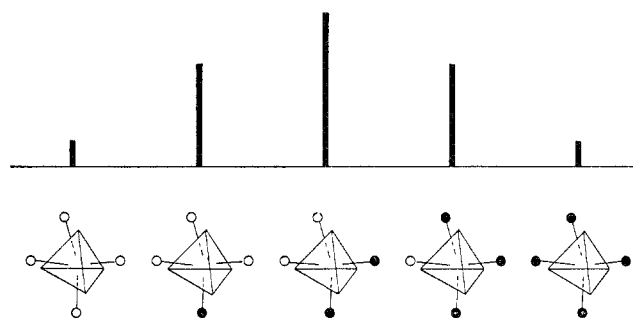
Table IV
Comparison of the Properties of Lithium Nuclides with the Proton

Nuclide	% abundance	Magnetic moment	Resonance freq in 14-kgauss field, MHz	Spin	Electric quadrupole moment
^{1}H	99.98	2.793	60.0	$1/2$	
^{6}Li	7.43	0.822	8.81	1	4.6×10^{-4}
^{7}Li	92.57	3.256	23.3	$3/2$	-0.1

Table V
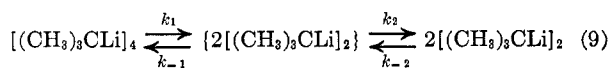### Chemical Shifts of ^{7}Li Magnetic Resonances in Organolithium Compounds[a]

Compound	δ, ppm[b]	Solvent
CH_3Li	-1.32	Ether
C_2H_5Li	-1.71	Cyclopentane
	-1.00	Benzene
	-0.6	Ether
	-1.38	Triethylamine
	$-1.21\ (-80°)$	Triethylamine
$n\text{-}C_4H_9Li$	-1.85	Cyclopentane
$(CH_3)_2CHLi$	-1.17	Cyclopentane
	-0.91	Triethylamine
$(CH_3)_3SiCH_2Li$	-1.36	Toluene
	-1.96	Cyclopentane
	-1.74	Hexane
	-2.26	Triethylamine
	$-2.64\ (-80°)$	Triethylamine
$(CH_3)_3CLi$	-0.40	Toluene
	-0.89	Cyclopentane
	-0.89	Triethylamine
C_6H_5Li	-1.2	Ether
$C_6H_5CH_2Li$	$+0.54$	Toluene–benzene
	-0.20	Ether

[a] Temperature near 25° unless otherwise noted. [b] Relative to 3 M aqueous LiBr in external capillary. Chemical shifts are uncorrected for bulk magnetic susceptibility effects.

Figure 6. Relative concentrations and structures of the five tetrameric species formed in a 1:1 mixture of $(LiR)_4$ and $(LiR')_4$, assuming random distribution of alkyl groups. The circles represent alkyl groups; the lithium atoms are located at the corners of the tetrahedra.

various possible mixed species. When the two components of the mixture do not share the same degree of association, the number of possible species is larger, and wider excursions from a purely random distribution may be expected.

To understand what the ^{7}Li spectrum of a mixture of two different organolithium compounds might look like, consider first a hypothetical system in which the two compounds LiR and LiR' are both tetramers, with significantly different ^{7}Li chemical shifts. If the distribution of the two types of alkyl groups among the bonding sites is random, we expect the five possible tetrameric species to be present in a 1:1 mixture in the proportions indicated in Figure 6. Assuming that this is the case, what may we expect to see in the ^{7}Li spectrum? There are three possible conditions: (a) a rapid intermolecular exchange among all the possible tetramers; (b) a slow intermolecular exchange among all the tetramers, but rapid intramolecular exchange within each tetramer, so that all of the lithiums within each of the different tetramers appear to be equivalent; (c) slow intra- as well as intermolecular exchange.

If condition a obtains, only one ^{7}Li resonance would be observed, at a chemical shift approximately intermediate between those of the two starting components, LiR and LiR'. For condition b we should see five lithium resonances, spaced roughly equally, in the intensity ratio 1:4:6:4:1. If condition c is prevalent, the spectrum might be quite complex, since there are eight chemically distinct lithium environments among the five species.

