

The Chemistry of Carbanions. XIII. The Nuclear Magnetic Resonance Spectra of Various Methylmagnesium Derivatives and Related Substances

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The Chemistry of Carbanions. XIII. The Nuclear Magnetic Resonance Spectra of Various Methylmagnesium Derivatives and Related Substances^{1a,b}

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The nmr spectra of solutions of dimethylmagnesium and methylmagnesium bromide have been studied in the presence of added magnesium alkoxides, methyl lithium, magnesium bromide, and manganese(II) salts. Of particular interest were the nmr spectra of the unsymmetrical magnesium reagents, methylecyclopentadienylmagnesium (4), phenylecyclopentadienylmagnesium (7), methylphenylmagnesium (2), and 3,3-dimethylbutylcyclopentadienylmagnesium (10). From studies of these spectra at several temperatures, it was possible to determine the rates of exchange of alkyl groups from one magnesium atom to another and to study the effect of various additives on the rate of this exchange. These exchanges are retarded by the good solvating agents 1,2-dimethoxyethane and, especially, N,N,N',N'-tetramethylethylenediamine and are catalyzed by magnesium bromide. The exchange of methyl groups between dimethylmagnesium and methylecyclopentadienylmagnesium (2) appears to be a bimolecular reaction which is first order in each reagent. A study of the exchange of alkyl groups between the mixed reagent 3,3-dimethylbutylcyclopentadienylmagnesium (10) and bis(3,3-dimethylbutyl)magnesium (9) indicates that the rate of exchange is substantially faster than the rate of configurational inversion at the CH₃-Mg bond. Consequently, the exchange reaction occurs primarily with retention of configuration.

In an effort to learn more about the structures of the organometallic reactants involved in the addition reactions of organomagnesium compounds,^{2,3} we have studied the nmr spectra of solutions containing various methylmagnesium derivatives and related compounds.⁴

Mixtures of Magnesium and Lithium Reagents.—Our initial measurements of ethereal solutions of

methyl lithium (containing lithium bromide), methylmagnesium bromide, dimethylmagnesium, and dimethylmercury are presented in Table I. In agreement with earlier observations for alkylmagnesium bromides and the corresponding dialkylmagnesiums,^{2b,4a-c,n} the spectra of methylmagnesium bromide and of dimethylmagnesium are very similar both in position of chemical shift and in ¹³C-H coupling constants. The position of the methyl signal for dimethylmagnesium was dependent on concentration^{4a,b} and moved to higher field as the concentration was lowered, suggesting that the extent of solvation or the degree of association of dimethylmagnesium varied with concentration. From a study of its crystal structure,⁵ solvent-free dimethylmagnesium is known to exist in polymeric chains with four methyl groups arranged in a tetrahedral fashion around each magnesium atom. We have determined the apparent degree of association of a 0.13 M solution of dimethylmagnesium in ether solution by isothermal distillation and find it to be approximately monomeric (apparent mol wt 1.20–1.28 × monomer) at this concentration level. This observation is in agreement with the results previously obtained for dilute ethereal solutions of diethylmagnesium and diphenylmagnesium.⁶

We examined the nmr methyl signals of ether solutions containing the various mixtures of magnesium

(1) (a) This research has been supported by research grants from the National Institutes of Health (Grant No. GM-08761) and the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Grant No. AF-AFOSR-573), and the U. S. Army Research Office (Durham); (b) calculations were carried out in part at the M.I.T. Computation Center, Cambridge, Mass.; (c) Halcon International Predoctoral Fellow, 1963–1964.

(2) References to our earlier studies in this area include (a) H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963); (b) H. O. House and D. D. Traficante, *ibid.*, **28**, 355 (1963); (c) H. O. House and H. W. Thompson, *ibid.*, **28**, 360 (1963); (d) H. O. House and W. L. Respass, *ibid.*, **30**, 301 (1965); (e) H. O. House, W. L. Respass, and G. M. Whitesides, *ibid.*, **31**, 3128 (1966).

(3) For reviews dealing with the structure of organomagnesium compounds, see (a) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954; (b) R. M. Salinger in "Survey of Progress in Chemistry," Vol. 1, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1963, pp 301–324; (c) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966).

(4) Previous studies of the nmr spectra of organomagnesium compounds include (a) D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 5125 (1962); (b) H. Roos and W. Zeil, *Ber. Bunsenges. Physik. Chem.*, **67**, 28 (1963); (c) G. Fraenkel, D. G. Adams, and J. Williams, *Tetrahedron Letters*, No. 12, 767 (1963); (d) G. M. Whitesides, F. Kaplan, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2167 (1963); (e) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *ibid.*, **87**, 2854 (1965); (f) G. M. Whitesides and J. D. Roberts, *ibid.*, **87**, 4878 (1965); (g) M. Witanowski and J. D. Roberts, *ibid.*, **88**, 737 (1966); (h) G. Fraenkel, D. T. Dix, and D. G. Adams, *Tetrahedron Letters*, No. 43, 3155 (1964); (i) G. Fraenkel and D. T. Dix, *J. Am. Chem. Soc.*, **88**, 979 (1966); (j) D. F. Evans and M. S. Khan, *Chem. Commun.*, No. 3, 67 (1966); (k) E. A. Hill, *J. Org. Chem.*, **31**, 20 (1966); (l) N. G. Kreighoff and D. O. Cowan, *J. Am. Chem. Soc.*, **88**, 1322 (1966); (m) F. R. Jensen and K. L. Nakamaye, *ibid.*, **88**, 3437 (1966); (n) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965), a general review.

(5) E. Weiss, *J. Organometal. Chem.*, **2**, 314 (1964).

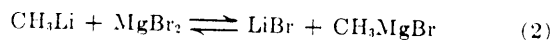
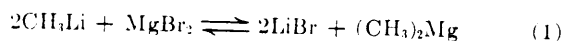
(6) (a) A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963). (b) A. D. Vreugdenhil and C. Blomberg, *ibid.*, **82**, 461 (1963); **83**, 1096 (1964); **84**, 39 (1965). (c) M. B. Smith and W. E. Becker, *Tetrahedron*, **22**, 3027 (1966).

TABLE I
THE NMR SPECTRA OF METHYL ORGANOMETALLIC
REAGENTS IN ETHER SOLUTION

Reagent	Concn., moles/l.	Temp., °C	Chemical shift upfield from internal TMS, ^a cps	J_{13C-H} , cps
CH ₃ MgBr	2.40	~30	92.5	107
CH ₃ MgBr	0.70	~30	92.5	...
CH ₃ MgBr	0.20	~30	92.3	...
CH ₃ MgI	1.08	~30	92	...
(CH ₃) ₂ Mg	0.71	~30	83	105.5
(CH ₃) ₂ Mg	0.18	~30	85	...
(CH ₃) ₂ Mg	0.090	~30	87	...
(CH ₃) ₂ Mg	0.028	~30	90	...
(CH ₃) ₂ Mg	0.84	33	84	...
(CH ₃) ₂ Mg	0.84	-29	87	...
(CH ₃) ₂ Mg	0.84	-54 ^b	88 ^c	...
CH ₃ Li ^e	1.90	~30	111	97
CH ₃ Li ^e	0.40	~30	110.5	...
CH ₃ Li ^e	0.20	32	110.5	...
CH ₃ Li ^e	0.20	-48	112.5 ^d	...
CH ₃ Li ^e	0.20	-65.5	114.5 ^e	...
CH ₃ Li ^e	0.20	-70.5	114 ^f	...
(CH ₃) ₂ Hg	<i>g</i>	~30	-16	<i>h</i>

^a Unless otherwise noted, the band width at half-height for each methyl peak is approximately 1 cps or less. ^b At -54°, some of the reagent had separated from solution as white needles. The band width of the methyl signal at half-height was 2.2 cps, probably because of the presence of this suspended crystalline material in the sample. ^c The ethereal solutions of methylolithium contained an equimolar quantity of lithium bromide. ^d The band width at half-height was 2.2 cps. ^e The band width at half-height was 6.0 cps. ^f The band width at half-height was 8.0 cps. ^g This spectrum was determined as a solution in carbon tetrachloride. ^h The value J_{13C-H} was 102 cps.

and lithium compounds summarized in Table II.⁷ The chemical shift and $^{13}C-H$ coupling constant values observed for the various mixtures containing magnesium bromide suggest the presence of equilibria 1 and 2, both of which lie relatively far to the right.⁸ We plan to examine addition reactions of the solution produced by mixing 1 mole equiv of magnesium bromide with 2 mole equiv of methylolithium (eq 1). If the di-



methylmagnesium reagent produced in this way is comparable in reactivity to the reagent obtained from dimethylmercury,² this procedure would offer a simple preparative route to dimethylmagnesium for synthetic purposes. Crude estimates of the reactivities of these

(7) (a) For a recent review of the exchange of alkyl groups between metal atoms, see J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965). (b) In a study published after completion of our work, L. M. Seitz and T. L. Brown [*J. Am. Chem. Soc.*, **88**, 4140 (1966)] were able to demonstrate the formation of 2:1 and 3:1 complexes of halide-free methylolithium and dimethylmagnesium which exchanged with excess methylolithium sufficiently slowly to allow separation of nmr methyl signals at low temperatures. In agreement with this study, our 2:1 mixture exhibited only a single methyl signal (for the 2:1 complex) at low temperatures, but this observation does not mean that exchange was rapid. We are grateful to Professor Brown for informing us of these results prior to publication.

(8) For simplicity, methylolithium will be represented as a monomer through this paper. However, current evidence indicates that halide-free methylolithium is a tetramer in ether solution. See (a) E. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, **2**, 197 (1964); (b) T. L. Brown, *ibid.*, **5**, 191 (1966); (c) L. M. Seitz and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 2174 (1966); (d) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1965). (e) H. Gilman and J. Swiss [*J. Am. Chem. Soc.*, **62**, 1847 (1940)] have presented evidence indicating that the reactivity of *n*-butyllithium is diminished by the addition of Grignard reagents or magnesium halides.

TABLE II
THE NMR METHYL SIGNALS FOR MIXTURES OF ORGANOMETALLIC
COMPOUNDS IN ETHER SOLUTION^a

Reagents (concn, moles l.) ^b	Temp., °C	Chemical shift upfield from internal TMS, ^a cps	J_{13C-H} , cps
(CH ₃) ₂ Mg (0.26) + LiBr (0.51)	~30	84.5	...
(CH ₃) ₂ Mg (0.53) + CH ₃ Li (0.36)	~30	88	103.5
(CH ₃) ₂ Mg (0.36) + CH ₃ Li (0.71)	~30	95	101.5
(CH ₃) ₂ Mg (0.18) + CH ₃ Li (1.06)	~30	102	99
(CH ₃) ₂ Mg (0.18) + CH ₃ Li (0.37)	33	96.5	...
(CH ₃) ₂ Mg (0.18) + CH ₃ Li (0.37)	-62.5	105 ^c	...
(CH ₃) ₂ Mg (0.18) + CH ₃ Li (0.37)	-89	106.5 ^d	...
CH ₃ MgBr (0.56) + CH ₃ Li (0.14)	~30	89.5	...
CH ₃ MgBr (0.35) + CH ₃ Li (0.35)	~30	85	...
CH ₃ MgBr (0.14) + CH ₃ Li (0.56)	~30	95.5	...
MgBr ₂ (1.42) + CH ₃ Li (0.95)	~30	93	108
MgBr ₂ (1.13) + CH ₃ Li (1.14)	~30	91.5	108
MgBr ₂ (0.71) + CH ₃ Li (1.42)	~30	83	105
MgBr ₂ (0.40) + CH ₃ Li (1.63)	~30	96	101
MgBr ₂ (0.07) + CH ₃ Li (0.70)	~30	105	...
(CH ₃) ₂ Mg ^e + (CH ₃) ₂ Hg ^e	~30	-15, 84	...

^a Unless otherwise noted, the band width at half-height for each methyl peak is approximately 1 cps or less. ^b In all cases the methylolithium employed contained an equimolar quantity of lithium bromide. ^c The peak width at half-height was 2.0 cps. ^d The peak width at half-height was 2.8 cps. ^e Approximately equimolar amounts of these two reagents in ether solution were measured. The concentrations of the reagents were not determined.

mixtures of magnesium and lithium compounds were obtained in two ways.⁸ Although ethereal solutions of methylolithium reacted immediately with fluorene to yield a yellow solution with nmr absorption characteristic of fluorenyllithium, an ethereal solution of dimethylmagnesium and fluorene remained colorless for at least 12 hr. The fact that no fluorenyllithium was formed upon addition of fluorene to an ether solution prepared from 2 mole equiv of methylolithium and 1 mole equiv of magnesium bromide therefore indicates that the concentration of free methylolithium must be low and, presumably, that the equilibrium represented by eq 1 lies far to the right.

