

# Molecular Dynamics at Equilibrium. Carbon–Magnesium Bond Exchange in the System Dineopentylmagnesium–Diphenylmagnesium

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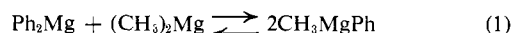
**Abstract:** The kinetics and thermodynamics of carbon–magnesium bond exchange in the system diphenylmagnesium–dineopentylmagnesium has been investigated with nmr methods. Thermodynamic parameters for the equilibrium  $R_2Mg + Ph_2Mg \rightleftharpoons 2RMgPh$  ( $R = \text{neopentyl}$ ) are  $\Delta H = 2.4 \text{ kcal/mol}$ ,  $\Delta S = -13.8 \text{ eu}$ ;  $\Delta F_{298^\circ} = -1.73 \text{ kcal/mol}$ . From nmr line-shape analysis using a Kubo–Anderson–Sack treatment, the dependence of  $\tau_{RMgPh}$  on concentrations of the different species at 301°K is found to be  $\tau_{RMgPh}^{-1} = 4.4[R_2Mg] + 12.2[RMgPh]$ , which is consistent with the following bimolecular steps, shown with rate constants in parentheses ( $M^{-1} \text{ sec}^{-1}$ ) and activation parameters  $\Delta H^\ddagger$  (kcal/mol) and  $\Delta S^\ddagger$  (eu):  $RMgR + R^*Mg^*Ph \rightleftharpoons RMg^*R^* + RMgPh$  (4.4),  $\Delta H_i^\ddagger = 16.1$ ,  $\Delta S_i^\ddagger = 0.7$ ;  $RMgR + PhMgPh \rightleftharpoons RMgPh + RMgPh$  (233),  $\Delta H_i^\ddagger = 8.3$ ,  $\Delta S_i^\ddagger = -22$ ,  $\Delta H_r^\ddagger = 6$ ,  $\Delta S_r^\ddagger = -36$ .

Organomagnesium compounds in ether solutions at equilibrium undergo a variety of fast exchange processes: inversion at carbon bound to magnesium,<sup>1</sup> carbon–magnesium bond exchange,<sup>2</sup> and magnesium–ether coordination exchange.<sup>3</sup> Of these processes, only inversion has been found to be slow enough to study with the methods of nmr line-shape analysis. A mechanism involving linear alkyl-bridged dimeric transition states was proposed to be responsible for inversion in organomagnesium compounds.<sup>1c</sup> The other processes are generally too fast to be measurable with nmr methods.

In previous work on exchange<sup>4</sup> between different organometallics, it has been shown that fast exchange occurs between dimethylmagnesium and dimethylzinc at  $-103^\circ$ ,<sup>5,6</sup> between dimethylmagnesium and dimethylcadmium in tetrahydrofuran at  $28^\circ$ ,<sup>3</sup> and between dimethylmagnesium and trimethylindium at  $-60^\circ$ .<sup>7</sup> Several studies have shown that complex formation occurs in the systems methyl lithium–dimethylmagnesium,<sup>6</sup> phenyllithium–diphenylmagnesium,<sup>8</sup> methyl lithium–diphenylmagnesium,<sup>9</sup> and phenyllithium with dimethylmagnesium.<sup>9</sup>

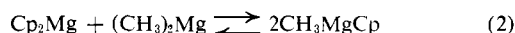
When diphenylmagnesium is added to dimethylmagnesium in ether or tetrahydrofuran, only one  $CH_3\text{-Mg}$  line is observed, implying fast carbon–magnesium bond exchange, while its average shift varies with the

composition of the sample in a manner quantitatively consistent with the operation of the equilibrium<sup>2</sup> 1.

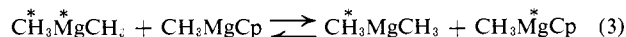


Only in the presence of *N,N,N',N'*-tetramethylethyldiamine is the exchange slow enough to give separate resonances for dimethylmagnesium and methylphenylmagnesium.

House, Latham, and Whitesides also investigated the system dicyclopentadienylmagnesium ( $Cp_2Mg$ ) with dimethylmagnesium with nmr methods and concluded



the slow step in the exchange process to be the degenerate reaction 3.<sup>2</sup>



It is not clear why intermolecular exchange among organomagnesium compounds in solution should be so fast. In this work, we have chosen to investigate, quantitatively, carbon–magnesium bond exchange processes in the system dineopentylmagnesium–diphenylmagnesium using nmr line-shape techniques. This system is more typical of common organomagnesium compounds than the constituents of (2) since it does not include the unusual bonding characteristics ascribed to dicyclopentadienylmagnesium. Furthermore, the results should be easily interpretable.