It is reasonable to expect, however, that the chemical shift of each lithium will be determined mainly by only the three alkyl groups immediately adjacent to it. This assumption, which we call the local environment approximation,[15] leads to the expectation that there will be only four different ^{7}Li lines, characteristic of the local environments (3R; 2R, R'; R, 2R'; 3R') in the intensity ratios 1:3:3:1. The first and last of these should appear at the chemical shifts characteristic of the

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

components going into the mixture; the intermediate two local environments should appear at intermediate chemical shifts. (It might be noted parenthetically that the local environment approximation, which applies in the limit of slow inter- and intramolecular exchanges, is equally applicable whether the species are associated as hexamer or tetramer.) All of the characteristics delineated for the three possible conditions named above apply only for the system at equilibrium, i.e., after the equilibrium distribution of groups R and R' on the various bonding sites has been arrived at.

When t-butyllithium (I) and trimethylsilylmethyllithium (II) are mixed in cyclopentane solution, the ^7Li spectrum initially shows no evidence of mixing.[16] Only the resonances characteristic of the starting components are seen, as shown in Figure 7. The spectrum does, however, change with time, until equilibrium is achieved. The very slow initial approach to equilibrium is quite remarkable and is a source of interesting information. It is clear from the manner in which the spectrum changes with time, as well as from other evidence, that the rate-determining step in the approach to equilibrium involves dissociation of the t-butyllithium moiety. We presume that this dissociation consists in the formation of dimers[17] and that it is a two-stage equilibrium involving an intermediate solvent-caged species (denoted by brackets in eq 9). By

$$[(CH_3)_3CLi]_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \{2[(CH_3)_3CLi]_2\} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2[(CH_3)_3CLi]_2 \quad (9)$$

contrast, the dissociation of II hexamer (or tetramer) is relatively rapid. The rate of dissociation of t-butyllithium to a solvent-separated species may be measured by observing the rate at which the ^7Li resonance line due to I disappears, beginning with an unequilibrated solution. Experiments in which we have made area measurements upon spectra of the type shown in Figure 7 have demonstrated that the process is indeed first order in t-butyllithium and independent of the concentration of II. Although the uncertainties in the data, occasioned by instrumental limitations, are larger than we might wish, experiments at 20, 29, and 39° yield an activation energy for dissociation on the order of 24 ± 4 kcal/mole.[18]

Solvent Effects on Organolithium Exchanges

If the intermolecular exchanges just alluded to are rate determined by dissociation of the t-butyllithium tetramer in a two-stage process of the form of eq 9, the question of the importance of the cage effect again arises. Unfortunately, the question cannot be answered as simply as it was in the case of the trimethylaluminum dimer, but some indications are available. The initial rate at which a 1:1 mixture of I and II changes in the direction of equilibrium in toluene solution at 20° has
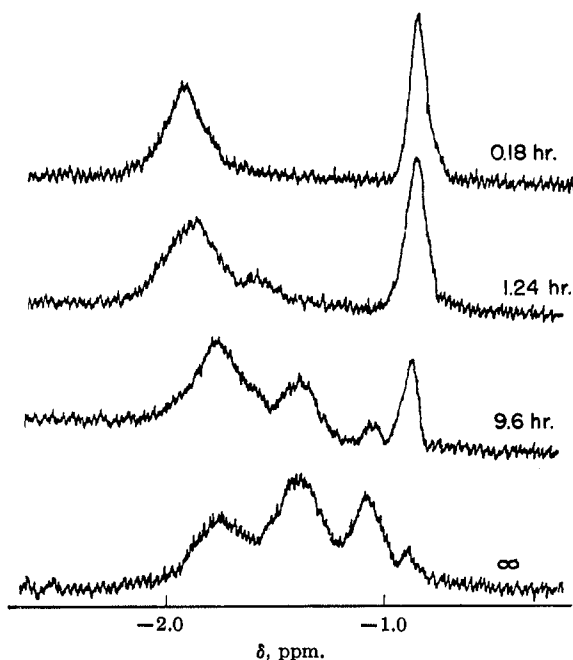