Although the reaction of ethylene dibromide with an ethereal solution of methylolithium to form ethylene and methylbromide is rapid,⁹ the corresponding reaction with ethereal dimethylmagnesium is relatively slow. As illustrated in Table III, the rate of re-

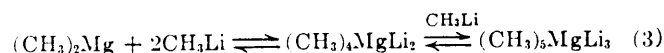
TABLE III
REACTION OF METHYL ORGANOMETALLIC REAGENTS WITH
ETHYLENE DIBROMIDE IN ETHER SOLUTION

Reagent (concn, moles l.)	Additive (concn, moles l.)	Time, min	Temp, °C	Reagent consumed, %
(CH ₃) ₂ Mg (0.24)	...	10	25	4-7
(CH ₃) ₂ Mg (0.055)	...	15	35	34
(CH ₃) ₂ Mg (0.051)	LiBr (0.057)	1	0	6
(CH ₃) ₂ Mg (0.051)	LiBr (0.057)	15	25	68
(CH ₃) ₂ Mg (0.051)	LiBr (0.057)	10	35	77
(CH ₃) ₂ Mg (0.065)	LiCl (0.13)	15	25	64
CH ₃ Li (0.95)	MgBr ₂ (0.47)	15	25	88-93
CH ₃ Li (0.63)	LiBr (0.63)	10	25	100

(9) (a) H. Gilman and R. G. Jones, *Org. Reactions*, **6**, 339 (1951); (b) R. D'Hollander and M. Anteunis, *Bull. Soc. Chim. Belges*, **72**, 77 (1963); (c) H. Gilman and F. K. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1964); (d) H. O. House and W. L. Respess, *ibid.*, **4**, 95 (1965).

action of dimethylmagnesium with ethylene dibromide is accelerated by the addition of lithium bromide or lithium chloride. One possible interpretation of this increased reactivity is to suppose that a very low concentration of methyllithium is formed by the equilibrium illustrated in eq 1.¹⁰

The equilibration of methyl groups in mixtures of dimethylmagnesium and methyllithium is believed to proceed *via* the formation of a series of complexes as illustrated in eq 3.^{7b} This type of complex formation



with organolithium compounds has been suggested (although in simpler form) for a number of metal derivatives^{2a,11} and appears to be applicable to the subsequently discussed reaction of methylmagnesium bromide with manganese compounds.

Effect of Manganese on the Methyl Signal of Methylmagnesium Reagents.—In our initial preparations of methylmagnesium bromide from ethereal methyl bromide and ordinary Grignard-grade magnesium turnings, the nmr spectra of the solutions were found sometimes to exhibit a sharp methyl peak and at other times to exhibit a broad methyl peak which became still broader as the solutions were allowed to stand. The centers of the broad and the sharp peaks were located at approximately the same position; the broad peak became sharp when it was observed at -54° and broadened when this solution was allowed to warm to room temperature. The variable results were traced to the fact that the solutions which gave broad peaks always contained methyl bromide. If such solutions were treated with additional magnesium metal to consume the excess methyl bromide, the broad peak sharpened. Exactly the same type of behavior was observed with the Grignard reagent prepared from methyl iodide. At this time we found that this phenomenon of peak broadening in the presence of excess methyl halide was not observed when specially purified (triply sublimed) magnesium¹² was used to prepare the Grignard reagent.¹³ This fact led us to the conclusion that the line-broadening phenomenon was associated with some trace impurity in ordinary Grignard-grade magnesium. Previous analyses¹⁴ of commercial magnesium samples suggested that the most likely impurities to cause the effect observed were iron, copper, or manganese. Although the addition of low concentrations of anhydrous iron(III) chloride or anhydrous copper(I) iodide^{2a} to ethereal solutions of methyl bromide and methylmagnesium bromide (prepared from triply

sublimed magnesium) did not lead to line broadening, the addition of small concentrations of manganese(II) iodide gave solutions with broad nmr methyl signals which behaved in just the same way (Table IV) as

TABLE IV
THE EFFECT OF LOW CONCENTRATIONS OF MANGANESE ON THE NMR SIGNALS FROM ETHER SOLUTIONS OF METHYLMAGNESIUM HALIDES

Reagent (concn, moles/l.)	Additive (concn, moles/l.)	Temp, $^\circ\text{C}$	Chemical shift upfield from internal TMS, cps	Band width at half-height, cps
CH_3MgBr^a (1.01)	CH_3Br (0.30)	~ 30 -54	90 98	34–40 ^b 2 ^c
CH_3MgBr^a (1.04)	CH_3Br (0.33)	~ 30	92	6–41 ^d
CH_3MgBr^a (1.04)	CH_3Br (0.33) + excess $\text{Mg}^{12,e}$	~ 30	90	2
CH_3MgI^a (0.92)	CH_3I (0.18)	~ 30	92	15 ^f
CH_3MgI^a (0.92)	CH_3I (0.18) + excess $\text{Mg}^{12,e}$	~ 30	91	1.5
CH_3MgBr^g (1.42)	CH_3Br (0.5)	~ 30	97	1.5
CH_3MgBr^g (1.42)	CH_3Br (0.5) + $\text{Mg}^{12,h}$	~ 30	97	9
CH_3MgBr^g (0.99)	MnI_2 (8.8×10^{-3})	~ 30	90	4–24 ⁱ

^a This reagent was prepared from ordinary Grignard-grade magnesium which contains small amounts of manganese. ^b The peak gradually broadened over a period of 23–600 hr. ^c When the cold solution was warmed to $\sim 30^\circ$, the methyl signal was located at 91 cps with a half-band width of 35 cps. ^d The peak gradually broadened over a period of 1–137 hr. ^e This solution was obtained from the one listed above it in the table by adding excess magnesium and stirring the mixture overnight. ^f The figure is the half-band width after the solution had been stirred for 10 hr. ^g This reagent was prepared from triply sublimed magnesium. ^h This solution was obtained from the one listed above it in the table by adding ordinary Grignard-grade magnesium and stirring the mixture for 5 hr. ⁱ The peak gradually broadened over a period of 5–32 hr.

the reagent prepared from ordinary magnesium. We therefore attribute the aforementioned line broadening in the presence of excess methyl halide to the presence of small amounts of manganese in ordinary Grignard-grade magnesium.

Although the reason for the above line broadening in the presence of manganese has not been established, the following possibility is consistent with presently available information. During the initial preparation of the Grignard reagent, the manganese (and other impurities in ordinary magnesium) remains among the colloidal and fine suspended particles which contribute the dark color to Grignard reagents prepared from ordinary Grignard-grade magnesium. If excess methyl bromide is present, the manganese is slowly converted to a methylmanganese derivative (written as dimethylmanganese in eq 4); the same material could arise by reaction of methylmagnesium bromide with manganese iodide (eq 5).¹⁵ Further equilibra-

(10) R. E. Dessy [AD611152, *U. S. Govt. Res. Rept.*, **40**, 35 (1965); *Chem. Abstr.*, **63**, 6809 (1965)] has reported that the rate of addition of butylmagnesium bromide to benzonitrile is accelerated by the presence of lithium perchlorate or tetrabutylammonium perchlorate. This effect is interpreted as a medium effect caused by an inert salt. Although our results with the ethylene dibromide reaction could be interpreted in the same way, we were unable to obtain a sufficiently concentrated solution of tetrabutylammonium perchlorate in ether to examine its effect.

(11) (a) G. Wittig, F. J. Meyer, and G. Lange, *Ann. Chem.*, **571**, 167 (1951); (b) W. Tochtermann, *Angew. Chem., Intern. Ed. Engl.*, **5**, 351 (1966); (c) R. Waack and M. A. Doran, *J. Am. Chem. Soc.*, **85**, 2861, 4042 (1963); (d) G. Wittig, *Quart. Rev. (London)*, **20**, 191 (1966).

(12) We are indebted to Dr. Francis Johnson of the Dow Chemical Co. for a generous sample of this purified magnesium.

(13) This possibility was suggested to us by Professor F. R. Jensen of the University of California at Berkeley.

(14) (a) R. E. Dessy, S. E. I. Green, and R. M. Salinger, *Tetrahedron Letters*, No. 21, 1369 (1964); (b) D. O. Cowan, J. Hsu, and J. D. Roberts, *J. Org. Chem.*, **29**, 3688 (1964).

(15) Reactions corresponding to eq 5 and 6 are known when methyllithium is treated with manganese(II) iodide. See (a) C. Beermann and K. Clauss, *Angew. Chem.*, **71**, 627 (1959); (b) R. Riemschneider, G. H. Kassahn, and W. Schneider, *Z. Naturforsch.*, **B15**, 547 (1960). Although these authors were not able to obtain stable products from manganese(II) iodide and the methyl Grignard reagent, it seems likely that low concentrations of complex ions (i.e., eq 6) are formed with Grignard reagents in the same way that methylcopper(I) evidently forms small amounts of soluble complexes with methylmagnesium bromide.¹⁶

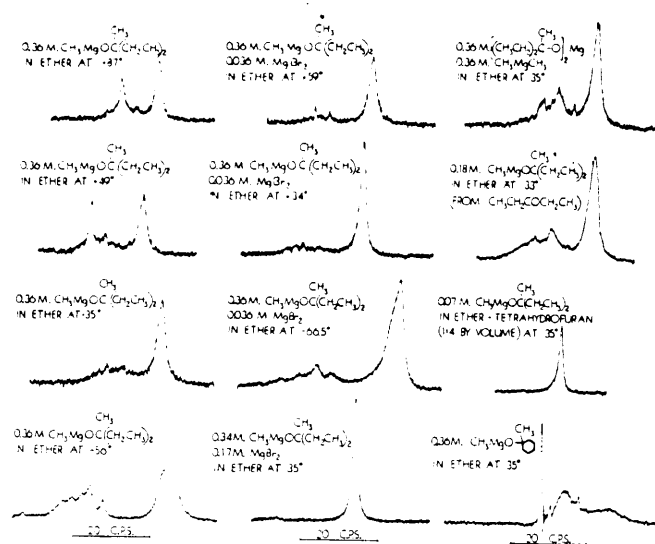
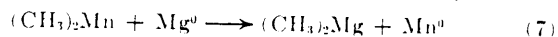
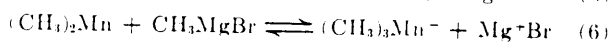
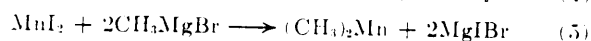
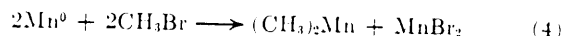


Figure 1.—Nmr spectra of the CH_3Mg^+ region of methylmagnesium alkoxide solutions. Unless otherwise indicated, the solutions of $\text{CH}_3\text{MgOC}(\text{CH}_2\text{CH}_3)_2\text{CH}_3$ were prepared from 3-methyl-3-pentanol.



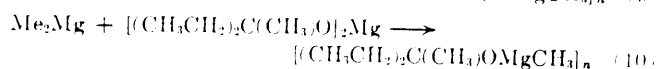
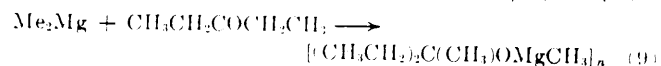
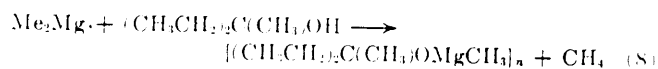
tion to form a complex manganese anion (eq 6) would then serve to equilibrate the methyl groups between magnesium(II) and manganese(II) species. As a result, each methyl group is bonded for a portion of the time to a paramagnetic manganese(II) species with the result that the average methyl signal is broadened. Apparently, at low temperatures the exchange of methyl groups (eq 6) is sufficiently slow that the sharp methyl signal attributable to methylmagnesium bromide remains.¹⁶ When these solutions with broad methyl signals are treated with excess magnesium metal, the manganese(II) species is presumably reduced to metallic manganese¹⁷ (eq 7) with the result that the normal sharp signal for methylmagnesium bromide remains. It might be noted that this line-broadening phenomenon is the only place in this study where we noted any differences in the nmr spectra which were dependent on whether the organomagnesium compound was obtained from ordinary Grignard-grade magnesium or triply sublimed magnesium. Furthermore, this line broadening was found only in instances where a limiting amount of magnesium was treated with excess methyl halide. Thus, in the normal preparative procedures where an excess of magnesium metal is employed, we have no reason to believe that the use of ordinary Grignard-grade magnesium would be objectionable.

Effect of Alkoxides on the Methyl Signal of Methylmagnesium Reagents.—In earlier studies (see ref 2b,

(16) Although we did not observe any signal for the methylmanganese(II) species at low temperature, this would be expected because of the low concentration of manganese species present, because their signals would be very broad, and because the apparent chemical shifts of such species would probably be large.

(17) Although we have no data for ether solutions, in aqueous media the oxidation potentials for magnesium and manganese [to manganese(II)] are 2.37 and 1.18 v, respectively: W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., 1952, p 528.