It will be shown below how kinetics of carbon–magnesium bond exchange have been extracted, in considerable detail, from nmr line-shape data and how this provides extensive information on the mechanism of an exchange process at equilibrium. Note that the study of chemical dynamics at equilibrium is uniquely accessible with the nmr line-shape technique.

## Results and Discussion

Dineopentylmagnesium and diphenylmagnesium were prepared by reacting the corresponding mercury compounds in tetrahydrofuran with sublimed magnesium.

(1) (a) M. Witanowski and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 737 (1966); (b) G. Fraenkel and D. T. Dix, *ibid.*, **88**, 979 (1966); (c) G. Fraenkel, C. Cottrell, and D. T. Dix, *ibid.*, **93**, 1704 (1971).

(2) H. O. House, R. A. Latham, and G. M. Whitesides, *J. Org. Chem.*, **32**, 2481 (1967).

(3) D. F. Evans and M. S. Khan, *Chem. Commun.*, 67 (1960); D. F. Evans and M. S. Khan, *J. Chem. Soc. A*, 1643, 1648 (1967); D. F. Evans and V. Fazarky, *Chem. Commun.*, 974 (1968); J. A. Magneson and J. D. Roberts, *J. Org. Chem.*, **37**, 133 (1972); G. E. Parris and E. C. Ashby, *J. Amer. Chem. Soc.*, **93**, 1206 (1971).

(4) (a) J. P. Oliver, *Advan. Organometal. Chem.*, **8**, 187 (1970); (b) N. S. Ham and T. Mole, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 91 (1969).

(5) R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *J. Amer. Chem. Soc.*, **85**, 1191 (1963).

(6) L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4140 (1966).

(7) See ref 4a, unpublished results.

(8) L. M. Seitz and T. L. Brown, *J. Amer. Chem. Soc.*, **89**, 1602, 1607 (1967).

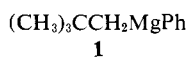
(9) J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 2538 (1969).

Table I. Equilibrium Data at Different Temperatures,  $R_2Mg + Ph_2Mg \rightleftharpoons 2RMgPh$ 

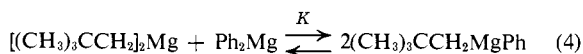
Sample	$[R_2Mg]_0, M$	$[Ph_2Mg]_0, M$	$T, ^\circ C$	Area ratio, $[RMgPh]/[R_2Mg]$	$K$
1	0.326	0.449	-15	$2.300 \pm 0.073$	9.61
	0.326	0.449	-32	$2.060 \pm 0.010$	8.03
	0.326	0.449	-50	$1.475 \pm 0.019$	4.55
2	0.408	0.387	-15	$1.469 \pm 0.016$	9.82
	0.408	0.387	-21	$1.393 \pm 0.018$	8.84
	0.408	0.387	-32	$1.245 \pm 0.015$	7.00
	0.408	0.387	-50	$0.956 \pm 0.006$	4.08
	0.408	0.387	-65	$0.856 \pm 0.131$	3.24
3	0.457	0.364	+3	$1.272 \pm 0.008$	13.62
	0.457	0.364	-15	$1.171 \pm 0.001$	10.98
	0.457	0.364	-50	$0.804 \pm 0.013$	4.43
	0.457	0.364	-60	$0.747 \pm 0.003$	3.74
4	0.507	0.319	+3	$0.923 \pm 0.006$	12.06
	0.507	0.319	-15	$0.860 \pm 0.007$	9.54
	0.507	0.319	-21	$0.833 \pm 0.016$	8.67
	0.507	0.319	-32	$0.780 \pm 0.005$	7.16
	0.507	0.319	-44	$0.699 \pm 0.009$	5.27
5	0.507	0.319	-65	$0.586 \pm 0.003$	3.34
	0.362	0.228	-15	$0.884 \pm 0.014$	10.38
	0.362	0.228	-65	$0.559 \pm 0.013$	2.96
9	0.610	0.243	-50	$0.429 \pm 0.002$	5.16

The  $^{199}Hg$ ,  $^1H^{10}$  coupling constants for dineopentylmagnesium are  $J(^{199}Hg, CH_2) = 93$  Hz and  $J(^{199}Hg, CH_3) = 5.5$  Hz.

When dineopentylmagnesium and diphenylmagnesium are mixed in tetrahydrofuran, new single lines appeared in the nmr spectra 12.04 Hz to lower field of the  $CH_2Mg$  resonance of dineopentylmagnesium and 3.77 Hz to lower field of the *tert*-butyl resonance, Figure 1. These new signals indicate the existence of another organomagnesium species in the solution, most likely a mixed species such as neopentylphenylmagnesium (1).



