Pt-OOC (glycine), and Pt-NH_3. This result may indicate that the strength of the coordinate bonds in these compounds is similar.

The Pt-Cl stretching force constant used in this investigation is the same as used previously for *trans*-$Pt(NH_3)_2Cl_2$.[18] Also the interaction constant between two Pt-Cl stretching modes takes a similar value as that used for *trans*-$Pt(NH_3)_2Cl_2$ (0.23 mdyne/A). The Pt-Cl (*trans*) stretching force constant is slightly less than the Pt-Cl (*cis*) stretching force constant. This is reasonable since the Pt-Cl (*trans*) bond is slightly weakened compared with the Pt-Cl (*cis*) bonds because of the *trans* effect of ethylene. Other bending and repulsive force constants used in this work are similar to those of other Pt(II) complexes.[17-19]

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[18] K. Nakamoto, P. J. McCarthy, J. Fujita, R. A. Condrate, and G. T. Behnke, *Inorg. Chem.*, 4, 36 (1965).

[19] See footnotes *a* and *b* in Table VII.

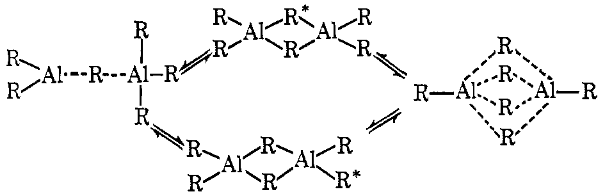
Organometallic Exchange Reactions. V. Proton Magnetic Resonance Study of Methyl Group Exchanges among the Trimethyl Derivatives of Group III. The Cage Effect in Organometallic Dissociations[1]

K. C. Williams and Theodore L. Brown[2]

Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801. *Received July 25, 1966*

Abstract: The exchange of methyl groups between bridge and terminal positions in trimethylaluminum has been studied in toluene solution using proton magnetic resonance spectroscopy. The rate and activation energy are essentially the same as reported for cyclopentane solution. The process is strictly first order in trimethylaluminum. Exchange of methyl groups between trimethylaluminum and trimethylgallium has been observed in cyclopentane and toluene. Trimethylaluminum–trimethylindium exchange has been observed in toluene. From a detailed study of the temperature and concentration dependences of the pmr spectra it is concluded that the over-all rate-determining process in these exchanges is formation of solvent-separated $Al(CH_3)_3$ from $Al_2(CH_3)_6$. Comparison of these exchange data with the results for bridge-terminal exchange in $Al_2(CH_3)_6$ leads to the conclusion that the latter process requires dissociation into solvent-caged monomers. The cage effect favors recombination of monomers in cyclopentane, whereas monomer–solvent interactions prevent extensive intracage recombination in toluene.

The nature of the association of trialkyl derivatives of the group III metals in solution has been extensively studied. It now appears that aluminum is the only metal whose saturated alkyl derivatives are associated in solution.[3] The bridge structure of dimeric trimethylaluminum in hydrocarbon solutions was nicely confirmed by Muller and Pritchard through observation of two peaks in the pmr spectrum of trimethylaluminum in cyclopentane at −75°.[4] At room temperature, only one pmr peak is observed, as a result of methyl group exchange between bridging and terminal positions. Two possible mechanisms were suggested for the exchange: (1) the breaking of one Al–C bond, which may re-form with a different methyl group in the bridging position; or (2) a deformation of the molecule in which no bonds are broken, leading to structure having four bridging methyl groups at the corners of a square. These processes are depicted in eq 1. Since the estimated activation energy (6–14 kcal/mole) was considerably less than the heat of dissociation of the dimer to the monomer, reported to be 20.2 ± 1 kcal/mole in the gaseous phase,[5] an intramolecular process was deemed the more likely. Ramey and co-workers[6] have carried out a more quantitative study of the temperature dependence of the pmr spectra of a number of trialkylaluminum compounds in an attempt to elucidate the mechanism by which alkyl groups are transferred from bridging to terminal positions. For $(Al(CH_3)_3)_2$ the enthalpy of activation for exchange of bridge and terminal groups was found to be 15.6 ± 0.2 kcal/mole. The authors suggested that the exchange occurs by one of the intramolecular processes suggested by Muller and Pritchard. They also studied the interconversion of mixed aluminum alkyls and concluded that the exchange involved rupture of one Al–C bond. Ziegler has discussed the interconversion of mixed aluminum alkyls in some detail.[7] He postulates the following reaction scheme to account for rapid exchange of alkyl groups.