2d, and references therein), we had noted that the addition of 1 mole equiv of a ketone or a tertiary alcohol to 1 mole equiv of a dialkylmagnesium compound in ether solution yielded a solution corresponding in stoichiometry to an alkylmagnesium alkoxide with chemical properties very different from the properties of an ether solution of the dialkylmagnesium. In particular, the reactivity of these solutions with ketones was diminished from the high level of reactivity associated with the dialkylmagnesium to an order of reactivity comparable to the corresponding alkylmagnesium bromide. Also, these reagents exhibited a strong tendency to convert ketones to their enolate anions rather than to add to the carbonyl function. In one case, the reduction of the carbonyl function rather than addition was enhanced. Also, the stereochemical requirements of these alkylmagnesium alkoxide reagents in addition reactions to carbonyl functions were different from the requirements exhibited by the dialkylmagnesium or alkylmagnesium bromide reagents. All of the foregoing differences were removed when these alkylmagnesium alkoxide reagents were treated with an equimolar quantity of magnesium bromide; the resulting solutions were comparable with solutions of the alkylmagnesium bromide. In view of these results, we were prompted to study the nmr spectra of the methylmagnesium alkoxide reagents obtained by treatment of ethereal solution of dimethylmagnesium with equimolar amounts of 3-methyl-3-pentanol, 3-pentanone, or magnesium di-3-methyl-3-pentoxide to obtain the reagent used in earlier studies^{2b,d,18} (eq 8, 9, and 10).



As summarized in Table V and Figure 1, the spectra of these solutions were essentially the same irrespective of the mode of formation. The spectra exhibited two general areas of absorption attributable to methyl groups bound to magnesium. The lower field broad absorption (ca. 70 cps upfield from TMS) exhibits more fine structure when cooled (-56°) and sharpens when heated (87°). As the sample is heated, the two regions of absorption sharpen and begin to move together. Since the two peaks observed at 87° did not exhibit any evidence of exchange broadening, it is not apparent whether or not these two peaks would coalesce at sufficiently high temperatures. We were unsuccessful in obtaining satisfactory spectra of these ether solutions at higher temperatures. The relative areas under the two regions of absorption were altered slightly when the solutions were diluted with ether and dilution with the better solvating solvent, tetrahydrofuran, caused these two regions of absorption to collapse to a single peak. The addition of even 10 mole % of magnesium bromide caused the absorption largely to collapse to a single peak and essentially a single peak was observed when the solutions were

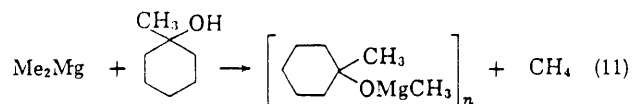
(18) The tertiary alcohol, 3-methyl-3-pentanol, was employed to obtain ether-soluble species. Attempts to use *t*-butyl alcohol or magnesium methoxide were thwarted by our inability to obtain reasonable concentrations of the corresponding methylmagnesium alkoxide species in ether solution.

TABLE V
 THE NMR METHYL SIGNALS FOR METHYLMAGNESIUM ALKOXIDES IN ETHER SOLUTION

Reactants (concn., moles/l.)	Temp, °C	Chemical shift upfield from internal TMS, cps	Band width at half-height, cps
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36)	87	76.6	1.8
		67.6	1.2
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36)	49	80.7	2.0
		67.8	1.0
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36)	35	82.3	2.5
		70	10
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36)	-56	96	3
		76	12
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36) + MgBr (0.036)	59	83.5 ^a	2.5
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36) + MgBr ₂ (0.036)	34	86 ^a	1.7
(CH ₃) ₂ Mg (0.36) + Et ₂ C(OH)Me (0.36) + MgBr ₂ (0.036)	-66.5	97.6 ^a	4
(CH ₃) ₂ Mg (0.34) + Et ₂ C(OH)Me (0.34) + MgBr ₂ (0.17)	35	88.8	1.4
(CH ₃) ₂ Mg (0.36) + [Et ₂ C(Me)O] ₂ Mg ^b (0.36)	~35	84	2.6
		74	8
(CH ₃) ₂ Mg (0.36) + [Et ₂ C(Me)O] ₂ Mg (0.36) + MgBr ₂ (0.36) ^c	~35	90	1
(CH ₃) ₂ Mg (0.18) + Et ₂ CO (0.18)	33	85	2.5
		74	11
(CH ₃) ₂ Mg (0.18) + Et ₂ CO (0.18)	-51	95	6
		75	7
(CH ₃) ₂ Mg (0.07) + Et ₂ CO (0.07) + tetrahydrofuran ^d	33	97	1.5
(CH ₃) ₂ Mg (0.07) + Et ₂ CO (0.07) + tetrahydrofuran ^d	-51	98	2
(CH ₃) ₂ Mg (0.36) +  (0.36)	~35	69	1
		75	12
(CH ₃) ₂ Mg (0.36) +  (0.36) + MgBr ₂ (0.36) ^c	~35	90.5	1

^a A broad diffuse peak at lower field was also apparent. ^b This material was initially insoluble and slowly dissolved in the organomagnesium reagent solution over a period of 48 hr. ^c The solution was obtained by adding magnesium bromide to the solution listed above it in the table. ^d This solution was prepared from the indicated concentration of reactants in a mixture of ether and tetrahydrofuran (1:4 by volume).

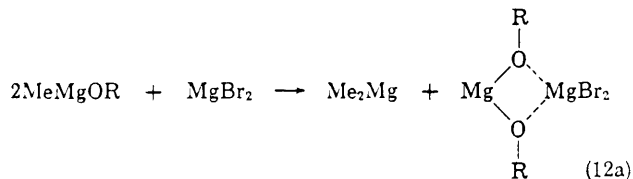
treated with either 0.5 or 1.0 mole equiv of magnesium bromide. A preliminary examination (Table V and Figure 1) of the methylmagnesium alkoxide derived from reaction of dimethylmagnesium with 1-methylcyclohexanol (eq 11) suggests similar behavior except



that the relatively broad peak was found at higher field in this case. The apparent degree of association of a 0.112 *M* solution of methylmagnesium 3-methyl-3-pentoxide in ether was determined by isothermal distillation to be 2.8, indicating that we are dealing with species at least some of whose degrees of aggregation are greater than monomeric.^{19,20}

The results of these nmr measurements are in complete agreement with earlier observations^{2d} that ether solutions of methylmagnesium alkoxides have chemical properties which differ from the properties of solutions of methylmagnesium bromide or dimethylmagnesium. However, apart from establishing that in the absence of tetrahydrofuran or magnesium bromide these solutions contain at least three different kinds of methyl-

magnesium species, two of which do not equilibrate readily, these measurements do little to define structures for these associated methylmagnesium alkoxides. The presence of either tetrahydrofuran or magnesium bromide apparently catalyzes the exchange of methyl groups among these methylmagnesium species. The effect of adding 0.5 mole equiv of magnesium bromide may well be to effect a reaction such as one of these illustrated in eq 12 which effectively prevents the magnesium dialkoxide from participating in other equilibria.



The Exchange of Methyl Groups between Dialkylmagnesium Reagents.—While the foregoing experiments provided information about the effect of various additives and impurities on the nmr signal of dimethylmagnesium, they provided no firm information about the nature of the reagent itself or about the ease and mechanism of transfer of a methyl group from one magnesium atom to another. To learn more about these latter questions, we elected to study mixtures of dimethylmagnesium and a second dialkyl- (or diaryl-) magnesium compound with the expectation that we could learn something about the rate of methyl group

(19) Our results suggest that the methylmagnesium alkoxides, at least in part, differ from the tetrameric methylead(II) methoxide and methylzinc methoxide. See (a) G. E. Coates and A. Lauder, *J. Chem. Soc., Sect. A*, 264 (1966); (b) H. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, No. 7, 194 (1966). (c) For other studies of alkylmagnesium alkoxides, see D. Bryce-Smith and B. J. Wakefield, *Proc. Chem. Soc.*, 376 (1963); 2483 (1964).

(20) Presumably the previously noted⁴ effect on oxygen on measurements of the apparent degree of association of ether solutions of dialkylmagnesium derivatives results from the partial conversion of the dialkylmagnesium reagents to alkylmagnesium alkoxides which are more highly associated.

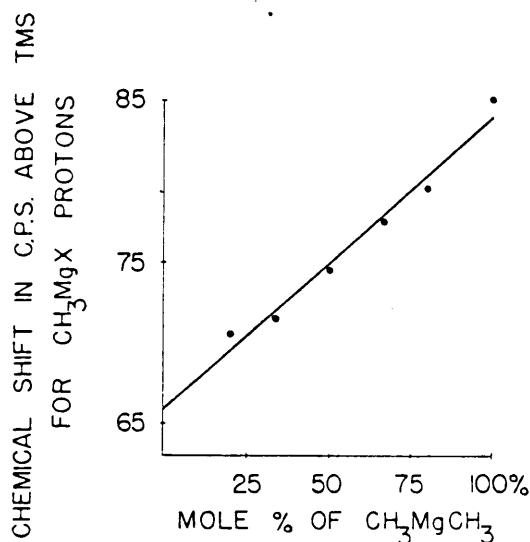
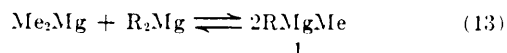
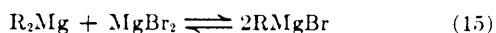
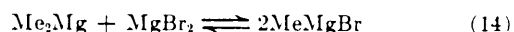


Figure 2.—Graph of nmr chemical shift for CH_3MgX protons vs. mole % dimethylmagnesium in dimethylmagnesium-diphenylmagnesium mixtures in ether solution (dimethylmagnesium concentration 0.21 M in all cases).

transfer and about the properties of mixed methylalkyl- (or aryl-) magnesium species (*i.e.*, 1) from studying the equilibrium illustrated in eq 13 by nmr techniques.



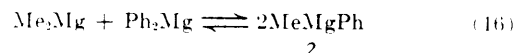
We anticipated that these studies would not be profitable with mixtures of methylmagnesium bromide and other alkylmagnesium bromides²¹ because the vast bulk of current evidence indicates that these Grignard reagents exist in dilute ether or tetrahydrofuran solution as the monomeric alkylmagnesium bromides (*i.e.*, both equilibria 14 and 15 lie relatively far to the right). As a result, the amount of mixed reagent 1 (eq 13) to be expected in such solutions would be very small. Although early isotope exchange studies²² had seemingly established that the equilibria illustrated in eq 14 and 15 did not occur in ether solution, a variety



of later investigations have all indicated that this early work must be in error. In particular, subsequent isotope labeling studies have indicated statistical exchange,^{22,23} crystalline samples of the dietherates of phenylmagnesium bromide and ethylmagnesium bromide have been crystallized from ether solution and their crystal structures have been determined by X-ray diffraction,²⁴ an investigation of infrared carbon-magnesium stretching frequencies indicated that equilibration occurred in ether solution,²⁵ thermochemical measurements indicated a rapid reaction of diethylmagnesium and magnesium bromide to form mono-

meric ethylmagnesium bromide,²⁶ and various measurements of the apparent molecular weights of ether solutions of alkylmagnesium halides²⁷ have indicated them to be monomeric in dilute solution.²⁸ As will be noted in the subsequent discussion, our data are entirely consistent with this view. In all cases where mixtures of Grignard reagents were examined or where solutions obtained by adding 2 mole equiv of magnesium bromide to equimolar mixtures of two different dialkylmagnesium reagents were examined, the spectra were consistent with the presence of alkylmagnesium bromides and we found no evidence for the presence of a mixed dialkylmagnesium reagent 1.

The first of a series of mixed methylaryl magnesium reagents 1 which we studied was methylphenylmagnesium 2 obtained as one of the components of an equilibrium mixture (eq 16) when dimethylmagnesium and



diphenylmagnesium were mixed (Table VI). In ether solution, only a single nmr methyl signal was observed whose position was dependent upon the ratio diphenylmagnesium-dimethylmagnesium in the solution (Figure 2). These results suggest that the single methyl signal observed is the average signal obtained for methyl groups which are rapidly exchanging between dimethylmagnesium and methylphenylmagnesium (2) with the methyl signal of the latter compound occurring at lower field because of decreased shielding by the phenyl ring. The fact that an approximately linear relationship is obtained (Figure 2) suggests that this exchange (eq 16) is approximately statistical. When an equivalent amount of magnesium bromide was added to these solutions (or when methylmagnesium bromide and phenylmagnesium bromide were mixed), the only high-field nmr signal observed was that corresponding to methylmagnesium bromide. As noted previously, this observation is in complete accord with the idea that the equilibria between dialkylmagnesium compounds and alkylmagnesium bromides (eq 14 and 15) lie far to the side of the Grignard reagents.

