Mixtures of the halo complexes and tin(II) chloride are less effective catalysts in a mixture of benzene and methanol than the pure halo complexes in benzene since the halo complexes are unstable in methanol solution.

Discussion

Bis(triphenylphosphine)nickel halides are effective homogeneous catalysts for both selective hydrogenation and isomerization of unsaturated compounds, thus resembling the mixture of dichlorobis(triphenylphosphine)platinum(II) and tin(II) chloride described earlier.[2a] It is especially interesting that with nickel complexes hydrogenation takes place more rapidly than isomerization. For example, the diiodo complex converted linoleate to monoene more rapidly than it changed oleate to the *trans* isomers in benzene solution under hydrogen pressure (expt 1 and 6). Similarly, in THF, linoleate was converted almost entirely to monoene, but oleate was only partially isomerized to the *trans* isomers (expt 2 and 7). Similar results were obtained with the bromo complex (expt 13 and 15). In the absence of hydrogen, neither the dibromo nor the diiodo catalyst brought about isomerization of oleate, but hydrogenation of linoleate occurred.

Two points are worthy of special note.

(1) Linoleate undergoes both rearrangement and reduction in an inert atmosphere (nitrogen), just as it does under hydrogen, though to a lesser extent. This might have been expected in those experiments in which THF was used as the solvent, for THF loses hydrogen fairly readily. It is unexpected, however, in the experiments in which benzene was used as the solvent. It may be that, in these cases, the methyl linoleate disproportionates to give monoenate and polyunsaturated esters. This point remains to be tested.

(2). Oleate undergoes *cis–trans* isomerization under hydrogen pressure, but not under nitrogen pressure.

We are of the opinion that, in an atmosphere of hydrogen, the catalyst combines with elemental hydrogen to form a hydrido complex which reacts with a double bond to bring about *cis–trans* rearrangement and migration. After the double bonds have become conjugated, reduction takes place as shown in our previous reports.[2]

No reaction intermediates were isolated in our experiments. However, several interesting papers have been published recently, suggesting that isomerization reactions of olefins take place through pathways involving π-allylmetal hydride intermediates[12] and the activation of hydrogen by metal complexes proceeds *via* an intermediate involving the expansion of the coordination sphere of the metal ion.[2,13]

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[12] For reactions involving iron carbonyls, see R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961); J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961); J. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962). For reactions involving rhodium chloride, see R. E. Rinehart and J. S. Lasky, *J. Am. Chem. Soc.*, **86**, 2516 (1964); J. F. Harrod and A. J. Chalk, *ibid.*, **88**, 3491 (1966); R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966). For reactions involving palladium complexes, see N. R. Davies, *Nature*, **201**, 490 (1964).

[13] L. Vaska, *Inorg. Nucl. Chem. Letters*, **1**, 89 (1965); J. F. Young, J. A. Osborn, F. H. Jardiene, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

Organometallic Exchange Reactions. VI. Lithium-7 and Proton Nuclear Magnetic Resonance Spectra of the Phenyllithium–Diphenylmagnesium and Phenyllithium–Diphenylzinc Systems in Ether[1]

L. M. Seitz and Theodore L. Brown[2]

Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received November 1, 1966*

Abstract: Proton and ^{7}Li spectra of ether solutions of phenyllithium with diphenylmagnesium and diphenylzinc have been examined over a large temperature range. Lithium-7 spectra show that the complex $Li_2M(C_6H_5)_4$ (M = Mg or Zn) is formed in solution when the Li:M ratio is ≥ 2, but no 3:1 complex is present, in contrast to the methyl systems. Furthermore, a 1:1 complex, $LiM(C_6H_5)_3$, appears to occur when Li:M < 2. Lithium and phenyl group exchange between phenyllithium and $Li_2M(C_6H_5)_4$ has been examined in the temperature range +34 to −58°. The lithium exchange parameters are very similar for Zn and Mg; the process is possibly rate-determined by formation of solvent-separated ion pairs. Phenyl group exchange is slower than lithium exchange; it appears to involve dissociation of the complex as a rate-determining step.

Wittig and co-workers have studied the reactions of phenyllithium with diphenylmagnesium or diphenylzinc[3] and have isolated complexes of 1:1 stoichiometry, $LiMg(C_6H_5)_3$ and $LiZn(C_6H_5)_3$. With zinc, they isolated an additional complex, $Li_3Zn_2(C_6H_5)_7$. They conclude further that the 1:1 complexes are dissociated in ether at room temperature and that the magnesium complex is dissociated to the greater extent.