(1)

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[1] This research was sponsored by a grant from the National Science Foundation.

[2] Alfred P. Sloan Research Fellow.

[3] N. Muller and A. L. Otermat, *Inorg. Chem.*, 4, 296 (1965).

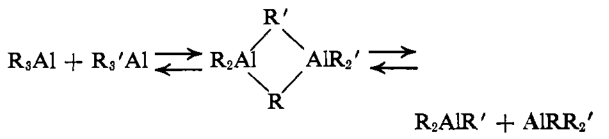
[4] N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, 82, 248 (1960).

[5] A. W. Laubengayer and W. F. Gilliam, *ibid.*, 63, 477 (1941).

[6] K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Barchert, *J. Phys. Chem.*, 69, 3418 (1965).

[7] H. Zeiss, Ed., "Organo-Metallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p 208.

$$(AlR_3)_2 \rightleftharpoons 2AlR_3$$



$$R_3Al + R_3'Al \rightleftharpoons R_2Al(\mu\text{-}R')(\mu\text{-}R)AlR_2' \rightleftharpoons R_2AlR' + AlRR_2' \quad (2)$$

This dissociation process accounts equally well for the pmr results. Swift and co-workers[8] have studied trialkylaluminum compounds using ^{27}Al magnetic resonance and have suggested that the bridge–terminal exchange in trimethylaluminum can be explained in terms of a mechanism based on monomer–dimer equilibrium. Other studies have also been carried out on the interconversion of aluminum alkyls.[9,10]

In this paper we report an investigation of intermolecular exchange of methyl groups between different members of trimethyl compounds of group III metals. Information obtained from this study indicates that the exchange of bridge and terminal groups in trimethylaluminum occurs by a dissociative process.

Experimental Section

Materials and Procedures. All operations were performed in a glove box under an argon atmosphere. Concentrations of group III alkyls were determined by decomposing aliquot samples with dilute nitric acid and mixing with an excess of standard 0.1 *N* EDTA. Excess EDTA was then titrated with a standard 0.1 *N* zinc chloride solution using dithizone as indicator.

Trimethylaluminum was obtained from Ethyl Corp. and was used without further purification. The solvents were passed through a silica gel column, distilled, and stored over sodium wire in an inert atmosphere. Gallium and indium metal were obtained from the Indium Corp. of America, and dimethylmercury was procured from Eastman Organic Chemicals.

Trimethylgallium was prepared from gallium trichloride and trimethylaluminum. After two fractional distillations inside the glove box, a colorless liquid was obtained, boiling at 54–55° (lit.[11] bp 56°). Since contamination with small amounts of halides and trimethylaluminum was a possibility, trimethylgallium was also prepared from gallium metal and dimethylmercury. In the latter preparation, dimethylmercury and excess gallium metal were heated at 100° for 5 or 6 days in a sealed tube (*Caution!*). The tube was then broken open and the trimethylgallium used after filtering without further purification. The purity of the trimethylgallium was assured by examination of the nmr spectrum.

Trimethylindium was prepared by heating excess indium and dimethylmercury at 100° for about 2 weeks in a sealed tube (*Caution!*). The trimethylindium was further purified by recrystallization from cyclopentane.

Measurements of nmr spectra were made in the manner previously reported. Samples were degassed and sealed under vacuum in standard size nmr tubes. Solution concentrations were normally in the range of 0.2 to 0.3 *M*.

Interpretation of Nmr Data. Two methods were used to estimate $1/\tau_e$, the reciprocal mean lifetime of methyl groups between exchanges. The first involves comparison of the experimental spectra with calculated spectra using the two-site program previously described.[12] The second involves examination of the individual line widths in the region of slow exchange. Under the condition of slow exchange, the resonances are broadened; the line width is related to the mean lifetime (τ_j) by the expression

$$1/\tau_j = (\Delta_{1/2} - \Delta_{1/2}^0) \qquad (3)$$

where $\Delta_{1/2}^0$ is the measured half-intensity width for the *j*th component in the absence of exchange. This procedure is valid regardless of the number of sites in the system, provided the broadening is not large enough to cause appreciable overlap of the signals.