Figure 7. ^7Li spectra of a 1:1 mixture of t-butyllithium (I) and trimethylsilylmethyllithium (II) in cyclopentane at 20°.
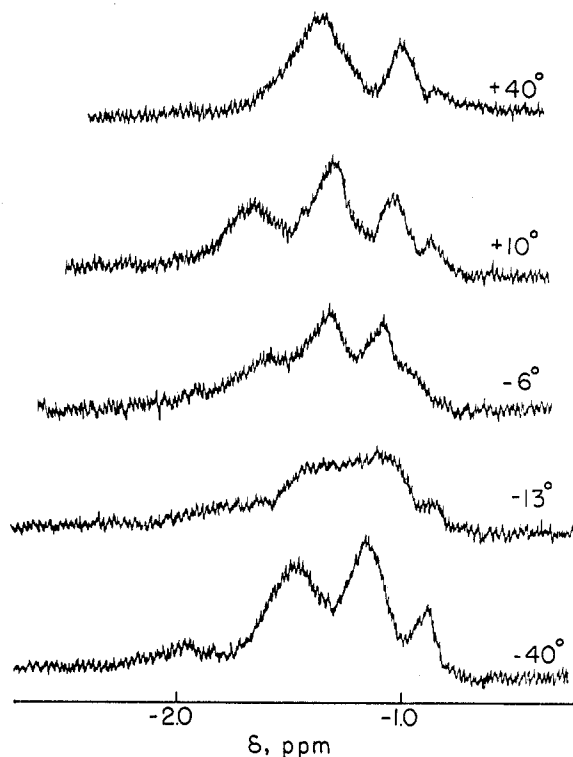

Figure 8. ^7Li spectra of an equilibrium 1:1 mixture of t-butyllithium (I) and trimethylsilylmethyllithium (II) in cyclopentane at various temperatures.[18]

been measured, using the area-measuring technique described above.[18] The rate is about 20 times faster than that observed for cyclopentane solutions at the same temperature. The effect is analogous and similar in magnitude to that observed in the trimethylaluminum system. The aromatic solvent thus appears to reduce the free-energy barrier to formation of the solvent-

(16) G. E. Hartwell and T. L. Brown, J. Am. Chem. Soc., 88, 4625 (1966).

(17) A subsequent rapid dissociation of dimers into monomer may occur, as suggested on the basis of kinetics studies,[14,18] but this is not important for the present discussion.

(18) S. Bywater, Advan. Polymer Sci., 4, 66 (1965).

separated dimers. It is doubtful, however, whether the cage effect has been completely quenched in toluene. The magnitude of the cage effect (*i.e.*, the ratio $k_{-1}:k_2$ of eq 7) no doubt varies with each organolithium species, and it is difficult to obtain an estimate for any one particular associated form. The best that can be said at this point, on the basis of the available ^{7}Li resonance data for alkyllithium compounds in cyclopentane and toluene, is that the cage effect in cyclopentane appears to be at least on the order of 20, and may in some cases be very much larger.

The ^{7}Li spectrum of an equilibrium mixture of I and II in either cyclopentane or toluene changes with temperature. A representative set of spectra for a cyclopentane solution is shown in Figure 8.[19] The spectra change from a type characteristic of rapid intramolecular exchange to the type characteristic of slow intramolecular exchange in the range from -20 to $-30°$, in *either* solvent. Intermolecular exchanges, on the other hand, which lead to collapse of the multiplet structure are much faster in toluene.[16] In either solvent, the intermolecular exchanges among the tetramers do not all occur at about the same rate. On the contrary, with increasing temperature the spectra exhibit a progressive collapse, beginning with the species richest in II. The same behavior is seen also with other pairs of organolithium compounds. In general, the rate of dissociation of an alkyllithium moiety is dependent on the bridging groups attached. This observation has important implications in connection with the kinetics of organolithium reactions. The effects of cross-association on the kinetic behavior of an organolithium system might in some cases be very important.