On the other hand, studies of the corresponding methyl systems, methyllithium + dimethylmagnesium or dimethylzinc, indicate that the stoichiometry of the complexes is 2:1. Hurd succeeded in isolating a 2:1 complex, $Li_2Zn(CH_3)_4$, by adding methyllithium to di-

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[1] The research was supported by the National Science Foundation.

[2] Alfred P. Sloan Research Fellow.

[3] G. Wittig, F. J. Meyer, and G. Lang, *Ann.*, **57**, 167 (1951).

methylzinc in ether.[4] In an investigation of the methyl systems,[5] employing ^{7}Li and proton magnetic resonance techniques, two complexes were discerned, one of 2:1 stoichiometry and the other of 3:1. The 2:1 complex is the more readily formed in both the Mg and Zn systems.

Since the predominant methyl complexes have been shown to be 2:1, the stoichiometry of the phenyl complexes in solution becomes a matter of some interest.

We report here ^{7}Li and proton magnetic resonance spectra that reveal the stoichiometry of the mixed complexes in solution. Data relating to the rates and mechanisms of various exchange processes are also presented.

Experimental Section

All operations were performed in a glove box under argon atmosphere as described previously.[6] The concentrations of phenyllithium were determined by decomposing aliquot samples with water and titrating to a phenolphthalein end point with 0.1 *N* hydrochloric acid. Concentrations of diphenylmagnesium and diphenylzinc were determined by decomposing aliquot samples with water and titrating with standard EDTA solution (NH_4Cl–NH_4OH buffer, pH 10) using Erichrome black T as indicator.[7]

Diphenylmercury was obtained from Eastman Organic Chemicals, and sublimed magnesium metal from Dow Chemical Co. The zinc metal was Mallinckrodt analytical reagent grade (granular 20 mesh). Mallinckrodt analytical reagent grade anhydrous ether was dried over sodium wire and used without further purification.

Solutions of phenyllithium in ether were prepared by slowly adding small pieces of lithium, with stirring, to a suspension of diphenylmercury in ether. Excess lithium was used to ensure complete reaction; it was added until it remained afloat and bright. The lithium amalgam and excess lithium were removed by filtration to produce a clear, but very slightly yellow, phenyllithium solution. This method was used to eliminate contamination by lithium halides. Since phenyllithium reacts with ether, the preparation was completed as quick as possible, usually within 2 hr. The solution was used immediately. In order to complete the preparation rapidly, only 25 or 30 ml of 1 *M* solution was prepared at a time.[8]

Ether solutions of diphenylmagnesium and diphenylzinc were prepared in a similar manner. The respective metals were added in large excess to a suspension of diphenylmercury in ether. These reactions required from 12 to 24 hr for completion. Judging from the proton resonance spectra, no diphenylmercury remained in the solutions.

After the concentrations (usually about 1 *M* for phenyllithium, 0.5 *M* for diphenylmagnesium and diphenylzinc) of the separate solutions were determined, they were mixed in the appropriate volume proportions. The solutions were degassed, sealed under vacuum in standard size nmr tubes, and stored in Dry Ice.

Lithium-7 magnetic resonance spectra were obtained at 23.3 Mc as described previously.[6] Aqueous lithium bromide solution (7 g of commercial grade LiBr/10 ml of solution) was employed as an external standard for the room temperature ^{7}Li chemical shift measurements.

Results and Discussion

Stoichiometries of Complexes. The ^{7}Li chemical shift of halide-free phenyllithium in ether at room temperature is somewhat concentration dependent. It appears at -1.26 ppm in 0.95 *M* solution and at -1.19 ppm in 0.72 *M* solution, relative to the aqueous LiBr external standard. When diphenylmagnesium or diphenylzinc is added, the resonance shifts considerably upfield (Table I), thus indicating the presence of a mixed complex whose chemical shift is substantially upfield. The position of the resonance is sensitive to the Li:M ratio,[9] in accord with rapid intermolecular exchange. The data for the magnesium system show a sharp break in a graph of chemical shift *vs.* $(C_6H_5)_2Mg:C_6H_5Li$ ratio, at a ratio of 0.5, indicating formation of a 2:1 complex. The less complete data for the zinc system suggest similar behavior.

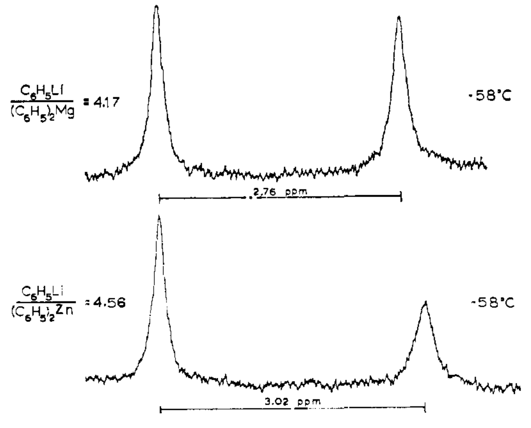

Figure 1. Low-temperature ^{7}Li spectra of LiC_6H_5–$Mg(C_6H_5)_2$ and LiC_6H_5–$Zn(C_6H_5)_2$ solutions.