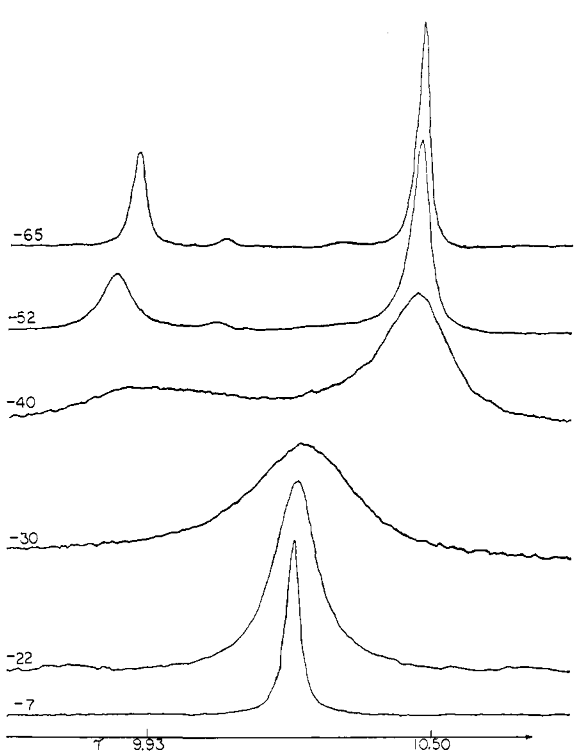


Figure 1. Temperature dependence of the pmr spectrum of $Al_2(CH_3)_6$ in toluene.

For $(Al(CH_3)_3)_2$ in toluene, both methods were used to estimate the reciprocal mean lifetimes. Since the internal chemical shift between bridge and terminal groups is temperature dependent in this solvent, use of the two-site program presented some problems. The fitting of calculated and observed line shapes can be carried out for a two-dimensional fitting of both τ_e and $\delta\omega$, but this clearly places a limitation on the accuracy attainable for τ_e. As an aid in choosing appropriate values of $\delta\omega$, the internal chemical-shift difference observed at the low temperatures in the region of slow exchange was extrapolated to higher temperatures. This technique made it possible to restrict consideration of $\delta\omega$ values to a reasonably small range and facilitated choice of best $\delta\omega$ and τ_e. To estimate transverse relaxation times for use in the two-site program, and as an estimate of $\Delta_{1/2}^0$ for eq 1, the half-intensity line width of cyclopentane was employed. This procedure, employed by Ramey and co-workers[6] in their study of the trimethylaluminum exchange in cyclopentane, gave results from use of eq 1 in agreement with those obtained from use of the two-site program for trimethylaluminum exchange in toluene.

Results and Discussion

It is convenient to initiate a discussion of the results by considering the exchange of bridge and terminal methyl groups of trimethylaluminum in toluene. The nmr spectrum of trimethylaluminum in toluene as a function of temperature is displayed in Figure 1. In general, the spectra are similar to those obtained in cyclopentane, except for the temperature dependence of the internal chemical shift, which results mainly from variation in the chemical shift of the bridge methyls. From analysis of the over-all line shape in the temperature region below the coalescence point, a plot of log $1/\tau_e$ *vs.* $1/T$ was obtained, as shown in Figure 2. The quantity τ_e is defined as $1/\tau_e = 1/\tau_t + 1/\tau_b$. For $(Al(CH_3)_3)_2$, τ_b refers to the average time a particular methyl group spends in the bridging position and τ_t to the corresponding time for the terminal position. An activation energy of 15.4 ± 2 kcal/mole is obtained

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[8] C. P. Poole, Jr., H. E. Swift, and J. F. Itzel, Jr., *J. Chem. Phys.*, 42 (7), 2576 (1965).

[9] E. G. Hoffman, *Trans. Faraday Soc.*, 58, 642 (1962).

[10] T. Mole and J. R. Surtess, *Australian J. Chem.*, 17, 310 (1964).

[11] G. E. Coates, *J. Chem. Soc.*, 1951, 2003.