The ^{7}Li spectra of ethyllithium–methyllithium mixtures have been observed in ether solution,[15] in which both organolithium species are presumably tetrameric. The spectra for a typical mixture at three different temperatures in the slow-exchange region are shown in Figure 9. Intermolecular exchanges are very much more rapid in this system than in the hydrocarbon solvents (this particular system cannot be studied in hydrocarbon solvents because of the low solubility of methyllithium). In the slow-exchange limit, the relative intensities observed for the lines are those characteristic of a four-line spectrum, indicating that exchange condition c is operative. With an increase in temperature above $-50°$ the spectrum collapses rapidly to a single-line spectrum. There is no evidence of an intermediate stage involving slow intermolecular and fast intramolecular exchange. Assuming that exchange occurs *via* dissociation of the tetrameric species to di-
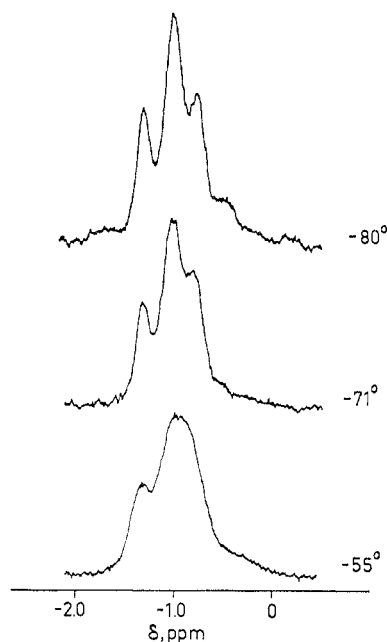

Figure 9. ^{7}Li spectra of an ether solution of a methyllithium–ethyllithium mixture (methyl:ethyl ratio = 1.55) at various temperatures. The ^{7}Li resonance due to a local environment of three methyl groups is farthest downfield. Note that the lines due to local environments richest in ethyl groups collapse first with increasing temperature.

mer, it thus appears that there is no cage effect operative. It is certainly reasonable to expect that the solvent participates extensively in a dissociative process.

It would be desirable to have a measure of the activation energy for dissociation of a tetrameric moiety in ether. The complexity of the spectrum precludes any quantitative evaluation of the temperature dependence with the aim of obtaining kinetic data. Fortunately, a system has been found in which dissociation of the methyllithium tetramer is rate determining and in which an accurate evaluation of the temperature dependence of the spectrum can be made.[2] Solutions containing either $LiAl(CH_3)_4$ or $LiB(CH_3)_4$ with CH_3Li exhibit rapid ^{7}Li exchange at room temperature. On lowering the temperature the slow-exchange limit in both instances is reached before $-50°$. Analysis of the kinetics of these systems indicates that the rate-determining step is dissociation of the methyllithium tetramer (eq 10).

$$(LiCH_3)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2(LiCH_3)_2 \qquad (10)$$
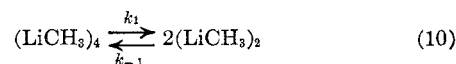
From the temperature dependences of the spectra, the kinetic parameters for this process, listed in Table II, were determined. The Arrhenius activation energy of about 11 kcal/mole is considerably lower than the value obtained for the analogous process for *t*-butyllithium in cyclopentane. How much of this may be ascribed to the difference in the alkyl groups, and how much to the effect of solvent, is not entirely clear. The equilibrium constant for the reaction

$$(CH_3)_3CLi + CH_3I \rightleftarrows (CH_3)_3CI + CH_3Li$$

(19) The recent discovery that II is hexameric in cyclopentane adds a complicating factor in attempts to compare the observed relative line intensities with those calculated on the basis of a random distribution. Nevertheless, if it is assumed that the only hexameric species possible are II$_6$ and II$_5$I, as seems quite reasonable, the relative concentrations of the tetramers richest in I: I$_4$, I$_3$II, I$_2$II$_2$, are affected very little by whether II is assumed to be hexamer or tetramer.

in ether is on the order of 750.[20] In the light of this result and the observation that ethyllithium tetramer dissociates more rapidly in ether than the methyllithium tetramer,[2,15] at least some of the difference in the two activation energies can be ascribed to the effect of solvent in lowering the activation energy for formation of solvent-separated species. Solvent participation is reflected also in the rather negative value obtained for $\Delta S^{\ddagger}$.