Table I. Lithium-7 Chemical Shifts in C_6H_5Li–$Mg(C_6H_5)_2$ and C_6H_5Li–$Zn(C_6H_5)_2$ Solutions in Ether at Room Temperature

$(C_6H_5)_2Zn$: C_6H_5Li	^{7}Li shift, ppm	$(C_6H_5)_2Mg$: C_6H_5Li	^{7}Li shift, ppm
0	-1.19^a	0	-1.19^a
	-1.26^b		-1.26^b
0.48	+1.52	0.376	+0.738
0.50	+1.46	0.500	+1.29
0.87	+1.81	0.750	+1.38
		0.950	+1.45
		1.42	+1.53

^{a} At 0.72 *M*. ^{b} At 0.95 *M*.

When the temperature is lowered to $-58°$, the intermolecular exchange is slowed sufficiently so that all the resonances representing the various species in solution are seen. Some representative low-temperature ^{7}Li spectra are shown in Figure 1. The spectra provide conclusive evidence that the stoichiometry of the predominant mixed complex in solution is 2:1, *e.g.*, $Li_2Mg(C_6H_5)_4$ and $Li_2Zn(C_6H_5)_4$, when Li:M $\geq$ 2. As the ratio Li:M becomes greater than 2, a downfield resonance representing free phenyllithium is observed. Furthermore, the relative areas of the resonances when Li:M > 2 are consistent with the formation of a 2:1 complex.

In the corresponding methyl compounds,[5] the presence of a 3:1 complex is evident when Li:M > 2. In the light of strong indications that methyllithium is tetrameric in ether,[6] it was proposed that the 3:1 complex results from replacement of one lithium atom in the

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(4) D. T. Hurd, *J. Org. Chem.*, 13, 711 (1948).

(5) Part III: L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, 88, 4140 (1966).

(6) L. M. Seitz and T. L. Brown, *ibid.*, 88, 2174 (1966).

(7) F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid," D. Van Nostrand Co., Inc., Princeton, N. J., 1958.

(8) Low-temperature ^{7}Li spectra of phenyllithium solutions containing lithium ethoxide consist of two resonances. From the relative areas of the resonances when the ethoxide concentration is known, it has been established that the species containing ethoxide is of the form $[Li_2(C_6H_5)OC_2H_5]_n$.

(9) Li:M will be used to represent the mole ratios phenyllithium: diphenylmagnesium and phenyllithium:diphenylzinc. The reciprocal of this ratio is listed in Table I.

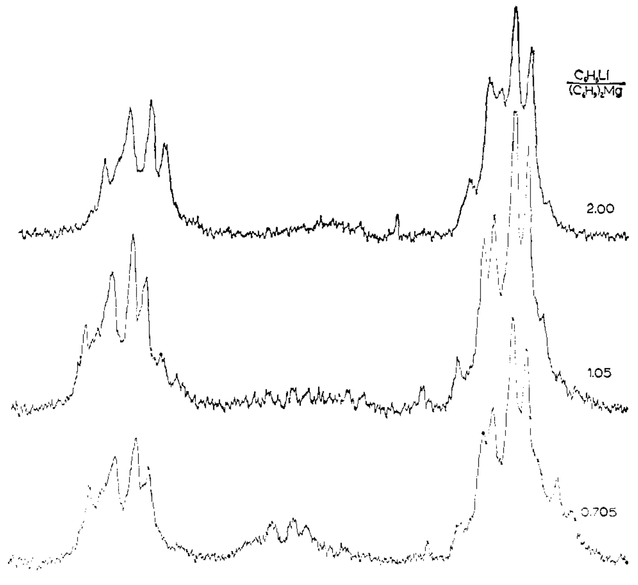

Figure 2. Proton spectra at −46° of C_6H_5Li–$Mg(C_6H_5)_2$ solutions when Li:Mg $\leq$ 2.