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

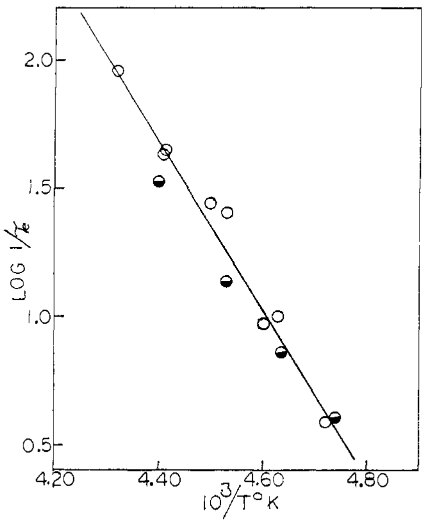


Figure 2. Log $1/\tau_e$ *vs.* $1/T$ for methyl group exchange in $Al_2(CH_3)_6$ in toluene: ◒, two-site exchange program data; ○, half-intensity line-width data. The Arrhenius activation energy is 15.4 ± 2 kcal/mole.

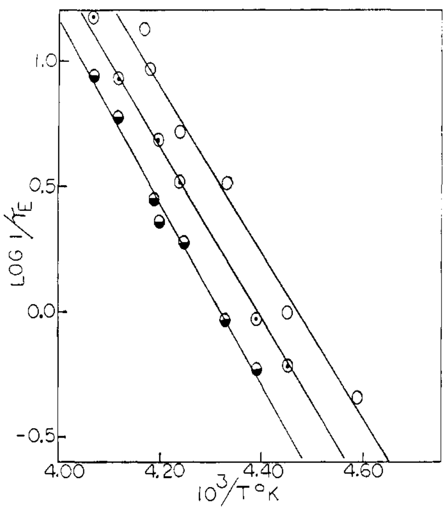


Figure 4. Log $1/\tau_e$ *vs.* $1/T$ for methyl group exchange in $Al_2(CH_3)_6$–$Ga(CH_3)_3$ mixtures in cyclopentane: ◒, (D)/(E) = 0.184; ⊙, (D)/(E) = 0.366; ○, (D)/(E) = 0.690. The Arrhenius activation energy is 15.9 ± 0.5 kcal/mole.

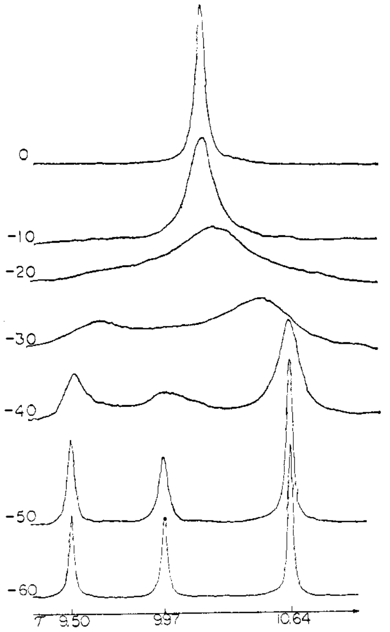


Figure 3. Proton magnetic resonance spectra of an $Al_2(CH_3)_6$–$Ga(CH_3)_3$ mixture in cyclopentane at various temperatures.

from the slope. This is the same value, within experimental uncertainty, as reported for cyclopentane solutions. The rather large error limit placed upon the estimated activation energy reflects the difficulties associated with temperature variation of the internal chemical shift. The concentration dependence of the bridge–terminal exchange was investigated over a concentration range greater than tenfold; the rate is independent of concentration over the range accessible by conventional nmr techniques. It is evident, therefore, that the exchange is first order in trimethylaluminum dimer.

The nmr spectra of a trimethylaluminum–trimethylgallium solution in cyclopentane at various temperatures are shown in Figure 3. At room temperature the spectrum consists of a single line; at low temperatures, of three lines, corresponding to the bridge and terminal methyls of trimethylaluminum, and trimethylgallium. All lines at low temperature occur at the chemical shifts found for the pure components. Log $1/\tau_E$ for the trimethylgallium absorption, obtained from measurements of the half-intensity width, is shown as a function of $1/T$ in Figure 4 for three different solutions of $Al_2(CH_3)_6$ and $Ga(CH_3)_3$ in cyclopentane. The quantity τ_E refers to the average time between exchanges for a methyl group on $Ga(CH_3)_3$. The lines, which are parallel within experimental uncertainty, yield an Arrhenius activation energy of 15.9 ± 0.5 kcal/mole for the exchange. Although the exchange rate is observed to depend on the ratio of concentrations of the two components, dilution of any one sample does not affect the exchange rate at all.