The deshielding of the neopentyl resonance in 1 compared to dineopentylmagnesium would be expected to result from the ring current in the phenyl moiety. This is proposed because, since all dialkylmagnesium compounds investigated to date are monomers,<sup>11,12</sup> in tetrahydrofuran such a mixed magnesium compound should be monomeric also. Then it would appear that the new species results from a redistribution equilibrium such as (4). We have tested this proposal by examining



The nmr spectra of mixtures of diphenylmagnesium and dineopentylmagnesium in tetrahydrofuran in the temperature range  $-65$  to  $+3^\circ$  (see Figure 1) using the original concentrations of organomagnesium compounds, together with the ratio of  $CH_2Mg$  proton absorption areas. We now proceed to show that the nmr data do in fact accord with the proposed equilibrium.

In the following procedure  $R_2Mg$  means dineopentylmagnesium and  $RMgPh$  is the mixed reagent 1. Here

$$p = [Ph_2Mg]_0/[R_2Mg]_0 \quad (5)$$

(10) R. E. Dessy, T. J. Flautt, H. H. Jaffé, and G. F. Reynold, *J. Chem. Phys.*, **30**, 1422 (1959); proton mercury coupling constants for other systems are quite similar to those for dineopentylmercury.

(11) E. C. Ashby, *Quart. Rev., Chem. Soc.*, **21**, 259 (1967); B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966).

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

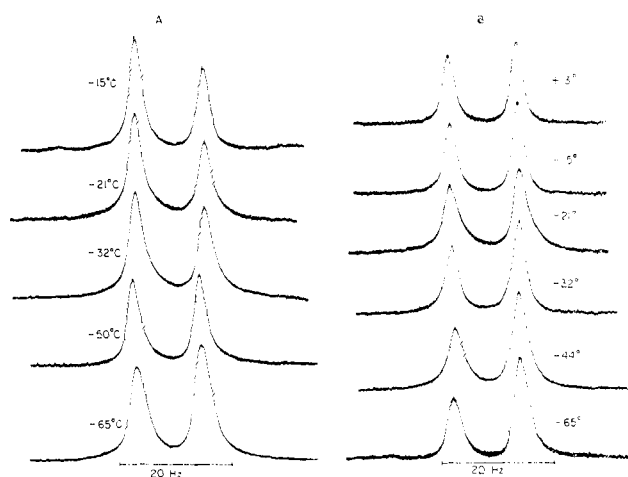


Figure 1. Temperature dependence of the  $CH_2Mg$  proton resonance, 100 MHz, in mixtures of dineopentylmagnesium ( $R_2Mg$ ) and diphenylmagnesium ( $Ph_2Mg$ ) in tetrahydrofuran: (a)  $[R_2Mg]_0 = 0.41$  M and  $[Ph_2Mg]_0 = 0.39$  M; (b)  $[R_2Mg]_0 = 0.51$  M and  $[Ph_2Mg]_0 = 0.32$  M.

$$r = [RMgPh]/2[R_2Mg] \quad (6)$$

$$[R_2Mg] = [1/(1+r)][R_2Mg]_0$$

$$[Ph_2Mg] = \frac{p+rp-r}{1+r}[R_2Mg]_0$$

$$[RMgPh] = [2r/(1+r)][R_2Mg]_0$$

$$K = \frac{[RMgPh]^2}{[R_2Mg][Ph_2Mg]} \quad (7)$$

$$K = 4r^2/(p+rp-r) \quad (8)$$

$[ ]_0$  means initial concentrations,  $[ ]$  are concentrations at equilibrium, and  $r$  is the nmr area ratio of the mixed reagent 1 to dineopentylmagnesium at equilibrium. The results, summarized in Table I, are quite compatible with the simple equilibrium shown in (4). As seen in Table I, the equilibrium is fairly evenly balanced around room temperature. This observation contrasts sharply with the results of House, Latham and Whitesides who found that equilibrium 2 lies far

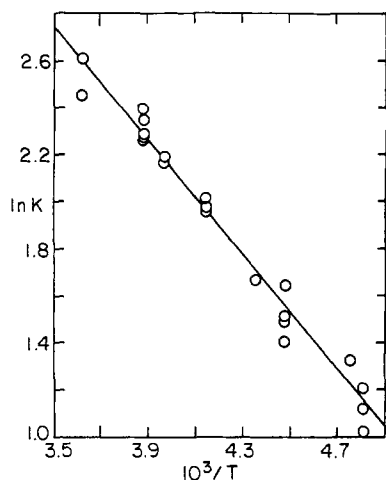


Figure 2. Temperature dependence of the equilibrium constant for  $R_2Mg + Ph_2Mg \rightleftharpoons 2RMgPh$ .