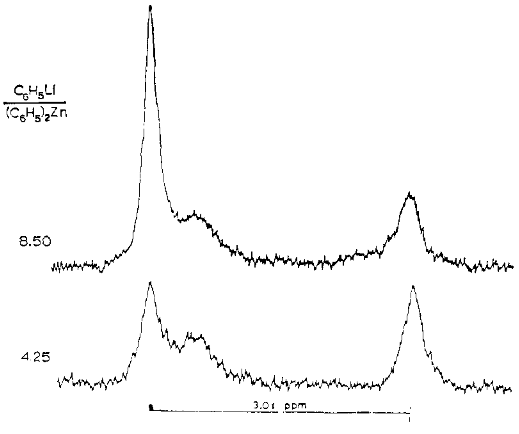

Figure 3. Lithium-7 spectra at −50° of LiC_6H_5–$Zn(C_6H_5)_2$ solutions containing lithium ethoxide.

tetramer with a magnesium or zinc atom. In solutions of the phenyl compounds, however, there is no evidence for a 3:1 complex. This is probably related to the association of phenyllithium in ether, which ebulliometric measurements suggest is dimeric.[3,10] In the absence of a tetrameric structure for the parent organolithium compound, the 3:1 complex is not expected.

The phenyl systems seem to differ from the corresponding methyl systems in another respect: there is no evidence for a 1:1 complex in the methyl systems, whereas in the phenyl systems the existence of such a complex seems probable. The data are not entirely conclusive, but the following observations point toward the existence of a 1:1 complex when Li:M < 2. (a) When M:Li is above 0.5, the room-temperature ^{7}Li chemical shift continues to shift upfield (Table I); the effect is most prominent in the zinc system. This phenomenon was not observed in the methyl–zinc system.[5] An analogous effect was observed in the methyl–magnesium system but was explained on the basis of dissociation of the 2:1 complex.[5] (b) In an attempt to prepare a sample with Li:Zn = 0.77, two layers appeared. (No phase separation was apparent in a sample of Li:Zn = 1.15.) The bottom layer, a clear viscous oil, contained lithium as shown by nmr; no ^{7}Li resonance was found for the upper layer. Also, in the proton spectra of the bottom layer, the chemical shift between the *ortho* and *meta–para* multiplets was intermediate between diphenylzinc and $Li_2Zn(C_6H_5)_4$ (*vide infra*). (c) A third, and probably the most conclusive, piece of evidence arises from a low-temperature proton spectrum of a Li:Mg = 0.705 sample (Figure 2). Resonances representing *ortho* protons of complex and free diphenylmagnesium are apparent. According to the Li:Mg ratio, the area ratio of complex:$(C_6H_5)_2Mg$ should be 3.6 if the sole complex is 1:1, 1.1 if it is 2:1; the measured ratio was 2.9.

The reasons for the apparently greater stability of a 1:1 complex in phenyl as compared with the methyl systems are not clear at present. The structure of the 1:1 complex is a matter of speculation.

When phenyllithium–diphenylzinc mixtures of Li:Zn > 2 are prepared using phenyllithium containing some lithium ethoxide (produced by allowing phenyllithium solution to stand overnight at room temperature), a third ^{7}Li resonance appears upfield from phenyllithium as shown in Figure 3. The ethoxide-containing species is of the form $[Li_2(C_6H_5)OC_2H_5]_n$.[8] Two observations support the conclusion that the phenyl group has a greater tendency than ethoxide to reside on the complex: (1) the species $[Li_2(C_6H_5)OC_2H_5]_n$ is observed, and (2) as the Li:Zn ratio is reduced, the resonance representing free phenyllithium decreases in intensity relative to the resonance representing $[Li_2(C_6H_5)OC_2H_5]_n$. The same phenomena are observed in the magnesium system.

Kinetics and Mechanisms of Exchange Reactions. At room temperature when Li:M > 2 only one ^{7}Li resonance is observed, indicating rapid lithium exchange between phenyllithium and the 2:1 complex, $Li_2Mg(C_6H_5)_4$ or $Li_2Zn(C_6H_5)_4$. As the temperature is lowered the ^{7}Li signal broadens and splits (−28°) into two resonances. At still lower temperatures, the two resonances continue to sharpen. The mean lifetime, τ, was obtained at each temperature by comparing the calculated line shape with the observed spectrum.[11] Data were obtained at temperatures both above and below the coalescence point. The T_2 values were estimated from the data for phenyllithium alone and for the Li:M = 2.0 solution at each temperature, but the chemical shift in the limit of no exchange, $\delta\omega$, was assumed constant. The plot of log $1/\tau$ *vs.* $1/T$(°K) is shown in Figure 4. The straight lines are least-square fits to the open circle and triangles for the magnesium and zinc systems, respectively. The solid circles and triangles represent data from samples of reduced concentration (factor of 2). It is apparent that the rate of lithium exchange is independent of total lithium concentration in the rather narrow concentration range accessible to the instrumental technique.

In contrast to the methyl systems, phenyl group exchange is decidedly slower than lithium exchange.

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(10) T. V. Talalaeva, A. N. Radinov, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **154**, 174 (1964).