Even at relatively low temperatures (-79°), only a slightly broadened average signal was observed for the methyl groups of mixtures of dimethylmagnesium and methylphenylmagnesium in ether solution. We

(26) (a) M. B. Smith and W. E. Becker, *Tetrahedron*, **22**, 3027 (1966); (b) T. Holm, *Tetrahedron Letters*, No. 28, 3329 (1966).

(27) (a) E. C. Ashby and M. B. Smith, *J. Am. Chem. Soc.*, **86**, 4363 (1964); (b) E. C. Ashby, *ibid.*, **87**, 2509 (1965).

(28) Certain of the foregoing molecular weight measurements²⁷ have been cited^{1,27} as evidence that alkylmagnesium halides are monomeric in dilute solution (*i.e.*, 0.05 M) but become dimeric in more concentrated solutions (*i.e.*, 0.5–1.0 M). However, it must be recalled that these molecular weight measurements (ebullioscopic determinations) were based on colligative properties of the solutions and, consequently, are only valid in dilute solutions where behavior approximating that of an ideal solution can be expected. There is no compelling reason to conclude that the apparently higher molecular weights reported for more concentrated solutions have an origin other than deviation from ideal solution behavior. Consequently, we are aware of no evidence requiring that alkylmagnesium halides are other than monomeric in ether solution. The aforementioned X-ray crystal structure data argue that the solvated Grignard reagents are monomeric in saturated solutions and, by inference, at all concentrations. The only case of which we are aware where a polymeric reagent is indicated is that of methylmagnesium halide which is converted to a mixture of polymeric dimethylmagnesium and magnesium halide when all the ether is removed from the reagent: E. Weiss, *Chem. Ber.*, **98**, 2805 (1965). The degree of association of ether solutions of magnesium halides at concentrations above 0.05 M appears to be even greater than the apparent association of alkylmagnesium halides;²⁶ it may well be that dimeric, trimeric, and polymeric structures are formed from the magnesium halides.

(21) Cf. G. Fraenkel, S. Kobayashi, and D. G. Adams, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 41N.

(22) For a summary of earlier studies (where no exchange was reported) and latter studies (where statistical exchange was found), see R. E. Dessy, S. E. I. Green, and R. M. Salinger, *Tetrahedron Letters*, No. 21, 1369 (1964).

(23) D. O. Cowan, J. Hsu, and J. D. Roberts, *J. Org. Chem.*, **29**, 3688 (1964).

(24) (a) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963); (b) *ibid.*, **86**, 4821 (1964); (c) L. J. Guggenberger and R. E. Rundle, *ibid.*, **86**, 5344 (1964).

(25) R. M. Salinger and H. S. Mosher, *ibid.*, **86**, 1782 (1964).

TABLE VII
THE NMR SPECTRA OF MIXTURES OF METHYLMAGNESIUM AND
CYCLOPENTADIENYLMAGNESIUM DERIVATIVES

Reagent (concn, moles/l.)	Solvent	Temp, °C	Chemical shift upfield from internal TMS (band width at half-height), ^a cps	
			Cyclopentadienyl signal	Methyl signal
(C ₅ H ₅) ₂ Mg (0.24)	Et ₂ O	~30	-360.5 ^b	...
		-75	-358.5	...
(C ₅ H ₅) ₂ Fe	Et ₂ O	~30	-245.5	...
(C ₅ H ₅) ₂ Mg (0.30) + (C ₅ H ₅) ₂ Fe (0.30)	Et ₂ O	~30	-246, -358	...
(CH ₃) ₂ Mg (0.36)	Et ₂ O-THF (1:1 by volume)	~30	...	106
C ₅ H ₅ MgCH ₃ (2.68)	THF	~30	-352	127
C ₅ H ₅ MgCH ₃ (2.11) + Et ₂ O (2.11)	THF	~30	-352.5	125.5
C ₅ H ₅ MgCH ₃ (1.72) + Et ₂ O (3.44)	THF	~30	-353.5	125
C ₅ H ₅ MgCH ₃ (1.27) + Et ₂ O (5.08)	THF	~30	-353.5	124
C ₅ H ₅ MgCH ₃ (0.35)	Et ₂ O-THF (85:15 by mole %)	31.5	-358.5	123
		-28	-359	127
		-82	-368	131.5 (1.3)
C ₅ H ₅ MgCH ₃ (0.32)	Et ₂ O-THF (8:92 by mole %)	~30	-355	126.5
C ₅ H ₅ MgCH ₃ (0.32) + MgBr ₂ (0.16)	Et ₂ O-THF (6:94 by mole %)	~30	-359	116.5
C ₅ H ₅ MgCH ₃ (1.34) + MgBr ₂ (1.42)	Et ₂ O-THF (1:1 by volume)	-12 ^c	-357 (2.5)	122.5 (3.4)
		33	-362.5	99.5
C ₅ H ₅ MgCH ₃ (0.54)	THF	~30	-356	126
C ₅ H ₅ MgCH ₃ (0.54) + LiCl (0.54)	THF	~30	-344	113
C ₅ H ₅ MgCH ₃ (0.54) + LiCl (1.08)	THF	~30	-336	108
C ₅ H ₅ MgCH ₃ (0.29) + CH ₃ MgCH ₃ (0.145)	Et ₂ O-THF (28:72 by mole %)	~30	-359 (0.7)	115 (0.9)
C ₅ H ₅ MgCH ₃ (0.24) + CH ₃ MgCH ₃ (0.24)	Et ₂ O-THF (36:64 by mole %)	~30	-356 (0.6)	112 (0.6)
		-84	-354 (1.0)	108 (1.5) + 128 (1.9)
C ₅ H ₅ MgCH ₃ (0.30)	Et ₂ O-DME ^d (12:88 by mole %)	31	-357 (0.8)	128.5 (0.8)
		-81	-358.5 (1.0)	131 (1.6)
C ₅ H ₅ MgCH ₃ (0.25) + CH ₃ MgCH ₃ (0.125)	Et ₂ O-DME (28:72 by mole %)	31	-359 (0.7)	115 (0.8)
		-81	-359 (1.3)	113 (3.5) + 131 (3.3)
C ₅ H ₅ MgCH ₃ (0.18)	Et ₂ O-THF-amine ^e (37:33:30 by mole %)	38.5	-358 (0.8)	121 (0.6)
		-67.5	-357 (0.8)	124.5 (1.2)
C ₅ H ₅ MgCH ₃ (0.18) + CH ₃ MgCH ₃ (0.09)	Et ₂ O-THF-amine ^e (45:30:26 by mole %)	38	-359 (0.8)	111.5 (2.3)
		-27	-359 (1.0)	104.5 (1.5) + 122.5 (1.5)
C ₅ H ₅ Mg(CH ₃) (0.23) + C ₅ H ₅ MgC ₃ H ₅ (0.115)	Et ₂ O-THF (69:31 by mole %)	30.5	-354 (0.8)	125 (0.7)
		-85	-355 (1.1) + -347 (1.2)	128
C ₅ H ₅ MgCH ₃ (0.17) + CH ₃ Mg(CH ₃) (0.084)	Et ₂ O-THF-Et ₃ N (26:50:24 by mole %)	~30	-355 (0.6)	116 (1.0)
		-74	-356 (1.1)	108 (2.1) + 129 (2.2)

^a In cases where no band width at half-height is specified, the value is approximately 1 cps or less. ^b An ether solution of cyclopentadiene has multiplets centered at -174 and -387 cps attributable to the cyclopentadiene protons. ^c Some solid precipitated when the solution was cooled to this temperature. ^d 1,2-Dimethoxyethane. ^e N,N,N',N'-tetramethylethylenediamine.

of 1 mole equiv were added. This behavior, which is in contrast to the behavior observed in mixtures of dimethylmagnesium and diphenylmagnesium (Figure 2), indicates that the equilibrium forming the mixed reagent **4** (eq 17) lies far to the right and a mixture obtained from equimolar amounts of dimethylmagnesium and dicyclopentadienylmagnesium contains primarily the mixed reagent. The fact that this mixed reagent **4** is more stable than its symmetrical disproportionation products (eq 17) suggested that the exchange of methyl or cyclopentadienyl groups with this mixed reagent might be slower than the aforementioned exchange reactions and led us to make the low-temperature measurements summarized in Table VII and Figures 4-7.

It is apparent from these data that exchange of both the methyl groups (with dimethylmagnesium) and the cyclopentadienyl groups (with dicyclopentadienylmagnesium) of the mixed reagent can be slowed sufficiently to observe the two separate signals attributable to the mixed reagent **4** and to the methyl or dicyclopentadienyl groups of the excess symmetrical reagent. The separation of the methyl groups was sufficient to permit calculation of the pre-exchange lifetimes for the methylmagnesium groups under several conditions. Typical observed and calculated curves for these measurements at various temperatures are presented in Figure 4 and the rates of exchange are summarized in Table VIII. Of particular interest is the observation that the rates of exchange are re-

TABLE VIII
 RATES OF EXCHANGE OF METHYL GROUPS IN ORGANOMETALLIC MIXTURES CONTAINING $\text{CH}_3\text{MgCH}_3^a$

Reagents (concn, moles/l.)	Solvent compn, mole %	Temp, °C	Typical values for $1/\tau$, sec ⁻¹	Arrhenius parameters E_a , kcal/mole	A	Rate constants ^c at -55°, M^{-1} sec ⁻¹
$\text{C}_3\text{H}_7\text{MgCH}_3$ (0.29) + CH_3MgCH_3 (0.145)	THF-ether (72:28)	-34.5 -46 -60.5	324 78.7 6.2	13.8	10^{+16}	124
$\text{C}_3\text{H}_7\text{MgCH}_3$ (0.25) + CH_3MgCH_3 (0.125)	DME ^b -ether (72:28)	-32.5 -55.5 -75.5	196 45 8.3	7.4	$10^{+9.9}$	25
$\text{C}_3\text{H}_7\text{MgCH}_3$ (0.18) + CH_3MgCH_3 (0.09)	Ether-THF-amine ^c (44:30:26)	38 10 -6.5	318 45.4 12	12.1	10^{+12}	0.63
$\text{C}_3\text{H}_7\text{MgCH}_3$ (0.24) + CH_3MgCH_3 (0.24)	THF-ether (64:36)	-38.5 -58.5 -69.5	476 ^d 44.6 10.5	12.2	$10^{+14.6}$	200
$\text{C}_3\text{H}_7\text{MgCH}_3$ (0.17) + CH_3MgCH_3 (0.084)	THF-ether-triethylamine (50:26:24)	-33.5 -50 -58	500 102 37.3	11.4	$10^{+14.2}$	500
PhMgCH_3 (0.10) + CH_3MgCH_3 (0.12)	THF-ether-amine ^c (56:28:16)	-5.5 -27 -52	310 ^d 73 9.5	8.6	$10^{+10.3}$	40

^a The methods used to calculate the data tabulated are presented in the Experimental Section. ^b 1,2-Dimethoxyethane. ^c N,N,N',N' -tetramethylethylenediamine. ^d The pre-exchange lifetime τ refers to the value for the methyl group of the mixed reagent, RMgCH_3 . ^e Calculated from the Arrhenius parameters assuming bimolecular kinetics.

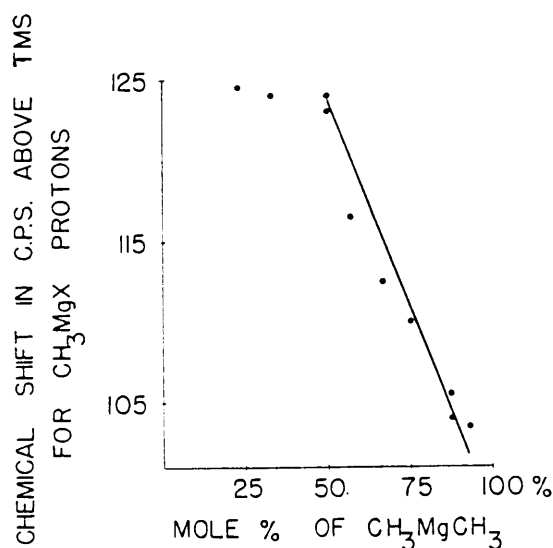
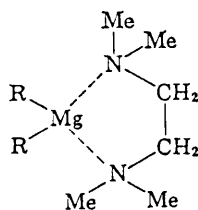


Figure 3.—Graph of nmr chemical shift for CH_3MgX protons vs. mole % dimethylmagnesium in dimethylmagnesium-dicyclopentadienylmagnesium mixtures in ether-tetrahydrofuran mixtures (65–85 mole % ether).

tarded slightly by increasing the concentration of tetrahydrofuran and markedly by adding the bidentate ligands 1,2-dimethoxyethane (5) or, especially, tetramethylethylenediamine (6).³² This diamine 6 is dis-

(32) Reaction of this diamine with several dialkylmagnesium compounds has been found to yield isolable monomeric complexes which are formulated as



(a) L. I. Zakharkin, *Zh. Obshch. Khim.*, **34**, 3125 (1964); *Chem. Abstr.*, **61**, 14697 (1964); *J. Gen. Chem. USSR*, **34**, 3166 (1964). (b) G. E. Coates and J. A. Heslop, *J. Chem. Soc., Sect. A*, 27 (1966).