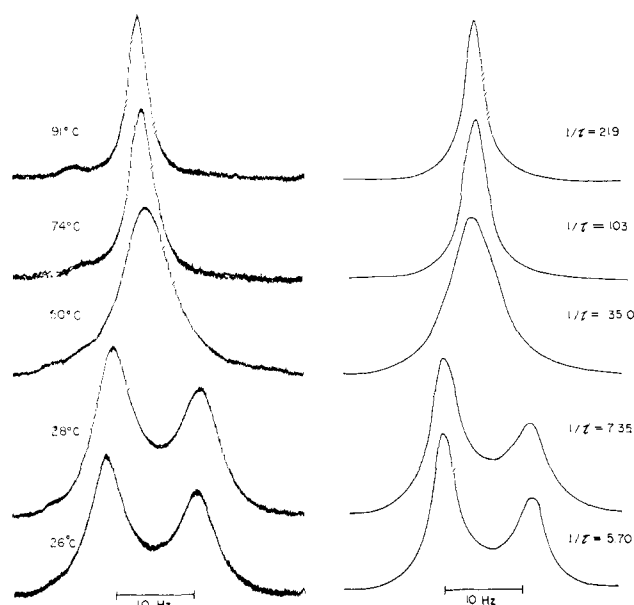
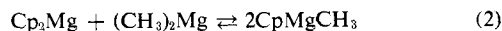


Figure 3. (Left) Nmr, 100 MHz, of  $CH_2Mg$  protons in a mixture originally  $[R_2Mg]_0 = 0.46 M$  and  $[Ph_2Mg]_0 = 0.36 M$  in THF. (Right) Calculated  $CH_2Mg$  line shapes for different preexchange lifetimes,  $\tau_{RMgPh}$ , sec.

to the right.<sup>2</sup> The temperature dependence of the equilibrium constant for (4) is illustrated in Figure 2,



which yields the following thermodynamic parameters:  $\Delta H = +2.40 \pm 0.08$  kcal/mol,  $\Delta S = +13.8 \pm 0.34$  eu,  $\Delta F_{298^\circ} = -1.73 \pm 9.1$  kcal/mol, and  $K_{298^\circ} = 18.8$ . While the enthalpy is nearly neutral, the entropy term largely determines the position of the equilibrium. This implies, in a qualitative way, that solvation differences are mainly responsible for the effects observed. However, very little is known about the mode of magnesium coordination with tetrahydrofuran in solution.

Above 20°, the nmr line shapes for equilibrium mixtures, which contain the components of reaction 4, exhibit the broadening and coalescence behavior of a system undergoing exchange at rates which are on the nmr time scale (see Figures 3 and 4). We have treated

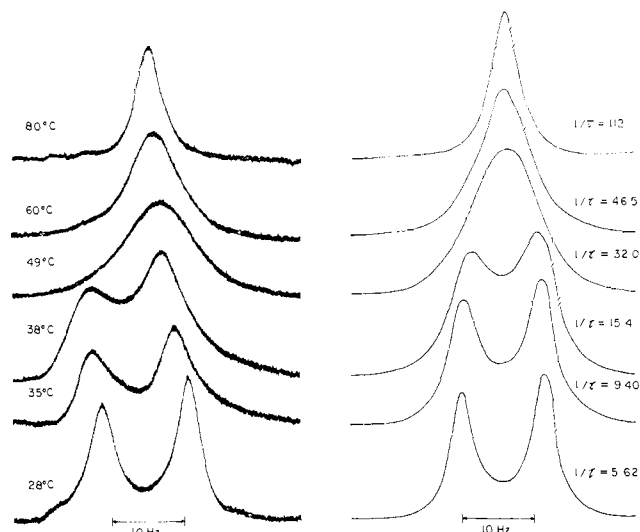


Figure 4. (Left) Nmr, 100 MHz, of  $CH_2Mg$  protons in a mixture originally  $[R_2Mg] = 0.43 M$  and  $[Ph_2Mg] = 0.23 M$ . (Right) Calculated  $CH_2Mg$  lines shapes at different values of  $\tau_{R_2MgPh}$ .

the methylene proton resonance of this system as a simple uncoupled two-site, exchange problem.

Using the shift and line widths obtained under conditions of slow exchange (Figure 1), together with the temperature dependence of the equilibrium constant, nmr line shapes were calculated as a function of the preexchange lifetime  $\tau_{R_2Mg}$  and  $\tau_{RMgPh}$ , recalling that

$$\frac{\tau_{RMgPh}}{\tau_{R_2Mg}} = \frac{[RMgPh]}{[R_2Mg]} \quad (9)$$

This calculation was carried out using the Kubo-Anderson-Sack method;<sup>13</sup> see Experimental Section. Then preexchange lifetimes of  $R_2Mg$  and  $RMgPh$  were determined for the different samples as a function of temperature by comparing theoretical line shapes<sup>13</sup> with the experimental spectra.