(11) For a description of the computer program and the equation on which the line-shape calculations are based, see ref 12.

(12) Part II: K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4134 (1966).

Mechanistic details are contained in the ensuing discussion, which will deal with lithium exchange first.

Concentration independence (Figure 4) rules out the possibility of the exchange occurring *via* only the bimolecular process, *e.g.*

$$(C_6H_5\overset{*}{Li})_2 + Li_2M(C_6H_5)_4 \longrightarrow Li\overset{*}{Li}M(C_6H_5)_2 + Li\overset{*}{Li}(C_6H_5)_2$$

The mechanism therefore appears to involve a dissociative process as a rate-determining step. The data can be interpreted in terms of an equilibrium between contact and solvent-separated ion-pair forms of $Li_2M(C_6H_5)_4$

$$\underset{C}{Li_2M(C_6H_5)_4} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_s}{Li^+\|LiM(C_6H_5)_4^-} \qquad (1)$$

Solvent-separated ion pairs appear to be more reactive than contact ion pairs.[13] An assumption that formation of solvent-separated ion pairs is rate determining in exchange of methyl groups between $Al(CH_3)_3$ and $LiAl(CH_3)_4$ led to a consistent interpretation of the kinetic data.[12] Accordingly, we assume that phenyllithium exchanges more rapidly with the solvent-separated species

$$\underset{D}{(C_6H_5\overset{*}{Li})_2} + \underset{C_s}{Li^+\|LiM(C_6H_5)_4^-} \xrightarrow{k_2} \underset{C_s{*}}{\overset{*}{Li}{}^+\|LiM(C_6H_5)_4^-} + \underset{D{*}}{Li\overset{*}{Li}(C_6H_5)_2} \qquad (2)$$

Following the steady-state approximation for C_s, the applicable kinetic expressions are

$$\frac{d(C_s)}{dt} = k_1(C) - k_{-1}(C_s) - k_2(D)(C_s) = 0$$

$$(C_s) = \frac{k_1(C)}{k_{-1} + k_2(D)}$$

$$\frac{d(C_s)}{dt} = k_2(D)(C_s) = \frac{k_1k_2(D)(C)}{k_{-1} + k_2(D)}$$

$$\frac{1}{\tau_D} = \frac{1}{2}\frac{1}{(D)}\frac{d(C_s)}{dt} = \frac{1}{2}\left(\frac{k_1k_2(C)}{k_{-1} + k_2(D)}\right)$$

$$\frac{1}{\tau_C} = \frac{1}{2}\frac{k}{(C)}\frac{d(C_s)}{dt} = \frac{1}{2}\left(\frac{k_1k_2(D)}{(k_{-1} + k_2(D)}\right)$$

for $k_{-1} \ll k_2(D)$

$$\frac{1}{\tau_D} = \frac{1}{2}\left(\frac{k_1(C)}{(D)}\right) \qquad (3)$$

$$\frac{1}{\tau_C} = \frac{k_1}{2} \qquad (4)$$

$$\frac{1}{\tau} = \frac{1}{\tau_C} + \frac{1}{\tau_D} = \frac{k_1}{2}\left(\frac{(C)}{(D)} + 1\right) \qquad (5)$$

If the mechanism is correct, $1/\tau_C$ should be invariant with concentration while $1/\tau_D$ should be sensitive to the (C)/(D) ratio. To test this, two samples of the magnesium system with different (C)/(D) ratios were examined in the slow exchange region at −41°. The data (Table II) reveal that $1/\tau_D$ is indeed dependent on (C)/(D) while $1/\tau_C$ is rather insensitive. Furthermore the rate constants, k_1, calculated from expressions 3–5 agree reasonably well with one another.