Solutions of either methyl- or ethyllithium and phenyllithium in ether are particularly interesting.[21] Since phenyllithium is dimeric in ether, whereas the alkyllithium compounds are tetrameric, it is of interest to know which mixed organometallic species subsist in the solution. By examining both the methyl group and ^7Li resonance spectra at low temperatures in methyllithium–phenyllithium mixtures and the low-temperature ^7Li spectra in ethyllithium–phenyllithium mixtures, we have been able to determine that just four organolithium species are present to a significant degree over a wide range of phenyl:alkyl ratios. These are $Li_2(C_6H_5)_2$, $Li_2C_6H_5R$, $Li_4R_3C_6H_5$, and Li_4R_4 (R = CH_3 or C_2H_5).

Mixed Organometallic Complexes

Beginning with Hein's work in the 1920's, there has been a continuing interest in compounds formed between organometallic compounds of different metals, most notably those of groups I, II, and III. A number of compounds have been isolated as solids of well-defined composition. More recently Wittig and co-workers have studied their properties in donor solvents.[22] Wittig refers to the mixed species as "ate" complexes and formulates them as largely ionic in character. Nuclear magnetic resonance techniques provide a powerful method for investigating the stoichiometries of the complexes in solution and for following the exchange equilibria which occur.

Methyllithium reacts with the trimethyl derivatives of the group III elements in ether or other donor solvent to form 1:1 compounds, $LiMR_4$.[2,23] The reactions proceed to completion. The interactions between $LiCH_3$ and $Mg(CH_3)_2$ or $Zn(CH_3)_2$ in ether give rise to more complicated systems. The zinc and magnesium systems behave almost identically, so we will consider here only the magnesium systems by way of example.[24] Addition of $Mg(CH_3)_2$ to an ether solution of $LiCH_3$ causes the chemical shift of the ^7Li resonance to change, but only one resonance is seen at room temperature. At low temperatures a multiplet structure is seen. By varying the Li:Mg ratio and observing the relative areas under the absorptions at temperatures on the
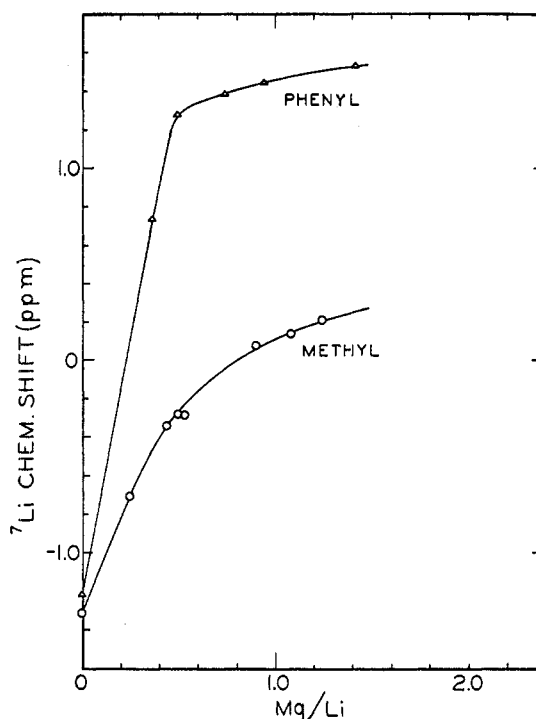
Figure 10. Chemical shifts in the ^7Li spectra of $Mg(CH_3)_2$–$LiCH_3$ and $Mg(C_6H_5)_2$–LiC_6H_5 mixtures in ether at room temperature.