A similar study was conducted on toluene solutions of trimethylaluminum and trimethylgallium. The Arrhenius plots for two different solutions are shown in Figure 5. Again, the exchange rate is found to depend on the ratio of concentrations only. An Arrhenius activation energy of 16.5 ± 1 kcal/mole is estimated for the toluene systems. The trimethylindium–trimethylaluminum system was also studied in toluene; the results for two different solutions, Figure 6, were the same as those obtained with trimethylgallium. The Arrhenius activation energy from these data is 16.4 ± 1 kcal/mole.

The above results immediately rule out at least one of the more obvious possible mechanisms of methyl exchange between trimethylgallium or trimethylindium and trimethylaluminum, namely a bimolecular reaction between $(CH_3)_3M$ and $(CH_3)_6Al_2$. The correct approach to a mechanism is suggested by the observations that (a) methyl exchange between trimethylindium and trimethylaluminum exhibits the same kinetic behavior as found in the analogous trimethylgallium system; (b) the Arrhenius activation energies obtained in both systems are, within experimental uncertainty, the same as found for bridge–terminal exchange of methyl groups in trimethylaluminum.

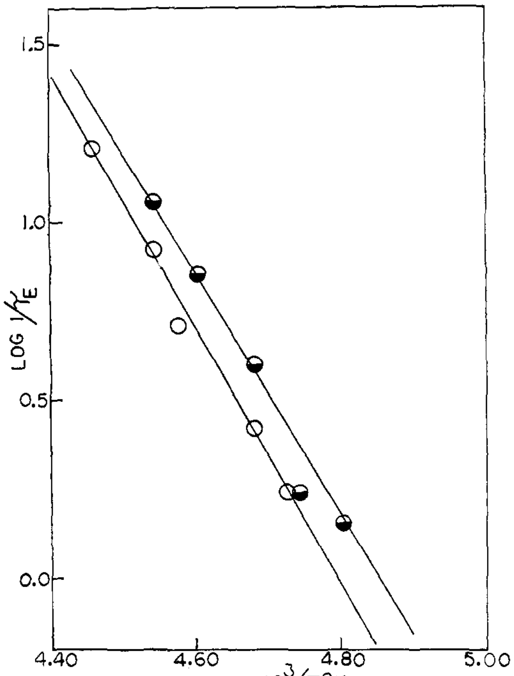


Figure 5. Log $1/\tau_E$ *vs.* $1/T$ for methyl group exchange in $Al_2(CH_3)_6$–$Ga(CH_3)_3$ mixtures in toluene: ○, (D)/(E) = 0.342; ◓, (D)/(E) = 0.470. The Arrhenius activation energy is 16.5 ± 1 kcal/mole.

We propose that trimethylaluminum is involved in a two-step equilibrium of the form

$$\underset{\substack{\text{dimer}\\ \text{D}}}{Al_2(CH_3)_6} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\substack{\text{solvent-caged}\\ \text{monomers}\\ \text{SCM}}}{2Al(CH_3)_3} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\substack{\text{solvent-separated}\\ \text{monomers}\\ \text{M}}}{Al(CH_3)_3 + Al(CH_3)_3} \quad (4)$$

The existence of solvent-caged monomers is not required to explain the exchange results with $Ga(CH_3)_3$ or $In(CH_3)_3$ *per se*, but is necessary in order to understand these data in relation to the bridge–terminal exchange in trimethylaluminum. If the steady-state concentration of solvent-separated monomers is small, as it certainly is in this system, the concentration of solvent-caged monomers is proportional to the concentration of dimer. This follows from the expression for the steady-state concentration of solvent-caged species[13,14]

$$D \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SCM \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2M \quad (5)$$

$$\frac{d(SCM)}{dt} = k_1(D) - k_{-1}(SCM) - k_2(SCM) + k_{-2}(M)^2 = 0 \quad (6)$$

$$(SCM) = \frac{k_1(D) + k_{-2}(M)^2}{k_{-1} + k_2} \quad (7)$$

Since the steady-state concentration of M is very small, $k_1(D) \gg k_{-2}(M)^2$