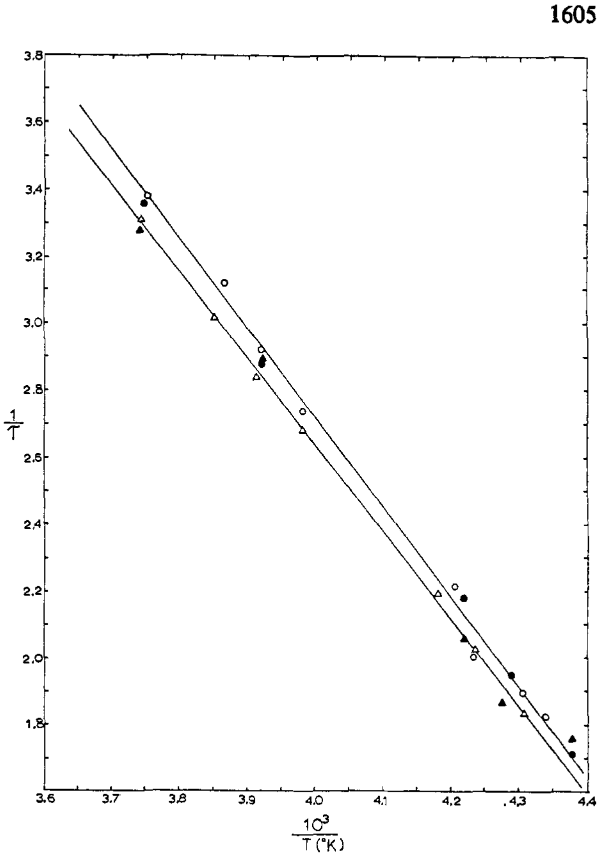

Figure 4. Log $1/\tau$ *vs.* $1/T$(°K) for ^7Li spectra: ○, $(C_6H_5Li)_2$ = 0.36 *M*, $(C_6H_5)_4MgLi_2$ = 0.30 *M*; △, $(C_6H_5Li)_2$ = 0.42 *M*, $(C_6H_5)_4ZnLi_2$ = 0.32 *M*. ● and ▲ represent solutions with concentrations one-half those of the corresponding solutions listed above.

Arrhenius activation energies from the slopes of the lines in Figure 4 are 12.3 and 11.8 kcal/mole for the magnesium and zinc systems, respectively, with an estimated uncertainty in each case of 1 kcal. These represent activation energies for the formation of solvent-separated ion pairs from contact ion pairs, as in eq 1. The rates for the two systems are nearly the same, although the zinc system appears to be slightly slower. As a comparison, the activation energy for the same process in $LiAl(CH_3)_4$, *i.e.*, $Li^+,Al(CH_3)_4^- \rightarrow Li^+\|Al(CH_3)_4^-$, was found to be 9.1 kcal/mole.[12]

Table II. Concentration Dependence of the Reciprocal Mean Exchange Time for ^7Li Exchange in the C_6H_5Li–$Li_2Mg(C_6H_5)_4$ System at −41°

			k_1, sec^{-1}		
(C)/(D)	$1/\tau_D$	$1/\tau_C$	From (3)	From (4)	From (5)
0.520	21.2	49.0	81.6	98.0	...
0.844	38.6	43.0	91.5	86.0	85.0

We now consider phenyl group exchange between phenyllithium and the 2:1 complexes. The temperature dependences of the proton spectra were examined from +34 to −27°. The spectra are too complex to provide a ready quantitative measure of the rate at each temperature, but qualitative changes in the spectra are revealing (Figure 5). The downfield multiplet represents the *ortho* protons of the aromatic ring; the position of the multiplet is dependent on the moiety to

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(13) J. Smid and T. E. Hagen-Esch, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).

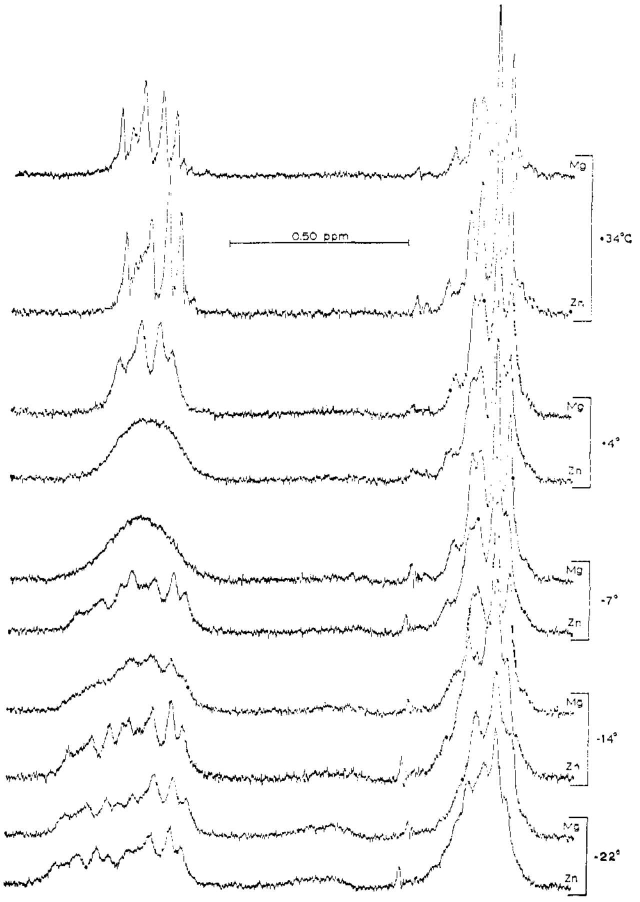

Figure 5. Temperature dependence of the proton spectra in the C_6H_5Li–$Li_2Mg(C_6H_5)_4$ and C_6H_5Li–$Li_2Zn(C_6H_5)_4$ systems.

which the phenyl group is attached.[14] The chemical shift of the upfield multiplet, *meta* and *para* protons, is less sensitive to the substituent. Thus attention is focused on the temperature dependence of the downfield multiplets (Table III). Since the multiplet separation in diphenylzinc is less than in diphenylmagnesium, about 0.38 and 0.65 ppm, respectively,[14] it is somewhat surprising that the separations in the complexes $Li_2Mg(C_6H_5)_4$ and $Li_2Zn(C_6H_5)_4$ are practically identical.