order of $-60°$ or so, it is possible to assign the absorptions to complexes of specific stoichiometry. The most abundant complex is the 2:1, $Li_2Mg(CH_3)_4$, but there is also a 3:1 complex, $Li_3Mg(CH_3)_5$, when $LiCH_3$ is present in excess. Deductions based on the ^7Li spectra are corroborated by the results obtained in the proton spectra. The structures of the 2:1 and 3:1 complexes are believed to be of the form
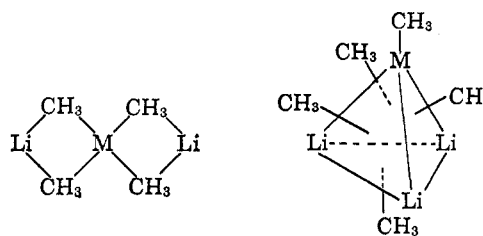
The 3:1 compound is analogous to a methyllithium tetramer; one lithium is replaced by a CH_3–Mg moiety. Since $Mg(CH_3)_2$ is not significantly associated in ether and $Zn(CH_3)_2$ does not self-associate under any solution conditions, the formation of the 3:1 complexes is rather remarkable. Recent work by Coates and co-workers shows, however, that organozinc compounds can self-associate if the appropriate bridging group is present.[25]

There is no evidence for a 3:1 complex in ether solutions of LiC_6H_5 and $Mg(C_6H_5)_2$, even at high Li:Mg ratios.[26] The principal species formed in these solu-

(20) J. F. Eastham, "Exchange Reactions," International Atomic Energy Agency, Vienna, 1965, p 335.

(21) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **89**, 1607 (1967).

(22) G. Wittig, *Proc. Robert A. Welch Found. Conf. Chem. Res.* *IX*, 13 (1966); see also ref 10 for leading references.

(23) J. P. Oliver and C. A. Wilkie, *J. Am. Chem. Soc.*, **89**, 163 (1967).

(24) L. M. Seitz and T. L. Brown, *ibid.*, **88**, 4140 (1966).

(25) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1870 (1965).

(26) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **89**, 1602 (1967).

tions is the 2:1 complex, $Li_2Mg(C_6H_5)_4$. There is only weak evidence for a 1:1 complex in solution, although this is reported to be the composition of the solid isolated from solution.

The exchanges between the complex or complexes and excess organolithium reagent are fast at room temperature in both the methyl and phenyl systems. It is possible, however, to learn something about the extent to which reaction 11 proceeds to the right by observing

$$nLiR + MgR_2 \longrightarrow Li_nMgR_{2+n} \qquad (11)$$

the ^7Li chemical shift in ether as a function of the ratio of Mg:Li. The results for the methyl and phenyl systems in ether at about 30° are shown in Figure 10. The phenyl system exhibits a sharp dependence of chemical shift on the ratio up to a value of 0.5, corresponding to the complex $Li_2Mg(C_6H_5)_4$. Beyond this point there is a further slight variation in chemical shift which may result from the formation of a small amount of 1:1 complex. It is clear that the equilibrium of eq 11 proceeds far to the right, and that the 2:1 complex is the predominant species formed. In the methyl system, by contrast, the ^7Li shift does not exhibit a sharp

break as a function of Mg:Li ratio, an indication that complex formation is incomplete at room temperature.

These studies of mixed organometallic complexes are of interest in furnishing a more complete picture than heretofore of the species present in solutions. There is need for a thorough study of solvent effects. The exchange properties of these systems are very probably sensitive to the donor character and polarity of the solvent. The entire area of exchanges in mixed organometallic complex formation involving alkyl and aryl derivatives of the transition metals is virtually unexplored. Most of the mixed compounds which have been prepared or which might be formulated are paramagnetic, and it remains to be seen whether nuclear magnetic resonance techniques will be useful under appropriate conditions. Exchanges may be quite rapid, and it may prove possible to observe very large isotropic contact shifts in either the proton or ^7Li resonances.