$$(SCM) = \frac{k_1(D)}{k_{-1} + k_2} \quad (8)$$

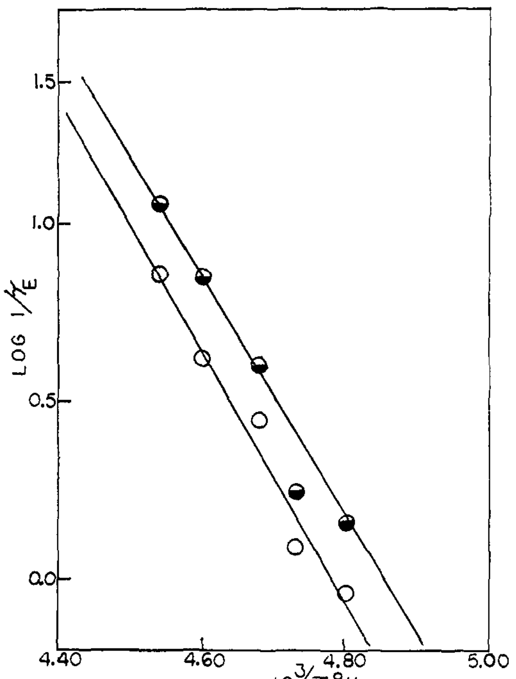
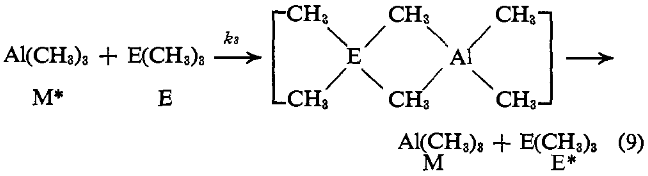


Figure 6. Log $1/\tau_E$ *vs.* $1/T$ for methyl group exchange in $Al_2(CH_3)_6$–$In(CH_3)_3$ mixtures in toluene: ○, (D)/(E) = 0.280; ◓, (D)/(E) = 0.496. The Arrhenius activation energy is 16.4 ± 1 kcal/mole.

Exchange of methyl groups with another group III trimethyl compound occurs in a rapid step



The steady-state concentration of monomer is given by the expression

$$(M) = \frac{2k_2(SCM)}{2k_{-2}(M) + k_3(E)} \quad (10)$$

We have also

$$\frac{d(E^*)}{dt} = k_3(M)(E) = \frac{2k_2k_3(SCM)(E)}{2k_{-2}(M) + k_3(E)} = \frac{2k_1k_2k_3(D)(E)}{(k_{-1} + k_2)\{2k_{-2}(M) + k_3(E)\}} \quad (11)$$

The reciprocal mean exchange lifetime is given by the expression

$$\frac{1}{\tau_E} = \frac{1}{3(E)}\frac{d(E^*)}{dt} = \frac{2}{3}\frac{k_1k_2k_3(D)}{(k_{-1} + k_2)\{2k_{-2}(M) + k_3(E)\}} \quad (12)$$

(The factor $^1/_3$ arises because the lifetime of a methyl group on an E site is three times the rate of exchange.) It is possible to distinguish two important cases for the relative values to be assigned the rate constant expressions.

Case A: $k_3(E) \gg k_{-2}(M)$, $k_{-1} \gg k_2$. The first of these conditions is completely consistent with the concentration dependences observed experimentally. The second condition corresponds to the situation in which there is a relatively rapid recombination of the mono-

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(13) (a) R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955); (b) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

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

mers within the solvent cage. It is the sort of behavior to be expected when the solvent does not interact to an appreciable degree with the dissociated monomers still trapped in the cage. Relative rates of recombination *vs.* separation into solvent-separated species have been evaluated in some free-radical systems; it has been found that recombination may be favored by factors of from 10 to 100.[14,15] These two conditions lead to the following expression for $1/\tau_E$.

$$\frac{1}{\tau_E} = \frac{2}{3}\left(\frac{k_2}{k_{-1}}\right)k_1\frac{(D)}{(E)} \tag{13}$$

The exchange rate is proportional to the rate constant for initial formation of solvent-caged monomers times a factor which is the ratio of the recombination to solvent-separation rate constants.

Case **B**: $k_3(E) \gg k_{-2}(M)$, $k_2 \gg k_{-1}$. The second condition in this instance corresponds to the situation in which the solvent interacts to an important degree with the dissociated species, so that solvent separation predominates over recombination.[14] The expression which results for $1/\tau_E$ in this instance is

$$\frac{1}{\tau_E} = \frac{2}{3}k_1\frac{(D)}{(E)} \tag{14}$$

The first condition stated in arriving at eq 13 and 14 can be readily tested by observing the effect of concentrations on the reciprocal mean lifetime of a methyl group on the E site. Table I shows data taken from the three lines of Figure 4 at $-37°$. A graph of the concentration ratio *vs.* $1/\tau_E$ extrapolates through the origin, with a slope of $11.5\ \text{sec}^{-1} = {}^2/_3k_{\text{eff}}$. The vertical separations observed in the Arrhenius plots for different solutions in toluene, Figures 4–6, also are in excellent agreement with the expectations based on eq 13 and 14. There is the further observation that dilution does not affect the exchange rate.