Table III. Temperature Dependence of the Chemical Shift Separation (ppm) between *ortho* and *meta-para* Proton Multiplets in Phenyllithium and the Complexes $Li_2M(C_6H_5)_4$ (M = Mg or Zn)

Temp, °C	$C_6H_5Li^a$	$Li_2Mg(C_6H_5)_4{}^a$	$Li_2Zn(C_6H_5)_4{}^a$
+34	0.984	0.915	0.895
+4	1.01	0.910	0.907
−7	1.04	0.907	0.903
−14	1.06	0.907	0.905
−22	1.10	0.903	0.907
−27	1.10	0.914	0.918
−36	1.11	0.914	. . .
−46	. . .	0.912	0.914
−56	. . .	0.910	0.910
−64	1.17	. . .	. . .
−66	. . .	0.914	0.914

[a] Measured from the most intense reasonance in each multiplet.

From the qualitative temperature dependence of the proton spectra such as those in Figure 5, the following conclusions can be drawn concerning *phenyl group* exchange between phenyllithium and the 2:1 complexes. (1) Phenyl group exchange is slower than lithium exchange. The separate *ortho*-proton resonances for phenyllithium and the complexes are apparent at −14°, although the separation between multiplets is only 9 cps. In comparison, the lithium resonances ($\delta\omega$ = 65 to 70 cps) coalesce at about −28°. (2) Phenyl group exchange is slower in the zinc system than the magnesium system. Notice in Figure 5 that the coalescence points are approximately +4 and −7° in the zinc and magnesium systems, respectively. (3) Phenyl group exchange is independent of the absolute concentrations of the species. A change in concentrations of the species by a factor of 2 caused no observable change in the spectra at each temperature. These observations suggest a mechanism which involves dissociation of the complex in a rate-determining step, possibly of the form

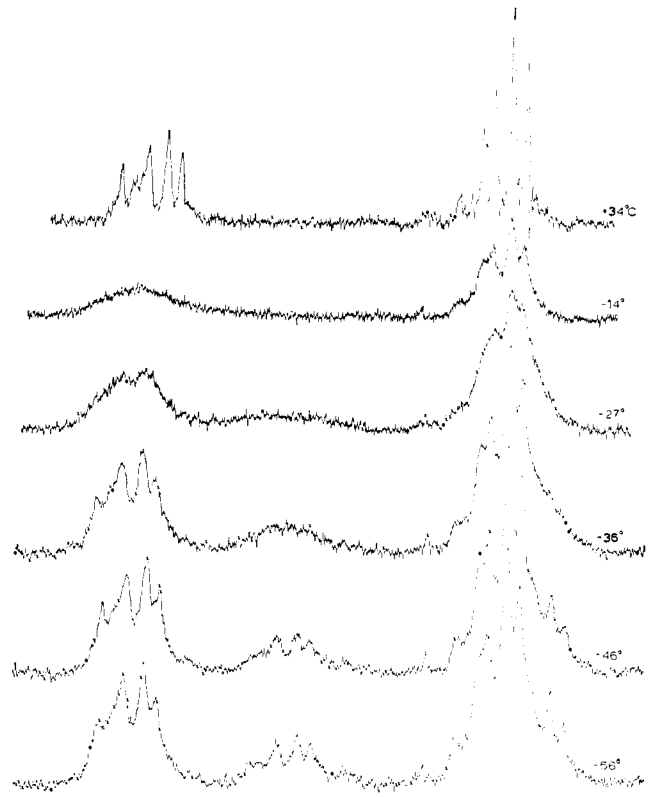

Figure 6. Temperature dependence of the proton spectra in the C_6H_5Li–$Mg(C_6H_5)_2$ system, Li:Mg = 0.705.

$$Li_2M(C_6H_5)_4 \rightleftharpoons (C_6H_5)_2M + (LiC_6H_5)_2 \qquad (6)$$

$$(\overset{*}{Li}C_6H_5)_2 + (LiC_6H_5)_2 \longrightarrow (LiLi(C_6H_5)_2) + (Li\overset{*}{Li}(C_6H_5)_2) \qquad (7)$$

The fact that phenyl group exchange is slower in the zinc system is consistent with the expectation that the zinc complex is more stable than the magnesium complex. Of course, lithium is also exchanged in this process, which must occur concurrently with the faster ion-pair process expressed by eq 1 and 2.