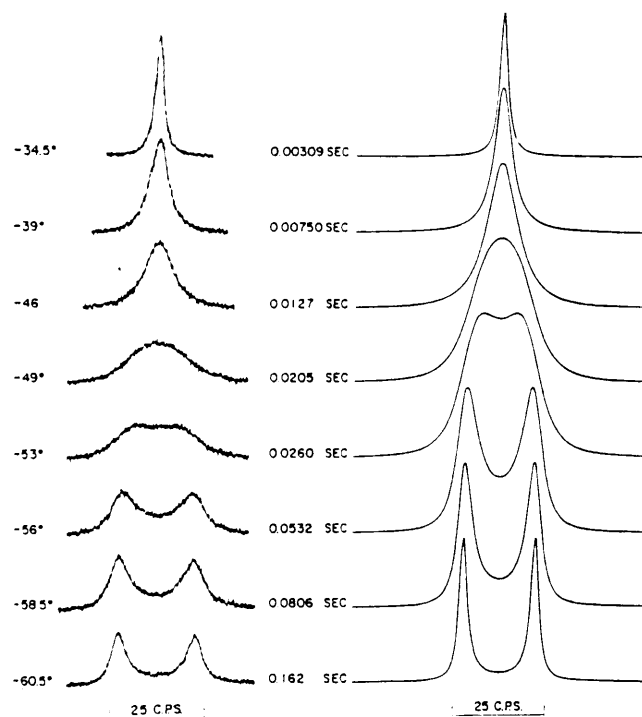
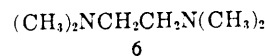
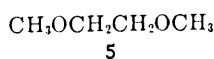


Figure 4.—Observed (C°) and calculated (pre-exchange lifetime τ) nmr spectra of CH_3Mg^+ protons in a mixture of $\text{C}_3\text{H}_7\text{MgCH}_3$ (0.29 M) and CH_3MgCH_3 (0.145 M) in tetrahydrofuran-ether (72:28 by mole %).



tinctly more effective in retarding the rate of exchange than is triethylamine which cannot function as a bidentate ligand. The striking ability of this diamine 6 to retard the rate of exchange was further demonstrated by adding it to mixtures of dimethylmagnesium and diphenylmagnesium. In the presence of this diamine, the exchange of methyl groups between dimethylmagnesium and the methyl phenyl mixed reagent 2 became sufficiently slow at low temperatures to permit

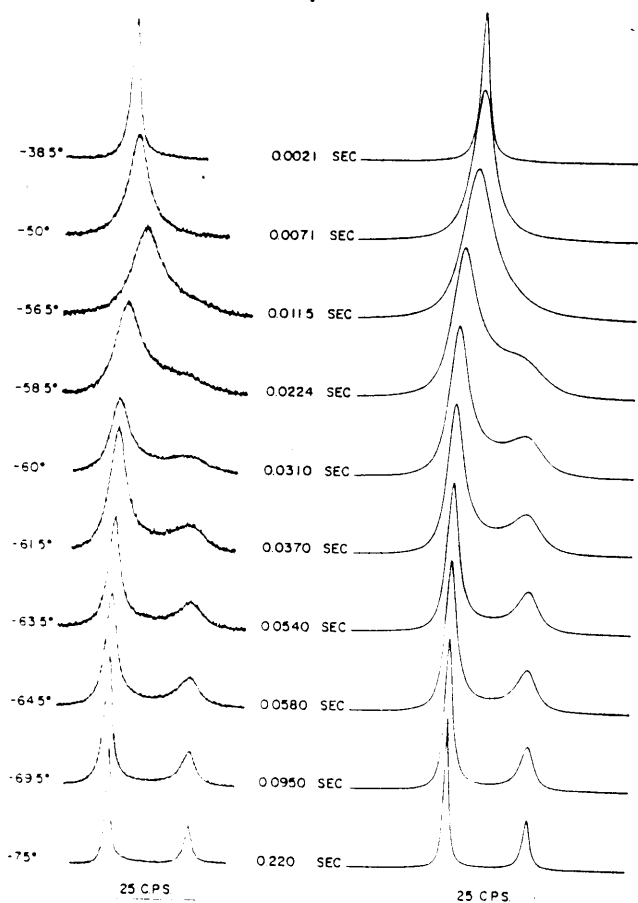
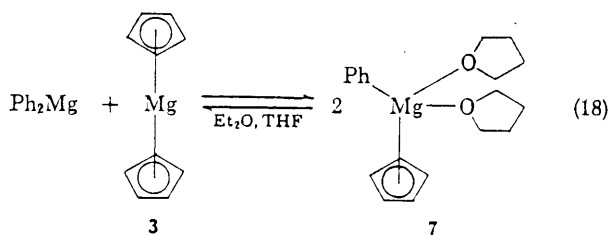


Figure 5.—Observed (C°) and calculated (pre-exchange lifetime τ) nmr spectra for CH_3Mg^- protons in a mixture of $\text{C}_5\text{H}_5\text{MgCH}_3$ (0.24 M) and CH_3MgCH_3 (0.24 M) in tetrahydrofuran-ether (64:36 by mole %). The pre-exchange lifetime τ refers to the methyl groups of the mixed reagent.

the observation of the nmr methyl signals associated with the two species and to permit calculation of pre-exchange lifetimes and exchange rates (Table VIII). The position of the equilibrium (eq 16) was also influenced by the presence of the diamine **6** such that the concentration of the mixed reagent was diminished. This observation presumably reflects the fact that at least one of the symmetrical reagents is more strongly solvated than the mixed reagent.

In an analogous manner, mixtures of diphenylmagnesium and dicyclopentadienylmagnesium (**3**) were found to form a mixed reagent (eq 18) which crystallized from an ether-tetrahydrofuran mixture as the disolvated mixed reagent **7**. The nmr signal (Table



IX) for the cyclopentadienyl protons of this reagent was shifted downfield with respect to the corresponding signal for the dicyclopentadienyl reagent **3** as would be expected from the decreased shielding by the phenyl ring in the mixed reagent. A 0.26 M solution of the mixed reagent **7** in tetrahydrofuran was found to be

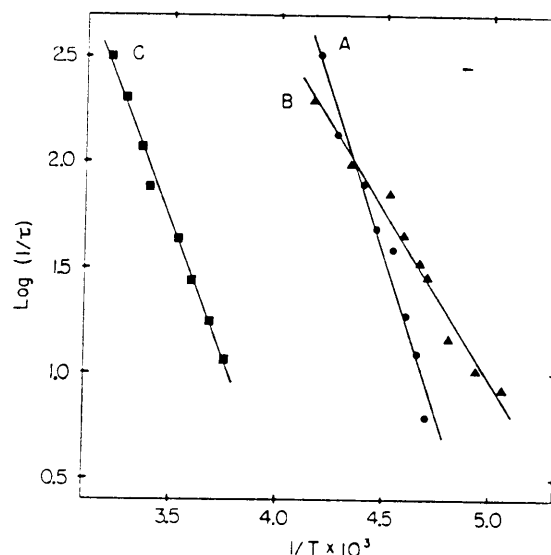


Figure 6.—Plot of $\log(1/\tau)$ as a function of $1/T$ for A, $\text{C}_5\text{H}_5\text{MgCH}_3$ (0.29 M) and CH_3MgCH_3 (0.145 M) in tetrahydrofuran-ether (72:28 by mole %); B, $\text{C}_5\text{H}_5\text{MgCH}_3$ (0.25 M) and CH_3MgCH_3 (0.125 M) in dimethoxyethane-ether (72:28 by mole %); C, $\text{C}_5\text{H}_5\text{MgCH}_3$ (0.18 M) and CH_3MgCH_3 (0.09 M) in ether-tetrahydrofuran- N,N,N',N' -tetramethylethylenediamine (44:30:26 by mole %).

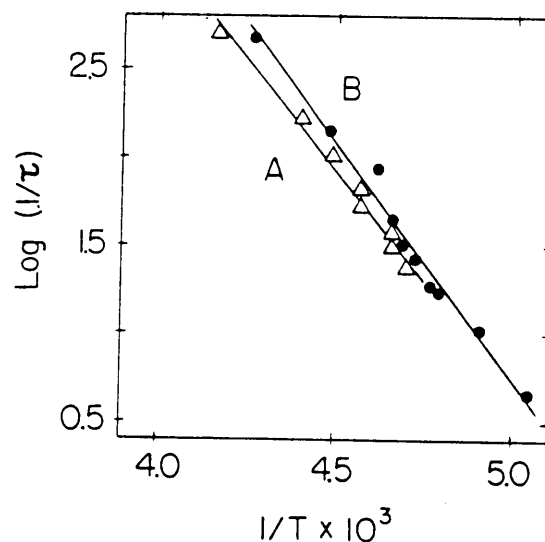


Figure 7.—Plot of $\log(1/\tau)$ as a function of $1/T$ for A, $\text{C}_5\text{H}_5\text{MgCH}_3$ (0.17 M) and CH_3MgCH_3 (0.084 M) in ether-tetrahydrofuran-triethylamine (26:50:24 by mole %); B, $\text{C}_5\text{H}_5\text{MgCH}_3$ (0.24 M) and CH_3MgCH_3 (0.24 M) in tetrahydrofuran-ether (64:36 by mole %). The pre-exchange lifetime τ refers to the methyl group of the mixed reagent in each case.

monomeric (apparent mol wt 1.07–1.11 \times monomer). These observations lead us to suggest the structure indicated in **7** for this substance.³¹ As was the case with the methylcyclopentadienyl reagent **4**, the exchange of cyclopentadienyl groups between the phenyl mixed reagent **7** and dicyclopentadienylmagnesium (**3**) was sufficiently slow at low temperatures to permit determination of pre-exchange lifetimes (Figure 8 and Table IX) and rates of exchange.

As had been the case with the methyl phenyl reagent **2**, addition of an equivalent amount of magnesium bromide to the mixed cyclopentadienyl reagents **4** or **7** led to solutions whose nmr spectra were consistent with the presence of cyclopentadienylmagnesium bromide and either methyl- or phenylmagnesium bromide.

TABLE IX
 RATES OF EXCHANGE OF CYCLOPENTADIENYL GROUPS IN ORGANOMETALLIC MIXTURES CONTAINING $C_5H_5MgC_5H_5$ ^a

Reagents (concn, moles/l.)	Solvent compn, mole %	Temp, °C	Typical values for $1/\tau$, sec ⁻¹	Arrhenius parameters E_a , kcal/mole	A
$C_5H_5MgC_5H_5$ (0.22) + $C_5H_5MgC_5H_5$ (0.11)	Ether-THF (65:35)	33 45 57.5	54.3 135 357	15.0 ± 0.6	$10^{+13.1 \pm 0.4}$
$C_5H_5MgC_5H_5$ (0.11) + $C_5H_5MgC_5H_5$ (0.055)	THF-ether (60:40)	32	25		
$C_5H_5MgC_5H_5$ (0.11) + $C_5H_5MgC_5H_5$ (0.054) + $MgBr_2$ (<0.025) ^b	THF-ether (59:41)	32	>10 ^{4c}		

^a The methods used to calculate the data tabulated are presented in the Experimental Section. ^b This solution was prepared by adding $MgBr_2(Et_2O)_2$ to the preceding solution listed in the table; not all of the $MgBr_2$ was soluble. ^c While two well-separated peaks (13.5 cps) were observed for the preceding solution ($1/\tau = 25$ sec⁻¹) at 32°, addition of $MgBr_2$ resulted in collapse to a sharp singlet (minimum value of $1/\tau$, 10³ sec⁻¹).

 TABLE X
 RATES OF EXCHANGE OF METHYL GROUPS IN ORGANOMETALLIC MIXTURES AT VARIOUS CONCENTRATIONS AT -55°^a

Reagent concn, moles/l.		Solvent compn, ether-THF, mole %	$1/\tau$ for the CH_3 group of $CH_3MgC_5H_5$, sec ⁻¹		$1/\tau$ for the CH_3 groups of $C_5H_5MgCH_3$, sec ⁻¹		Arrhenius parameters E_a , kcal/mole	
$CH_3MgC_5H_5$	$C_5H_5MgCH_3$		Obsd	Calcd ^b	Obsd	Calcd ^b		A
0.32	0.16	67:33	150	128	150	128	14.2 ± 1.1	$10^{17.1 \pm 1.1}$
0.11	0.055	67:33	49	44	49	44	13.5 ± 0.8	$10^{16.4 \pm 0.8}$
0.053	0.026	68:32	21	21	21	21	12.8 ± 0.7	$10^{15.8 \pm 0.7}$
0.051	0.053	74:26	63 ^c	42	34 ^c	20		
0.040	0.168	72:28	150 ^c	134	18 ^c	16		
0.23	0.052	68:32	45 ^c	42	100 ^c	92		

^a The methods used to calculate the data tabulated are presented in the Experimental Section. ^b Using eq 20a and b and setting $k = 800$ M⁻¹ sec⁻¹. ^c These values were obtained by calculating the arithmetic mean of values at temperatures -53 and -57.5°.