Table I. Dependence of the Reciprocal Mean Lifetime of a Methyl Group on Trimethylgallium on the Trimethylaluminum/Trimethylgallium Ratio (Data from Figure 4 at $-37°$)

$[Me_6Al_2]$/ $[Me_3Ga]$	$1/\tau$ $(GaMe_3)$
0.184	1.98
0.336	3.32
0.690	5.88

An additional experimental observation, which indirectly supports the above conclusions, is that trimethylgallium and trimethylindium mixtures in toluene exhibit rapid exchange of methyl groups at the lowest temperature studied, $-65°$. Since both these species are monomeric, the fact that the exchange is rapid is support for the assumption that the analogous process in the trimethylaluminum system, eq 9, is fast. These considerations are consistent also with the observation of Maher and Evans,[16] that methyl group exchange of trimethylthallium in toluene occurs through a bimolecular process, with a relatively low activation energy of 6.3 kcal/mole. It thus appears that the assumption $k_3(E) \gg k_{-2}(M)$ is justified.

To further test the proposed mechanism it is necessary to compare the rate of exchange between trimethylaluminum and a second trimethyl compound with the rate of bridge–terminal exchange in trimethylaluminum itself. Table II shows rate constants for bridge–terminal exchange in solutions of trimethylaluminum in cyclopentane and toluene. The rate constants listed are based on the assumption of a dissociative process; *i.e.*, we assume that the rate-determining process in the bridge–terminal exchange is the formation of solvent-caged monomers, with rate constant k_1 (eq 4). In view of the difficulties encountered in obtaining accurate rate constants in toluene, it may be doubted whether the rate of exchange is significantly different in this solvent than in cyclopentane. Table III lists for comparison the quantity $k_{\text{eff}} = {}^3/_2(1/\tau_E)(E)/(D)$ for trimethylgallium–trimethylaluminum exchange. This is equal to k_1 in the case of eq 14, and to $k_1(k_2/k_{-1})$ in the case of eq 13.

Table II. Rate Constants for Bridge–Terminal Exchange in Trimethylaluminum in Cyclopentane and Toluene Solutions[a]

Temp, °C	k_1,[a] sec^{-1} Cyclopentane[b]	Toluene
−55	7.65	12.3
−50	18.8	26.3
−45	46.2	52.5

[a] The rate constant, k_1, is related to τ_T and τ_B by $k_1 = 3/\tau_T$ and $k_1 = {}^3/_2\tau_B$; therefore, $k_1 = 1/\tau_e$. [b] Based on data in ref 6, after modification of statistical factors in relating τ_e to k_1.

Table III. Effective Rate Constants for Methyl Group Exchange between Trimethylaluminum and Trimethylgallium in Cyclopentane and Toluene

Temp, °C	k_{eff}, sec^{-1} Cyclopentane	Toluene
−55	0.9	18.8
−50	2.1	43.2
−45	4.5	92.0

It is clear that in toluene the rate constant for trimethylaluminum–trimethylgallium exchange is numerically the same, within experimental uncertainty, as the rate constant for bridge–terminal exchange. *This fact strongly rules against the possibility that bridge–terminal exchange is rate determined by an intramolecular process such as depicted in eq 1.* Substitution of one of the intermediates of eq 1 for solvent-caged monomers (SCM) in eq 4 and 5 would require that the intermediate dissociate to solvent-separated monomers with essentially zero activation energy. This does not seem plausible, since there still exists relatively strong bridge bonding in the intermediate. It is plausible, on the other hand, for solvent-caged monomers. A direct bimolecular process between $Ga(CH_3)_3$ and any form of $Al_2(CH_3)_6$ has been ruled out as the rate-determining step in this exchange. The dissociation to the monomeric form which is required for exchange with $Ga(CH_3)_3$ provides a pathway for bridge–terminal exchange as well. It is not necessary to postulate any intramolecular bridge–terminal exchange; if it occurs at all,

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(15) (a) R. K. Lyon and D. H. Levy, *J. Am. Chem. Soc.*, **83**, 4290 (1961); (b) S. Fujita, S. Kodama, and O. Toyama, *Bull. Chem. Soc. Japan*, **39**, 1323 (1966).