A kinetic analysis of these results is started by recalling the definition of  $\tau$  (eq 10).<sup>14</sup> Then we require

$$\frac{1}{\tau_{\text{species}}} = \frac{\text{rate of exchange}}{[\text{species}]} \quad (10)$$

some assumption about the mechanism of exchange. In principle, there are many paths as a result of which a neopentyl group in a  $R_2Mg$  species can be later found in a  $RMgPh$ . One can easily eliminate steps involving free carbanions since there is no evidence that they exist, even fleetingly in ether solutions of organomagnesium compounds. Furthermore, steps involving free ions of any kind can be similarly discounted. We can assume, as discussed above, that all species are monomers in tetrahydrofuran.<sup>11,12</sup> Then there are three bimolecular steps by which the molecular environment of a neopentyl group can be changed. This bare bones kinetic scheme contains for the moment no implications of stereochemistry.

(13) P. W. Anderson, *J. Phys. Soc. Jap.*, **9**, 316 (1954); R. Kubo, *ibid.*, **9**, 935 (1954); R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

(14) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957).

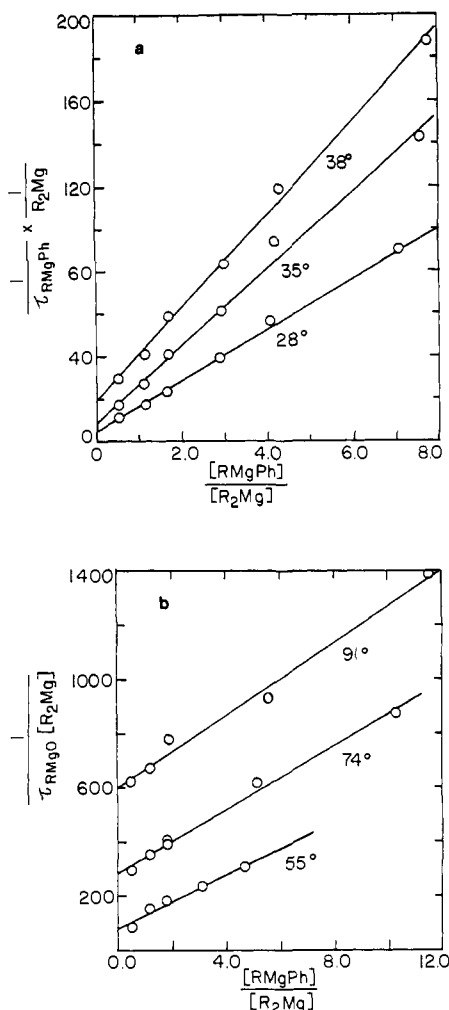
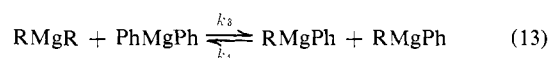
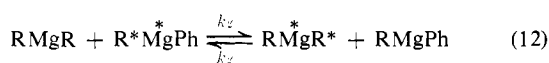


Figure 5. Kinetic plots for the exchanging system at different temperatures: (a) 28–38°, (b) 55–91°.

#### Scheme I



The mean lifetime of  $\text{RMgPh}$  in Scheme I is given by

$$\frac{1}{\tau_{\text{RMgPh}}} = (k_1 + k_2)[\text{R}_2\text{Mg}] + k_4[\text{RMgPh}] \quad (14)$$

Then, if this treatment is justified, a plot of  $(\tau_{\text{RMgPh}} \cdot [\text{R}_2\text{Mg}])^{-1}$  vs. the ratio  $[\text{RMgPh}]/[\text{R}_2\text{Mg}]$  should be linear with a slope of  $k_4$  and intercept  $(k_1 + k_2)$ . Kinetic plots of eq 14 for temperatures between 28 and 91° are shown in Figure 5. The linearity of these plots implies that exchange might indeed take place by all three steps.

Eyring plots of the temperature dependence of the rate constants  $k_2$ ,  $k_3$ , and  $k_4$  are shown in Figure 6. (It will be shown later how  $k_1$  can be neglected.) The activation parameters are listed in Table II.

Having established the analytical nature of the data, it is appropriate to inquire into the broader details of the mechanism.

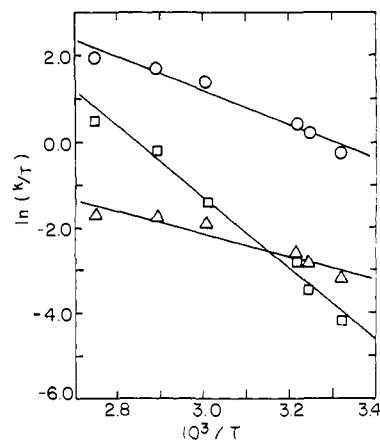
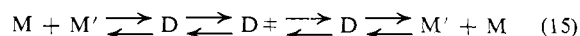


Figure 6. Eyring plots for rate constants for exchanging system: □,  $k_2$ ; ○,  $k_3$ ; △,  $k_4$ .