A smaller concentration of magnesium bromide was added to a mixture of dicyclopentadienylmagnesium (3) and phenylcyclopentadienylmagnesium (7) to learn the effect of magnesium bromide on the rate of exchange of cyclopentadienyl groups. The data, presented in Table IX, indicate that small amounts of magnesium bromide increase the rate of exchange substantially.

To learn the kinetic order of one of the aforementioned exchange processes, the rates of methyl group exchange between dimethylmagnesium and methylcyclopentadienylmagnesium (4) were determined at several concentrations. The reaction was found to be second order over-all, first order in dimethylmagnesium, and first order in methylcyclopentadienylmagnesium.

For a bimolecular reaction, the rate of exchange of methyl groups is given by

$$\text{rate} = k[CH_3MgCH_3][CH_3MgC_5H_5] \quad (19)$$

Consequently

$$1/\tau_{CH_3MgC_5H_5} = k[CH_3MgCH_3] \quad (20a)$$

$$1/\tau_{CH_3MgCH_3} = (k/2)[CH_3MgC_5H_5] \quad (20b)$$

Table X lists the experimental values measured for $1/\tau$ for the two kinds of methyl groups at each concentration; for comparison, the corresponding values for these quantities obtained from 20a and b by setting $k = 800$ M⁻¹ sec⁻¹ are also given.³³ The agreement between the two sets of numbers is satisfactory. These rate data clearly do not support a mechanism for the exchange which is zero order in either one of the

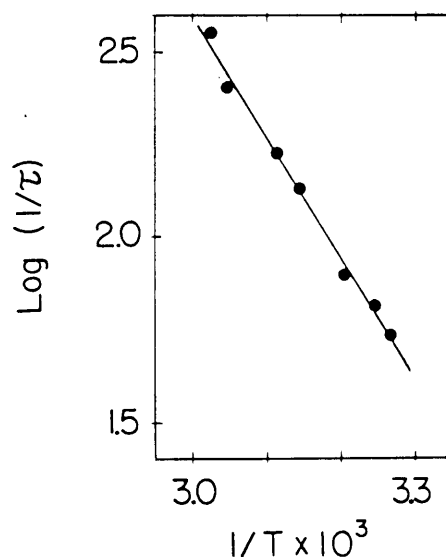


Figure 8.—Plot of $\log (1/\tau)$ as a function of $1/T$ for $C_5H_5MgC_5H_5$ (0.22 M) and $C_5H_5MgCH_3$ (0.11 M) in ether-tetrahydrofuran (65:35 by mole %).

components since in this circumstance $1/\tau$ for the second component would be independent of the concentration of the first. Similarly, a mechanism that was bimolecular in either component would predict that $1/\tau$ for that component would depend upon its own concentration; this prediction is again not in agreement with the data in Table X.

Consideration of both these results and the aforementioned retardation of exchange caused by the addition of substances (*i.e.*, 5 and 6) which serve as effective bidentate donor ligands suggest that the mechanism illustrated in eq 21 and 22 is applicable to this metal-metal exchange process. A rapid preequilibrium in-

(33) This value was obtained somewhat arbitrarily from the Arrhenius parameters obtained by examination of the temperature dependence of a solution 0.053 M in methylcyclopentadienylmagnesium and 0.026 M in dimethylmagnesium (third entry, Table X). Uncertainties in the concentrations of these solutions, together with significant variations in solvent compositions, make it difficult to choose a single value for k which would fit all of the solutions in this table.

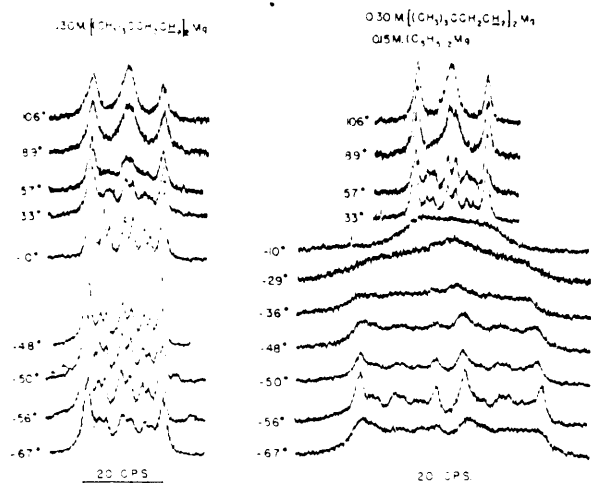
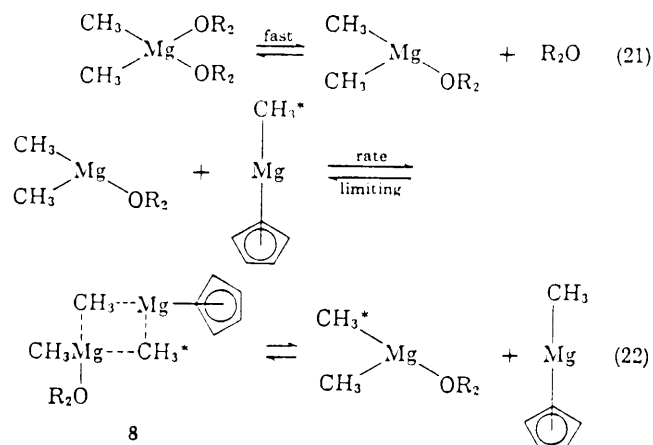


Figure 9.—Observed (C^{13}) nmr spectra for the CH_2Mg protons of bis(3,3-dimethylbutyl)magnesium (0.30 M) in ether-tetrahydrofuran (89:11 by mole %) and for a mixture of bis(3,3-dimethylbutyl)magnesium (0.30 M) and dicyclopentadienylmagnesium (0.15 M) in ether-tetrahydrofuran (81:19 by mole %).

volving dissociation of one or more solvent molecules from one of the organomagnesium compounds (presumably the dimethylmagnesium) explains the rate depression observed on adding the chelating ligands 1,2-dimethoxyethane and N,N,N',N' -tetramethylethylenediamine.³⁴ Since details of the methyl

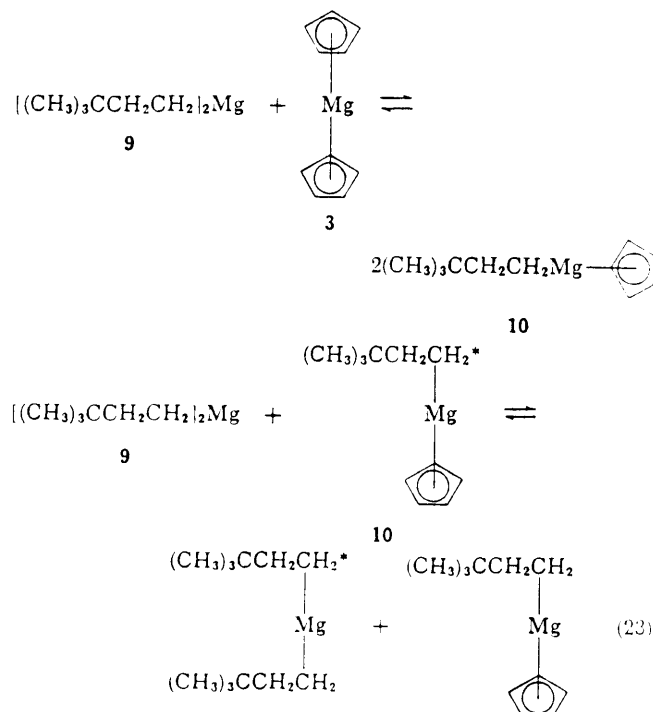


exchange step are not known in this case, we have represented the exchange of methyl groups as the customary four-center process 8 proceeding with retention of configuration.

To obtain more information about the stereochemistry of this step, we have examined mixtures obtained from bis(3,3-dimethylbutyl)magnesium (9) and dicyclopentadienylmagnesium (3). In ether solution, the dimethylbutylmagnesium derivative 9 undergoes a relatively slow inversion of configuration at the carbon atom adjacent to magnesium, requiring a temperature of approximately 100° to give an nmr signal in which the two protons at C-1 have become equivalent.^{4d-e} A question of interest is whether the rate k_e of exchange of dimethylbutyl groups from one magnesium atom to another is much faster than the rate k_i of configurational inversion (*i.e.*, $k_e > k_i$, exchange with retention)

(34) In ether-tetrahydrofuran mixtures, we presume that the bulk of the magnesium species are coordinated with tetrahydrofuran rather than ether in view of the fact that the tetrahydrofuran solvates are favored at equilibrium; see C. A. Hollingsworth, E. W. Smalley, and S. K. Podder, *Inorg. Chem.*, **3**, 222 (1964).

or whether the two rates are equivalent (*i.e.*, $k_e = k_i$, exchange with inversion). By examining the rate of exchange of dimethylbutyl groups (eq 23) between the symmetrical derivative 9 and the mixed reagent 10



(summarized in Figure 9), it is apparent that exchange of dimethylbutyl groups is substantially faster than the rate of configurational inversion. Consequently, the exchange reaction occurs primarily with retention of configuration.

The low-temperature spectrum observed for the mixture of 9 and 10 consists of two similar AA'XX'-type multiplets separated by 25.8 cps. As the temperature is raised, these first broaden and collapse to one AA'XX' spectrum as the chemical-shift difference between 9 and 10 is averaged by intermolecular exchange, then collapse to an A_2X_2 spectrum as inversion of configuration at the CH_2Mg group becomes rapid. Although the complexity of the line shapes in the intermediate exchange region make detailed rate calculations difficult, it is clear that corresponding lines in the multiplets of 9 and 10 coalesce at approximately -20°. Hence at this temperature, the rate of exchange of alkyl groups is approximately 57 sec⁻¹. From the known Arrhenius parameters for the inversion reaction,^{4e} the inversion rate at this temperature can be estimated to be approximately 10⁻³–10⁻⁴ sec⁻¹. Consequently, in this example, the rate of inversion of configuration is slower than the rate of exchange by a factor of 10⁴–10⁵. Whether the reaction leading to exchange is related to that leading to inversion is not apparent from the available data. By analogy with the exchange reaction between dimethylmagnesium and methylenecyclopentadienylmagnesium, the rate of exchange in eq 23 is probably concentration dependent. By contrast, Roberts and Witnowsky^{4e} have observed that the rate of inversion of configuration of bis-(3,3-dimethylbutyl)magnesium in ether is independent both of its concentration and of its method of preparation. (In particular, this dialkylmagnesium compound gave the same spectra irrespective of whether it

was prepared from the corresponding Grignard reagent by precipitation of magnesium chloride with dioxane or from the dialkylmercury compound by transmetalation.) It appears possible, therefore, that exchange and inversion may take place by reactions having different kinetic orders.

Comparison of the spectra of Figure 9 with those published previously⁴⁶ indicate that the temperature dependences observed in both sets of spectra are quite comparable. This agreement provides adequate justification for our use of Robert's and Witanowski's activation parameters to estimate the rate of configurational inversion of bis(3,3-dimethylbutyl)magnesium at -20° .