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

it must be slow in relation to the dissociative process. The second point which needs to be made about the equality of rate constants in these two processes is that the toluene solutions correspond to case **B**, in which the solvent-caged monomers proceed preferentially to the solvent-separated species, as opposed to recombination. The reason for this behavior in toluene lies in the strongly Lewis acid character of the monomeric species, coupled with the donor character of the aromatic system.[17]

The cyclopentane data correspond to case A, in which the solvent-caged monomers preferentially recombine as opposed to forming solvent-separated species. The rate constant for bridge–terminal exchange is about ten times larger than the effective rate constant for trimethylaluminum–trimethylgallium exchange. This implies that the ratio k_2/k_{-1} is about 10, which is in very reasonable accord with information available from studies of free-radical systems for the relative propensities of recombination *vs.* solvent separation in a relatively inert solvent.

The apparent Arrhenius activation energies obtained in this work fully support the proposed mechanism. It is to be expected that in both toluene and cyclopentane the activation energy for exchange is that associated with formation of the solvent-caged monomers. The identity of the rate-determining process for bridge–terminal exchange with that for trimethylaluminum exchange with trimethylgallium or trimethylindium is thus reflected in the essentially identical values obtained for the activation energies.

The assumption that the rate-determining process for bridge–terminal exchange is dissociation of the dimer into solvent-caged monomers raises the question of how well the activation energy for dissociation, on the order of 15–16 kcal/mole, compares with the heat of dissociation of $Al_2(CH_3)_6$ in the gas phase, about 20 kcal/mole. It is difficult to assess the absolute error in either of these estimates, but the comparison does not seem unreasonable. It is unlikely that the activation energy for dissociation is much greater than the enthalpy of dissociation, and some decrease in the latter may be expected in a condensed phase as opposed to the gas phase. Nevertheless it would be of interest to have further data regarding the thermodynamics of dissociation of trialkylaluminum systems, in both the gas and condensed phases.

The present results are important for a correct understanding of certain other exchange data in the literature. Intermolecular exchange between trimethylaluminum and dimethylcadmium has been observed[18] and was interpreted in terms of a bimolecular rate-determining process. The present results make it extremely unlikely, however, that the exchange is a simple second-order process. Brunner, Wailes, and Kaesz[19] have observed that the adduct $(C_5H_5)_2WH_2Al(CH_3)_3$ undergoes rapid exchange with $Al_2(CH_3)_6$. From the reported temperature dependence it appears that the exchange may involve dissociation of the dimer as the rate-determining step.

The solvent cage effect should be operative in a variety of organometallic exchange systems in which a rate-determining dissociation is operative. The much slower exchange between *t*-butyllithium and lithiomethyltrimethylsilane in cyclopentane as compared with toluene[20] no doubt results from a cage effect.

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The Donor Properties of Pyrophosphate Derivatives. III. A Colorless Copper(II) Complex

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Abstract: Complexes of octamethylpyrophosphoramide (OMPA) with Cu(II), Co(II), Fe(III), Ag(I), and Hg(II) have been prepared and characterized. These include $[Cu(OMPA)_3](ClO_4)_2$, $[Cu(OMPA)_2][CuBr_4]$, $[Ag(OMPA)_2]ClO_4$, $[Hg(OMPA)_3](ClO_4)_2$, $[Co(OMPA)_3][CoBr_4]$, and $[Fe(OMPA)_3](ClO_4)_3$. The most unique compound of these is $[Cu(OMPA)_3](ClO_4)_2$, believed to be the first cationic, six-coordinate complex of Cu(II), which is colorless.

We have previously reported the isolation of complexes of octamethylpyrophosphoramide (OMPA) with a wide variety of metal ions.[2,3] Octamethylpyrophosphoramide is believed to form a six-membered ring with the metal ion[4] in which the phosphoryl oxygens are the donor sites. We have attributed the stability of metal complexes of OMPA

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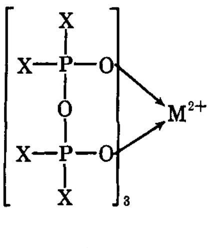

where X = $N(CH_3)_2$.