In light of the lithium and phenyl group kinetic behavior, it appears that the 2:1 phenyl complexes are similar in some respects to group III complexes, *e.g.*, $LiAl(CH_3)_4$ or $LiAlH_4$. It is interesting that the ^7Li chemical shifts of $Li_2M(C_6H_5)_4$ (Table I) and group III

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(14) J. A. Ladd, *Spectrochim. Acta*, 22, 1157 (1966).

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

The only kinetic evidence relating to the systems that arise when $Li:M < 2$ derives from the downfield (*ortho*-proton) multiplet in the proton spectra. In the samples $Li:Zn = 1.15$ and $Li:Mg = 1.05$, only one *ortho*-proton multiplet was evident at all the temperatures investigated, from +34 to −66°. However, in a sample of $Li:Mg = 0.705$, two *ortho*-proton multiplets did appear; the one furthest downfield presumably represents a 1:1 complex while the other represents free diphenylmagnesium. The temperature dependence of the spectrum is shown in Figure 6. It appears that phenyl group exchange between diphenylmagnesium and the 1:1 complex, whatever its nature, is slower than methyl group exchange between dimethylmagnesium and the 2:1 complex, $Li_2Mg(CH_3)_4$.[5]

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

Organometallic Exchange Reactions. VII. Distribution of Phenyl and Alkyl Groups on Lithium and Lithium–Magnesium Species in Ether[1]

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Abstract: Low-temperature lithium-7 and proton nuclear magnetic resonance spectra have been employed to observe equilibria in ether solutions of the following systems: methyllithium–phenyllithium, methyllithium–diphenylmagnesium, and phenyllithium–dimethylmagnesium. In the first, mixed species $[Li_2(CH_3)(C_6H_5)]_n$ and $Li_4(CH_3)_3(C_6H_5)$ are observed. In the lithium–magnesium systems, mixed 2:1 complexes, $Li_2Mg(CH_3)_{4-n}(C_6H_5)_n$, are observed. Phenyl exhibits a strong tendency to reside on the complex in preference to the more highly bridge-bonded $Li_4(CH_3)_3(C_6H_5)$. The systems observed here may serve as prototypes for benzylic or allylic lithium species in equilibria with excess saturated alkyllithium, as in initiation of anionic polymerizations.

Results reported in this series of papers have served to demonstrate a striking difference between methyl and phenyl groups in lithium and group II organometallic compounds.[2,3] Most of the differences observed can be accounted for by the statement that methyl is a stronger bridge-bonding group than phenyl. Nuclear magnetic resonance spectra of ether solutions containing methyllithium are most readily interpreted in terms of a methyllithium tetramer in solution.[2,4] Phenyllithium, on the other hand, is dimeric in ether solution.[5] In the tetramer the organic group is directly bonded to three metal atoms, in the dimer to two. In the mixed systems only the 2:1 phenyl complex, $Li_2M(C_6H_5)_4$ (M = Mg or Zn), is observed, whereas in the methyl series a 3:1 complex is also formed.[2] The latter is presumably a tetramer with four bridging methyl groups and one terminal $M-CH_3$ group. Also, in hydrocarbon solvents triphenylaluminum is apparently less strongly bonded in the dimer than trimethylaluminum.[6] The weaker bridge-bonding tendency of phenyl is understandable, since the phenyl group is more electron-withdrawing than a saturated alkyl group and has a larger steric requirement than methyl.

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

Experimental Section

The instrumental methods and details of sample preparation have been discussed in previous papers.[2,3]

Results and Discussion

Ethyllithium–Phenyllithium. Ethyllithium–phenyllithium mixtures were examined to take advantage of the ^{7}Li chemical shift difference for the two substances in ether (−0.70 and −1.25 ppm, for C_2H_5Li and C_6H_5Li, respectively). With this chemical shift difference (13 cps), it is feasible to look for the ^{7}Li resonances of mixed species. The ^{7}Li spectra of three typical mixtures at −80° are shown in Figure 1. By examining a number of spectra spanning a wide range of phenyl:ethyl ratios, it was possible to ascertain that there are but four distinguishable resonances. The end members of the set of four are separated by 13 cps and can be assigned with confidence to phenyllithium and ethyllithium. In the sample with a 2.44 phenyl:ethyl ratio,

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(3) Part VI: L. M. Seitz and T. L. Brown, *ibid.*, **89**, 1602 (1967).

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