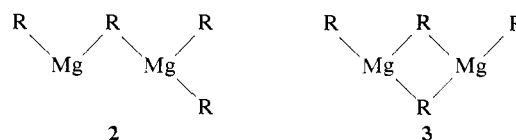
Table II. Activation Parameters for Exchange,  $\text{R}_2\text{Mg} + \text{Ph}_2\text{Mg} \rightleftharpoons 2\text{RMgPh}$

	Kinetic step		
	$k_2$	$k_3$	$k_4$
$k_{301}^\circ \text{K}, M^{-1} \text{sec}^{-1}$	$4.37 \pm 1.1$	$233 \pm 8$	$12.1 \pm 0.3$
$\Delta E, \text{kcal/mol}$	$+17 \pm 1$	$+8.3 \pm 1$	$+6 \pm 1$
$\Delta S^\ddagger, \text{eu}$	$+0.7 \pm 3$	$-22 \pm 3$	$-36 \pm 3$
$\Delta H^\ddagger, \text{kcal/mol}$	$+16.1 \pm 1$	$+7.6 \pm 1$	$+5.6 \pm 1$

Since organomagnesium compounds are known to form dimers in some ethers,<sup>11,15</sup> we must assume that small, though undetectable, concentrations of  $\text{R}_2\text{Mg}$  dimers exist in our tetrahydrofuran solutions also. Furthermore, it is clear from the results described above that dimeric transition states are involved in the exchange process under study. Then the outline of a mechanism would be (15) for the degenerate sequence,



where M and D stand for  $\text{R}_2\text{Mg}$  monomer and dimer, respectively. Next we need to know something about the structure of the dimer. Actually, although very little is known about these dimers, they are undoubtedly held together with alkyl or phenyl bridges. This assumption is based on the known methyl bridging in solid dimethylmagnesium polymer<sup>16</sup> (from crystallography) and on results in other systems such as organoaluminum<sup>17</sup> compounds. Then dimers could be singly or doubly bridged giving rise to structures such as 2 or 3 where the coordination of tetrahydrofuran has been omitted because of lack of information.



Rearrangement within the dimer could take place most simply by concerted migration *via* a four-center,

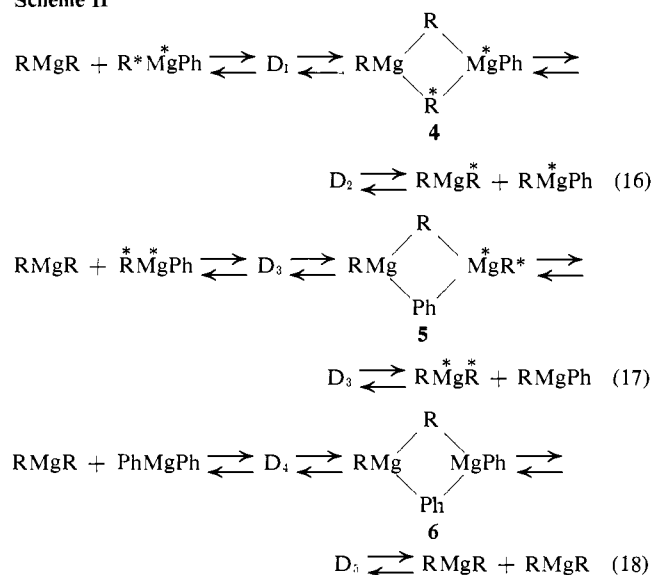
(15) E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, **86**, 4363 (1964); E. C. Ashby and F. W. Walker, *J. Org. Chem.*, **33**, 3821 (1968).

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

(17) K. S. Pitzer and R. K. Sheline, *J. Chem. Phys.*, **16**, 552 (1948); P. M. Lewis and R. A. Rundle, *ibid.*, **21**, 986 (1953).

doubly bridged transition state. The expanded mechanism title for (11)–(13) is proposed to be Scheme II.

## Scheme II



In terms of Scheme II, we can discount the contribution of (16) to the exchange process for the following reasons. It is now well known from work on organoaluminum compounds that phenyl is a far better bridging group than alkyl. It has been claimed that there is an exchange interaction between the  $\pi$  system and vacant orbitals on the metal.<sup>18</sup> For instance, in methylphenylaluminum compounds, the phenyl group is preferentially located at the bridge position, and in  $(\text{CH}_3)_3\text{PhAl}_2$  phenyl is exclusively at the bridge.<sup>18</sup> Thus, on the basis of these observations, transition state **4** can be dropped from consideration since it should be far less stable than **5**, and, hence,  $k_1$  can be ignored and the activation parameters applied to steps 12 and 13.