Experimental Section³⁵

Preparation of Reagents.—Ethereal solutions of methylmagnesium bromide, dimethylmagnesium (from dimethylmercury), diethylmagnesium (from diethylmercury), phenylmagnesium bromide, diphenylmagnesium (from diphenylmercury), and magnesium bromide (from ethylene dibromide) were prepared as previously described.² Each of the organomagnesium reagents was filtered through a Celite filter suspended on a sintered-glass funnel into a storage buret. The organometallic reagents were each standardized by an acid-base titration. In addition, the methyl reagents were standardized by reaction with dimethylphenylsilyl chloride followed by gas chromatographic analysis.³⁴ The magnesium bromide was purified by repeated recrystallization from ether-benzene mixtures. An ethereal solution of this purified magnesium bromide was standardized by a volumetric analysis for bromide ion. Except in certain specified preparations where Eastman Kodak Grignard-grade magnesium turnings were employed, the magnesium metal used in this study was used as turnings from a special sample of triply sublimed magnesium.³² 3-Methyl-3-pentanol was prepared as previously described.³⁴ Ethereal solutions of methylolithium were prepared from methyl bromide and excess lithium in the usual way. After the solutions had been filtered, they were standardized by acid-base titration, by reaction with dimethylphenylsilyl chloride,³⁴ and by reaction with ethylene dibromide.⁹ Dicyclopentadienylmagnesium was prepared either by passing a mixture of cyclopentadiene vapor and nitrogen over metallic magnesium in a hot (550 – 600°) tube³⁶ or by heating cyclopentadienylmagnesium bromide (from cyclopentadiene and ethereal methylmagnesium bromide) to *ca.* 270° under reduced pressure (*ca.* 0.05 mm) in such a way that the dicyclopentadienylmagnesium sublimed from the heated portion of the vessel.^{37b} In all cases, the solvent-free dicyclopentadienylmagnesium was sublimed under reduced pressure [*ca.* 90° (0.05 mm)] prior to use. The solvents ether, tetrahydrofuran, and 1,2-dimethoxyethane were distilled from lithium aluminum hydride immediately prior to use. Distilled commercial N,N,N',N' -tetramethylethylenediamine and triethylamine were each redistilled from lithium aluminum hydride immediately prior to use. An ethereal solution of bis(3,3-dimethylbutyl)magnesium was prepared by the addition of slightly more than 1 mole equiv of dioxane to an ether solution of 3,3-dimethylbutylmagnesium chloride followed by centrifugation to separate the insoluble magnesium salts.

Reaction of the Organometallic Reagents with 1,2-Dibromoethane.—The results summarized in Table III were obtained

by treating ethereal solutions containing the organometallic reagents and any specified additives with excess 1,2-dibromoethane and then stirring the solutions for the reaction times and at the reaction temperatures specified. The resulting solutions were quenched in a known excess of standard aqueous hydrochloric acid. After these mixtures had been saturated with sodium chloride (to improve the end point), they were titrated with standard aqueous sodium hydroxide to a phenolphthalein end point. In cases where analysis³⁴ of the starting organometallic reagent indicated the presence of some alkoxide, the titration values listed in Table III were corrected for this additional base which was present.

A solution of fluorene in ether was treated with excess ethereal methylolithium to give an orange solution which was 0.39 *M* in 9-fluorenyllithium and 0.07 *M* in methylolithium. The nmr spectrum of this solution lacked absorption attributable to unionized fluorene and exhibited, in addition to peaks attributable to ether and methylolithium, peaks attributable to fluorenyllithium.³⁷ The spectrum has two low-field doublets ($J = 8$ cps for each with further splitting apparent but not resolved) at δ 7.42 (2 H) and 7.99 (2 H) attributable to the 1 and 8 and to the 4 and 5 protons of the 9-fluorenyllithium. In addition, the 9-fluorenyllithium spectrum has a peak at δ 5.81 [1 H with partially resolved splitting ($J < 1$ cps), C_9 -H] and multiplets centered at δ 6.98 (2 H) and 6.6 (2 H) attributable to the protons at positions 2, 3, 6, and 7. The latter multiplets, each of which has the gross appearance of a triplet of closely spaced doublets, appear to result from coupling constant values of 8.0, 6.5, and *ca.* 1 cps.

Preparation of the Methylmagnesium Alkoxides.—The methylmagnesium alkoxide samples whose nmr spectra are summarized in Table V were obtained by adding the indicated amounts of freshly distilled samples of 3-methyl-3-pentanol, 3-pentanol, or 1-methylcyclohexanol as ether solutions to solutions of dimethylmagnesium in either ether or ether-tetrahydrofuran mixtures. To obtain the di(3-methyl-3-pentoxy)magnesium sample employed, a solution of 3.6 mmoles of dimethylmagnesium in 10 ml of ether was treated successively with two 0.37-g (3.6 mmole) portions of 3-methyl-3-pentanol. Although all the material remained in solution after the addition of the first mole equivalent of the tertiary alcohol, addition of the second mole equivalent resulted in the separation of a white solid which was insoluble in ether and in tetrahydrofuran. When 10 ml of an ether solution containing an additional 3.6 mmoles of dimethylmagnesium was added to this suspension and the mixture was stirred at room temperature, the white solid slowly redissolved. After 48 hr a clear solution was obtained with the nmr absorption indicated in Table V.

A solution prepared from 3.6 mmoles of dimethylmagnesium and 3.6 mmoles of 3-methyl-3-pentanol in 10 ml of ether was treated with 10 ml of an ether solution containing a known amount of cumene (as an internal standard) and excess dimethylphenylchlorosilane. After the reaction mixture had been stirred for 24 hr, it was hydrolyzed with saturated, aqueous ammonium chloride and analyzed by gas chromatography.³⁸ The calculated amounts of 3-methyl-3-pentanol and phenyltrimethylsilane (from methylmagnesium groups)³⁴ were 3.6 and 3.5 mmoles, respectively.

Determination of Molecular Weights.³⁹—Samples of methylcyclopentadienylmagnesium (4) and phenylcyclopentadienylmagnesium (7) were dissolved in tetrahydrofuran and aliquots of these solutions were hydrolyzed and titrated for total base to determine the concentration of the organometallic solutions. The organometallic solutions were placed in one arm of an isothermal distillation apparatus (Scientific Glass Apparatus Co., Inc., Bloomfield, N. J.) and tetrahydrofuran solutions containing known concentrations of phenanthrene were placed in the second arm of the apparatus. In each case, the apparatus containing the solutions was degassed by cooling to -80° , evacuating, and rewarming to room temperature. After the degassing process had been repeated two additional times, the system was cooled to -80° , evacuated, sealed, and then allowed to equilibrate at 40° until the volume of solution in each arm of the apparatus remained constant. At least two determinations

(37) J. A. Dixon, P. A. Gwinner, and D. C. Lim, *J. Am. Chem. Soc.*, **87**, 1379 (1965).

(38) A gas chromatography column packed with Carbowax 20 M, suspended on Chromosorb P was employed for this analysis.

(39) The general procedure employed is described by A. Steyermark, "Quantitative Organic Microanalysis," Blakiston Co., New York, N. Y., 1951, pp 292–297.

(35) All preparations and transfers of organometallic reagents were done under a nitrogen atmosphere. All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated, magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. The nmr spectra were determined at 60 Mc with a Varian Model A-60 nmr spectrometer, equipped with a V-6040 variable-temperature probe and controller. Sweep widths were calibrated using a Krohn-Hite Model 450 oscillator. The frequency output of this oscillator was checked periodically using a Hewlett-Packard Model 524C electronic counter. Calibration of the temperature controller was accomplished by measuring peak separations in a methanol or ethylene glycol sample. The nmr peak positions are expressed in cycles per second above tetramethylsilane as an internal standard or in δ values (parts per million relative to tetramethylsilane as an internal standard). Unless otherwise noted, all mass spectra were determined with a CEC Model 21-130 mass spectrometer.

(36) W. A. Barber and W. L. Jolly, *Inorg. Syn.*, **6**, 11 (1969).

TABLE XI
 NMR SPECTRA OF MIXTURES CONTAINING PHENYLCYCLOPENTADIENYLMAGNESIUM

Reagents (concn. moles/l.)	Solvent, mole %	Temp, °C	Chemical shift downfield from internal TMS (band width at half-height, ^a cps)
$C_6H_5MgC_5H_5$ (0.26)	THF	47	366
		-35	365.5 ^b
		-55.5	366
$C_6H_5MgC_5H_5$ (0.24) + $MgBr_2$ (ca. 0.26) ^c	THF-ether (92:8)	47	364.5
		-35	365
$C_6H_5MgC_5H_5$ (0.11) + $C_6H_5MgC_5H_5$ (0.055)	THF-ether (60:40)	32	366.5 (3.8), 352.5 (4.8)
		-55.5	366 (1.0), 348 (1.0)
$C_6H_5MgC_5H_5$ (0.11) + $C_6H_5MgC_5H_5$ (0.054) + $MgBr_2$ (<0.025) ^c	THF-ether (59:41)	32	365.5 (0.7)
$C_6H_5MgC_5H_5$ (0.22) + $C_6H_5MgC_5H_5$ (0.11)	Ether-THF (65:35)	9	367 (3.2), 352 (3.2)

^a In cases where no band width at half-height is specified, the value is approximately 1 cps or less. ^b The chemical shift for a 0.10 *M* solution of dicyclopentadienylmagnesium in ether-tetrahydrofuran (70:30 by mole %) is 351 cps at 37.5°. ^c Not all of the magnesium bromide was soluble.

were done for each organometallic reagent studied. For 0.117 and 0.0882 *M* solutions of methylcyclopentadienylmagnesium (4) in tetrahydrofuran, the molecular weight values found were 112 and 107, respectively. These values correspond to 1.07 and 1.03 times the molecular weight of the monomer. Solutions of phenylcyclopentadienylmagnesium (7) (0.26 *M*) in tetrahydrofuran gave molecular weight values of 332 and 345, corresponding to 1.07 and 1.11 times the molecular weight of the solvated monomer. Ether solutions of dimethylmagnesium and methylmagnesium 3-methyl-3-pentoxide were prepared, standardized, and equilibrated with standard ethereal solutions of phenanthrene by use of the previously described procedures. Ethereal solutions of the methylmagnesium alkoxide (0.112 *M*) gave molecular weight values of 378 and 402 corresponding to 2.69 and 2.86 times the value for the monomer. Ethereal solutions of dimethylmagnesium (0.13 *M*) gave molecular weight values of 65.3 and 69.8 corresponding to 1.20 and 1.28 times the value for the monomer.

Preparation of Methylcyclopentadienylmagnesium (4).—Solutions of 3.29 mmoles of dicyclopentadienylmagnesium in 7.0 ml of ether and 3.31 mmoles of dimethylmagnesium in 4.3 ml of ether were mixed. The mixed reagent began to separate as white needles almost immediately. After the mixture had been cooled to 0°, the supernatant liquid was removed with a syringe and the crystalline mixed reagent was washed with two portions of ether and then dried under reduced pressure (0.05 mm) at room temperature to leave 467.8 mg (68%) of the crystalline mixed reagent 4. A tetrahydrofuran solution of this material has nmr singlets at δ 5.87 (352 cps downfield from TMS, 5 H, cyclopentadienyl protons) and -2.12 (127 cps upfield from TMS, 3 H, methyl protons). The maximum concentration of ether which could have been present in this solution could be determined from integration of the nmr spectrum to be less than 0.03 mole/mole of mixed reagent. The compound was sublimed at 100° (0.05 mm). Weighed samples of the reagent were dissolved in tetrahydrofuran, hydrolyzed with aqueous hydrochloric acid, neutralized, and titrated with the disodium salt of ethylenediaminetetraacetic acid for magnesium content.⁴⁰

Anal. Calcd for C_6H_5Mg : Mg, 23.29. Found: Mg, 22.30; 22.56.

A sample of the mixed reagent 4 which had been sublimed into the source of a CEC Model 21-110 mass spectrometer gave molecular ion peaks at *m/e* 104 and 154 corresponding to the mixed reagent 4 and to dicyclopentadienylmagnesium (3).³⁹ Throughout a series of scans, the *m/e* 154 peak remained six to seven times as intense as the *m/e* 104 peak. The spectrum also exhibited abundant fragment peaks at *m/e* 89 ($C_5H_5Mg^+$) and 24 (Mg^+). Each of the aforementioned peaks was accompanied by isotope peaks corresponding to the 10% ²⁵Mg and 11% ²⁶Mg isotopes present in magnesium.

Reaction of Methylcyclopentadienylmagnesium with Benzophenone.—An authentic sample of 1,1-diphenylethanol [white needles from a benzene-petroleum ether (bp 30–60°) mixture; mp 78.5–79.5° (lit.⁴¹ 80.–80.4°)] was obtained from reaction of benzophenone with methylolithium. Authentic samples of diphenyl-

cyclopentadienylcarbinol, mp 122–126° (lit.⁴² 123°), and diphenylfulvene, mp 82–82.5° (lit.⁴³ 82°), were obtained from McNeil Laboratories. A solution of 51.9 mg (0.284 mole) of benzophenone, 48.3 mg of phenanthrene (an internal standard), and 1.62 mmoles of methylcyclopentadienylmagnesium in 50 ml of tetrahydrofuran and 10 ml of ether was stirred at room temperature for 8 hr. After the reaction mixture had been hydrolyzed with an aqueous solution (pH 8) of ammonia and ammonium chloride, the organic layer was separated, combined with the ether extract of the aqueous phase, and concentrated. A solution of the residue in 10 ml of benzene containing 3 mg of *p*-toluenesulfonic acid was refluxed for 5 min and then washed with aqueous sodium bicarbonate, dried, and analyzed by gas chromatography.^{38,44} The calculated yields of products (in order of increasing retention time) were diphenylethylene (10%), benzophenone (1%), and diphenylfulvene (68%). Collected³⁸ samples of the two olefins were identified with authentic samples by comparison of infrared spectra.