With regard to the role of solvent in the double bridging mechanism, nothing is known about the structures of complexes of dialkylmagnesium compounds with tetrahydrofuran in solution or even as to how many THF molecules are attached. Reports in the literature show magnesium to coordinate four to six THF molecules.<sup>19</sup> Still, it is safe to assume that formation of a bridged dimer would be accompanied by loss of one or more molecules of THF.

Qualitative experiments show that in the presence of bases stronger than THF, such as *N,N,N',N'*-tetramethylethylenediamine or triethylamine, the rates of exchange in reaction 4 are slower than in THF alone, whereas in ether the exchange is too fast to measure down to  $-90^\circ$ . These observations accord nicely with the proposed mechanism, since the higher dimer concentrations present in less basic solvents should give rise to faster rates of exchange.

The activation parameters obtained from the Eyring plots for three rate constants show that these steps still differ in the smaller details of mechanism. The results qualitatively reflect a linear free-energy relationship in that, while the rate constants are very similar, within a factor of  $<50$ , the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are

(18) G. Hata, *Chem. Commun.*, 7 (1968).

(19) M. C. Percaud and M. T. LeBihan, *Acta Crystallogr., Sect. B*, 24, 1502 (1968); M. Vallino, *J. Organometal. Chem.*, 20, 1 (1969).

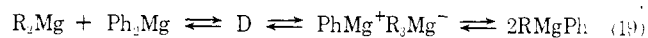
enormously different,  $\Delta H^\ddagger$  by 8 kcal/mol. Comparing the results for (17) and (18), it would appear that the degenerate rearrangement involves the looser transition state with more bond breaking and thus not much change in order; for (18) the transition state is more ordered.

The entropy changes, coming from a combination of aggregation of  $\text{R}_2\text{Mg}$  species and release of THF, are more ambiguous to interpret since the two effects lead to contributions to  $\Delta S^\ddagger$  of opposite sign. Altogether, both transition state, **5** and **6**, seem to lie equidistant between the two sides of (17) and (18). This is qualitatively so for (18) and exactly the case for (17) because of the degenerate character of this step.

House, Latham, and Whitesides' study of reaction 2 leads to conclusions very similar to ours. They used nmr line shapes to measure rates of exchange and proposed a mechanism with a doubly bridged transition state. Their exchange rates were slower in the presence of stronger bases. A kinetic plot of the data presented for  $\tau_{\text{CH}_3\text{MgCp}}$  at  $55^\circ$  vs.  $(\text{CH}_3)_2\text{Mg}$  gives a rate constant of  $10^3 \pm 80 \text{ M}^{-1} \text{ sec}^{-1}$ . Thus, the slow step in the exchange is the degenerate step 3. The other step could not be detected because of the low concentration of dicyclopentadienylmagnesium in the system or because of its low rate constant compared to that for (3).

An alternative to the mechanism involving the double bridge is one in which the organic groups transfer from one magnesium to the other in two separate steps *via* a tight ion-pair intermediate and linear, singly bridged transition states. Such a process for step 13 is envisaged as shown in Scheme III. The stereochemical

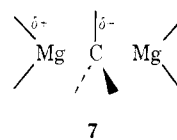
## Scheme III



or



*via*



difference between the two proposed mechanisms is that the four-center group transfer should proceed with retention of configuration, while the two-step process would be accompanied by inversion. In fact, a minor variation of this mechanism was proposed to account for the rates of inversion in the 2-methylbutylmagnesium compound.<sup>10</sup>

There is no way now to distinguish between the two mechanisms since we cannot measure the inversion rate of  $\text{CH}_2\text{Mg}$  in our system. However, House, *et al.*,<sup>2</sup> did investigate the system bis(3,3-dimethylbutyl)magnesium with dicyclopentadienylmagnesium and noted that at  $-20^\circ$  the exchange rate was  $10^4$  times as fast as the inversion rate. Thus, at this point we discount the importance of a two-step ion-pair mechanism.

Thus, in summary we have found that carbon-magnesium bond exchange in the dineopentyl-

magnesium diphenylmagnesium proceeds *via* bridged dimeric transition states.

### Experimental Section

**Chemicals.** All air- and moisture-sensitive compounds were handled under a nitrogen atmosphere. All glassware used was flamed in a current of dry nitrogen.

Triply sublimed magnesium (Dow Chemical) was used to prepare organomagnesium compounds. Neopentyl chloride (from K & K Laboratories) was purified by distillation. Diphenylmercury (Eastman Kodak) was recrystallized from hexane. Tetrahydrofuran (DuPont, anhydrous) was distilled straight into reaction vessels from lithium aluminum hydride (Ventron).

**Dineopentylmercury.** Neopentyl chloride (98.9 g, 0.928 mol) was allowed to react with triply sublimed magnesium turnings (30 g, 1.23 mol) in 750 ml of tetrahydrofuran under reflux (argon atmosphere) with stirring for 2 days. A 1.2 M solution of the Grignard reagent was obtained giving a 95% yield. After filtering out the unreacted magnesium, the Grignard solution was allowed to react with mercuric chloride (90 g, 0.331 mol) under reflux, with stirring, for 5 days. Subsequent hydrolysis and extraction afforded dineopentylmercury, a glassy solid, bp 55° (0.75 mm).

**Dineopentylmagnesium.** Dineopentylmercury (15 g, 0.044 mol) and magnesium turnings (4 g, 17 mol) were refluxed in 50 ml of tetrahydrofuran for 15 days affording a solution 1.5 M in dineopentylmagnesium.

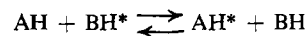
**Diphenylmagnesium.** Diphenylmercury (30 g, 0.0845 mol) and magnesium (3.5 g, 0.144 mol) were allowed to react in tetrahydrofuran at reflux (argon atmosphere) for 3 days. After cooling to room temperature, diphenylmagnesium crystallized out.

**Handling of Samples.** Standard solutions of dineopentylmagnesium and diphenylmagnesium and their mixtures were prepared in the drybox by dilution of stock THF solutions and their concentrations determined by means of Gilman's acid-base titration using phenolphthalein as indicator. All nmr samples were thoroughly degassed and then sealed off with a torch.

**Nmr Spectra.** All spectra were obtained with a Varian HA-100 nmr spectrometer in the frequency sweep mode using a voltage-driven Wavetech audio oscillator to sweep the audiomodulation. Spectra were recorded at a rate of 0.1 Hz sec<sup>-1</sup> at a sweep width of 1 Hz cm<sup>-1</sup>. Four sweeps in both directions through the required line shape were averaged for comparison to theoretical line shapes.

**Nmr Line Shapes.** The transfer of a neopentyl group between dineopentylmagnesium and neopentylphenylmagnesium, magnetic

environment, respectively may be treated as an uncoupled two site exchange.



The density matrix equations for this system in the low-power high-temperature approximation are

$$\rho^B_{\alpha,\beta} \left[ i(\nu - \nu_B) - \frac{1}{\tau_B} - \frac{1}{T_B} \right] + \frac{\rho^A_{\alpha,\beta}}{\tau_B} = \frac{+i\nu_0\nu_1}{2kT}$$

$$\rho^A_{\alpha,\beta} \left[ i(\nu - \nu_A) - \frac{1}{\tau_A} - \frac{1}{T_A} \right] + \frac{\rho^B_{\alpha,\beta}}{\tau_A} = \frac{+i\nu_0\nu_1}{2kT}$$

where A and B indicate the two sites,  $\nu_A$  and  $\nu_B$  are the chemical shifts,  $T$ 's are the phenomenological line-width parameters,  $\tau$ 's are preexchange lifetimes,  $\nu$  is the frequency,  $\nu_1$  is the rf power, and  $\nu_0$  is the average spectrometer frequency. The right-hand side is a constant whose value is assigned ultimately to conveniently scale the intensity. Equations are solved for  $\rho^A_{\alpha,\beta}$  and  $\rho^B_{\alpha,\beta}$  as a function of the frequency  $\nu$ . In matrix form this is given by

$$\begin{pmatrix} \frac{\rho^B_{\alpha,\beta}}{\rho^A_{\alpha,\beta}} \end{pmatrix} = \frac{i\nu_0\nu_1}{2kT} \times \begin{pmatrix} i(\nu - \nu_B) - \frac{1}{\tau_B} - \frac{1}{T_B} & + \frac{1}{\tau_B} \\ + \frac{1}{\tau_A} & i(\nu - \nu_A) - \frac{1}{\tau_A} - \frac{1}{T_A} \end{pmatrix}^{-1}$$

Then the intensity is

$$I(\nu) = (A)\text{Tr}\rho^A I_A^\nu + (B)\text{Tr}\rho^B I_B^\nu = \text{Im}[(A)\rho^A_{\alpha,\beta} + (B)\rho^B_{\alpha,\beta}]$$

This calculation has been carried out by use of a computer program by Saunders<sup>20</sup> derived from the Kubo-Anderson-Sack formulation<sup>13</sup> for nmr line shapes in exchanging systems. Since we are dealing with a first-order uncoupled system, the density-matrix equations reduce to McConnell-style equations, and their solution may be handled with this program.

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