Preparation of Phenylcyclopentadienylmagnesium (7).—After 2.40 mmoles of diphenylmagnesium in 2.0 ml of ether, 2.40 mmoles of dicyclopentadienylmagnesium in 5.1 ml of ether, and 2.0 ml of tetrahydrofuran had been mixed and cooled to 0° in an ice bath, the mixed reagent 7 crystallized as white needles. The supernatant liquid was removed and the residual product was recrystallized from a mixture of ether (5 ml) and tetrahydrofuran (1 ml). The resulting crystalline product was washed with ether and dried under reduced pressure (0.05 mm) at room temperature for 2 hr. The mixed reagent 7 as its ditetrahydrofuran solvate amounted to 1.229 g (82%). The magnesium content was determined as previously described.

Anal. Calcd for $C_{11}H_{10}Mg(C_4H_8O)_2$: Mg, 7.83. Found: Mg, 7.53, 7.79.

Attempted sublimation of phenylcyclopentadienylmagnesium ditetrahydrofuranate resulted in decomposition: nmr spectra of the sublimate and the residue indicated that dicyclopentadienylmagnesium sublimed, leaving a residue with intense nmr signals for phenylmagnesium species and a weak signal for a cyclopentadienylmagnesium species. A solution of this product in 1,2-dimethoxyethane exhibits nmr multiplets in the regions δ 6.7–7.6 (5 H, phenyl C–H), 3.5–4.0 (tetrahydrofuran α C–H bonds with solvent absorption superimposed), and 1.5–2.0 (8 H, tetrahydrofuran β C–H bonds) with a singlet at 6.17 (5 H, cyclopentadienyl C–H). The effect of additives on the cyclopentadienyl signal is summarized in Table XI.

The Nmr spectra of Ethylmagnesium and Neopentylmagnesium Derivatives.—An ether solution of neopentylmagnesium chloride was prepared by reaction of neopentyl chloride with magnesium.⁴⁵ Reaction of this Grignard reagent with mercuric chloride and subsequent reduction of the neopentylmercuric chloride with

(42) C. Courtot, *Ann. Chim.*, **4**, 86 (1915).

(43) J. Thiele, *Ber.*, **33**, 666 (1900).

(44) Suitable control experiments with authentic samples established that diphenylcyclopentadienylcarbinol was dehydrated to diphenylfulvene by this procedure. Calibration factors for the gas chromatographic analysis were obtained by subjecting known mixtures of alcohols to this dehydration procedure and subsequent analysis.

(45) (a) F. C. Whitmore and R. S. George, *J. Am. Chem. Soc.*, **64**, 1239 (1942); (b) H. Zimmer, I. Hechenbleikner, O. A. Homberg, and M. Danz, *J. Org. Chem.*, **29**, 2632 (1964).

(40) G. Schwarzenbach, "Complexometric Titrations," Methuen and Co., Ltd., London, 1957, p. 62.

(41) N. M. Bikales and E. I. Becker, *Can. J. Chem.*, **41**, 1329 (1963).

hydrazine in aqueous sodium hydroxide afforded, after distillation, dineopentylmercury⁴⁶ as a glassy solid, mp 38–38.5° (lit.^{46d} mp 39–40°).

A mixture of 46.6 g (0.14 mole) of dineopentylmercury, 7.30 g (0.30 g-atom) of magnesium turnings, ~20 drops of metallic mercury, 200 ml of ether, and 100 ml of tetrahydrofuran was heated under reflux with stirring. The extent of reaction was followed by nmr and gas chromatographic analysis.⁴⁷ A reaction period of 40 days was required to consume all the dineopentylmagnesium. The solution was filtered through Cellite on sintered glass and solvent was removed, first at atmospheric pressure and then under reduced pressure (75–85° (0.3 mm)). The residue was dissolved in 100 ml of dry ether and filtered through Cellite on sintered glass into a storage buret. The titration data for this solution is given in Table XII. Alternatively, dineopentyl-

TABLE XII
CONCENTRATIONS AND NMR SPECTRA OF
NEOPENTYLMAGNESIUM REAGENTS IN ETHER SOLUTION

Reagent	Concn (titration for total base content after hydrolysis), M	Concn (gas chromatographic determination of neopentyl bromide), M	Chemical shift upfield from internal TMS, ^a cps
(CH ₃) ₃ CCH ₂ MgCl	2.66	2.11	18
[(CH ₃) ₃ CCH ₂] ₂ Mg ^b	0.31	0.24	20 ^c
[(CH ₃) ₃ CCH ₂] ₂ Mg ^d	0.95	0.61	20.5 ^c

^a This column lists the position of the peak for the methylene group adjacent to magnesium. In addition each spectrum has a peak ca. 70 cps downfield from internal TMS attributable to the C-methyl groups of the neopentyl reagent. ^b This solution was prepared by the precipitation of the magnesium chloride-dioxane complex from an ethereal solution of neopentylmagnesium chloride. The concentration of residual halide ion in this solution was 0.02 M. ^c An additional peak was present at ca. 13 cps which may be due to a neopentylmagnesium alkoxide. The relative intensity of this peak was enhanced when 3-methyl-3-pentanol was added to the organometallic solution. ^d This solution was prepared from dineopentylmercury.

magnesium was obtained by adding slightly more than 1 equiv of dioxane to ethereal neopentylmagnesium chloride and separating magnesium salts by centrifugation. The total concentration

Typical values for total base concentration and concentration of neopentylmagnesium species are summarized in Table XII along with the nmr data for these reagents.

Because of the apparent presence of alkoxide impurities, the nmr spectra of these reagents were not investigated further. Table XIII summarizes nmr measurements obtained with a number of solutions containing diethylmagnesium.

TABLE XIII
NMR SPECTRA OF MIXTURES CONTAINING
DIETHYLMAGNESIUM IN ETHER SOLUTION

Reagents (concn, moles/l.)	Temp, °C	Chemical shift upfield from internal TMS, ^a cps
(CH ₃ CH ₂) ₂ Mg (0.75)	~35	37
	-34	42.5
(CH ₃ CH ₂) ₂ Mg (0.44)	~35	37.5
(CH ₃ CH ₂) ₂ Mg (0.75) + (C ₆ H ₅) ₂ Mg (0.76)	~35	33
	-34	40.5
(CH ₃ CH ₂) ₂ Mg (0.43)	~35	37
(CH ₃ CH ₂) ₂ Mg (0.43) + CH ₃ Li (0.43) ^b	~35	43.5 ^c (methyl at 90.5 cps)
(CH ₃ CH ₂) ₂ Mg (0.44) + CH ₃ MgBr (0.44)	~35	35 ^d (methyl at 79 cps)
(CH ₃ CH ₂) ₂ Mg (0.53) + CH ₃ MgCl (0.53)	~35	38 (methyl at 78 cps)

^a In all cases at room temperature, the nmr signal for the methylene portion of the ethylmagnesium group appeared approximately as a quartet ($J \approx 8$ cps), centered at the position indicated. ^b The ethereal solutions of methyl lithium contained an equimolar quantity of lithium bromide. ^c The values reported for the methylene group of ethyllithium in ether solution are 60⁴⁸ and 66 cps: T. L. Brown, R. L. Gertus, D. A. Bafus, and J. A. Ladd, *J. Am. Chem. Soc.*, **86**, 2135 (1964), and ref 8d. ^d The value reported for the methylene group of ethylmagnesium bromide in ether solution is 41 cps.^{2b,49}

Kinetic Studies.—The rates of exchange of methyl groups between magnetically nonequivalent positions were obtained by comparing the widths and peak separations of the observed exchange-broadened spectra with the corresponding parameters for spectra calculated using eq 24.^{49,50} Here, ω_A and ω_B are the

$$I(\omega) = Re \left\{ [1 - \chi, \chi] \left[\begin{array}{c} -i(\omega_A - \omega) - \frac{1}{T_2^A} - \frac{\chi}{(1 - \chi)\tau_B} \\ \frac{1}{\tau_B} \end{array} \right] \frac{\chi}{(1 - \chi)\tau_B} \right. \\ \left. - i(\omega_B - \omega) - \frac{1}{T_2^B} - \frac{1}{\tau_B} \right] \begin{bmatrix} 1 \\ 1 \end{bmatrix} \right\} \quad (24)$$

of base in neopentylmagnesium chloride and in dineopentylmagnesium was determined by hydrolysis and subsequent acid-base titration. In addition, the concentration of neopentylmagnesium species was measured by adding a slight excess of bromine to a cold, stirred aliquot of the organometallic solution containing a known amount of toluene (as an internal standard). The aliquot was quenched in aqueous ammonium chloride solution and excess bromine was removed by reaction with sodium sulfite. Vapor phase chromatographic analysis⁴⁸ was employed to determine the amount of neopentylbromide which corresponded to the concentration of neopentylmagnesium species. An authentic sample of neopentylbromide [bp 105–106°, n_D^{25} 1.4375; lit.^{46b} bp 104.8° (732 mm), n_D^{20} 1.4370] was prepared by bromination of neopentylmercuric chloride.^{46b} Control experiments indicated that the solutions did not contain alkoxides of neopentyl alcohol. The solutions obtained from neopentylmagnesium chloride also contained 2,2,5,5-tetramethylhexane.

(46) (a) H. Gilman and G. F. Wright, *J. Am. Chem. Soc.*, **55**, 3302 (1933); (b) F. C. Whitmore, E. L. Wittle, and B. R. Harriman, *ibid.*, **61**, 1585 (1939); (c) F. C. Whitmore and E. Rohrmann, *ibid.*, **61**, 1591 (1939); (d) R. Criegee, P. Dimroth, and R. Schempff, *Chem. Ber.*, **90**, 1337 (1957).

(47) A gas chromatograph fitted with a flame ionization detector and a column packed with 5% SE30 silicone gum suspended on Chromosorb P was employed for this analysis.

(48) A gas chromatography column packed with Dow Corning No. 710 silicone oil suspended on base-washed Chromosorb P was employed for this analysis.

chemical shifts (radians per second) characterizing the two sites involved in the exchange. T_2^A and T_2^B are the relaxation times of the protons at these sites in the absence of exchange, χ is the fraction of the methyl groups occupying site B, and τ_B is the mean pre-exchange lifetime for the methyl groups at site B. $I(\omega)$ is the relative intensity of the absorption spectrum at the frequency ω and Re indicates that only the real part of the expression in brackets is considered. Spectral calculations were carried out on an IBM 7094 computer and spectra were plotted using a Calcomp plotter. Several cycles of comparison of observed and calculated spectra were usually required to achieve a satisfactory fit.

$$1/\tau_{CH_3MgCH_3} = [CH_3MgCH_3]A \exp(-Ea/RT) \quad (25)$$

The kinetic order of the exchange process was established only for the exchange of methyl groups between dimethylmagnesium and cyclopentadienylmethylmagnesium in ether-THF solution (Table X). Arrhenius parameters for this reaction were obtained from a least-squares fit of the temperature dependence of the

(49) (a) A. Abragam, "The Principles of Nuclear Magnetism," The Clarendon Press, Oxford, 1961, Chapter 10; (b) R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957); (c) R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

(50) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

exchange rates to eq 25. For each of the other exchange reactions (Tables VIII and X), it was assumed that the exchange was first order in each component and an analogous kinetic treatment was applied. This assumption concerning the kinetic order clearly has no influence on the values of E_a reported in these tables; it does however influence the values of A . Consequently, the values of A for exchange reactions in solutions containing DME or tetramethylethylenediamine might be in error by some factor related to the concentrations and exponents in eq 25; this factor should not exceed 10^2 . Attempts to obtain activation parameters for exchange of methylenecyclopentadienylmagnesium and dicyclopentadienylmagnesium yielded an Ar-

renius plot with a positive curvature. The reason for this behavior was not investigated.

Registry No.— CH_3MgBr , 75-16-1; CH_3MgI , 917-64-6; $(\text{CH}_3)_2\text{Mg}$, 2999-74-8; CH_3Li , 917-54-4; $(\text{CH}_3)_2\text{Hg}$, 593-74-8; LiBr , 7550-35-8; MgBr_2 , 7789-48-2; $\text{CH}_3\text{MgOC}(\text{CH}_3)(\text{CH}_2\text{CH}_3)_2$, 13132-19-9; $[(\text{CH}_3\text{CH}_2)_2\text{C}(\text{CH}_3)\text{O}]_2\text{Mg}$, 13132-20-2; $(\text{CH}_3\text{MgO})(\text{CH}_3)-1,1-\text{C}_6\text{H}_{11}$, 13132-21-3; PhMgBr , 100-58-3; Ph_2Mg , 555-54-4; $(\text{C}_5\text{H}_5)_2\text{Fe}$, 102-54-5; **9**, 4469-61-8; $(\text{CH}_3)_3\text{CCH}_2\text{MgCl}$, 13132-23-5; $(\text{CH}_3)_2\text{Mg}$, 557-18-6.