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INTRAMOLECULAR EXCHANGE OF METHYL GROUPS IN μ-METHYL-μ-DIPHENYLAMINOTETRAMETHYLDIALUMINUM AND ITS INTERMOLECULAR EXCHANGE WITH TRIMETHYLGALLIUM

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Summary

Intramolecular exchange of the methyl groups in μ-methyl-μ-diphenylaminotetramethyldialuminum (I) proceeds via a first order process with activation parameters, E_a = 13.7 ± 0.45 kcal/mol, $\Delta H^{\ddagger}$ = 13.0 ± 0.6 kcal/mol and $\Delta S^{\ddagger}$ = —5.8 ± 3.6 e.u. at 290 K. A mechanism involving a single bridge opening is proposed for this exchange.

The exchange between I and trimethylgallium was examined and found to proceed via a process first order in I and independent of the concentration of $Ga(CH_3)_3$ with activation parameters E_a = 20.7 ± 0.8 kcal/mol, $\Delta H^{\ddagger}$ = 20.1 ± 0.8 kcal/mol and $\Delta S^{\ddagger}$ = +16.0 ± 4.2 e.u. at 290 K. A mechanism for this process is proposed in which the rate-determining step is the opening of the methyl bridge accompanied by substantial distortion in I.

Introduction

The exchange reaction of alkyl groups in bridged organometallic compounds has been of major interest since the first reports on the exchange among bridge and terminal groups in trimethylaluminum dimer [1]. There have been numerous studies on this system [2], and reports also have appeared on various other exchange processes, both in systems containing equivalent bridging groups [3—6] and in systems in which dissimilar bridging groups occur [7—10]. It has been suggested that at least three mechanisms occur for these exchange processes. The first is a dissociative mechanism which takes place in the "weakly bridged" systems such as trimethylaluminum. The second process is thought to involve a single bridge opening or some other intramolecular process where one bridge is "strong" and the second "weak". The evidence for the latter process is excellent for the dissimilar bridged systems [7] and also seems convincing for the similar bridged tolyl systems [6]. The third process proposed for inter-

molecular exchange does not involve bridge opening and occurs in systems in which one of the species involved has two strong bridging groups. An example of this appears to be the exchange between trimethylaluminum and bis(μ-phenylethynyl)tetramethyldialuminum in which pentacoordinate aluminum was suggested in the transition state [5].

We now wish to report a detailed study on the intramolecular bridge-terminal exchange of μ-methyl-μ-diphenylaminotetramethyldialuminum (I), first observed by Magnuson and Stucky [8,9], and on the intermolecular exchange of this species with trimethylgallium.

Experimental

Bis(μ-diphenylamino)tetramethyldialuminum was prepared by the method of Kawai et al. [11] directly from diphenylamine (Baker reagent grade) and trimethylaluminum (Ethyl Corp.). This product was used without further purification. The purity, however, was checked by examination of the NMR spectrum which gave a broad unresolved set of lines at δ 7.1 ppm, due to the phenyl groups and a sharp singlet at δ —0.58 ppm for the methyl groups with an intensity ratio of 5/3. The reactions and properties of this compound have been described in detail elsewhere [12].

μ-Methyl-μ-diphenylaminotetramethyldialuminum was prepared by reaction of a large excess of trimethylaluminum (Ethyl Corp.) with bis(μ-diphenylamino)-tetramethyldialuminum as shown in eq. 1. The compounds were mixed in a tube which was then sealed and heated for approximately two weeks at 115°C. The tube

$$Al_2(CH_3)_6 + (\mu\text{-NPh})_2Al_2(CH_3)_4 \rightleftharpoons 2(\mu\text{-CH}_3)(\mu\text{-NPh}_2)Al_2(CH_3)_4 \qquad (1)$$

was then reattached to the vacuum line and the volatile products (primarily the excess $Al_2(CH_3)_6$ necessary to drive the reaction to the right) were removed. The white solid product, thus obtained, was 90—97% I as determined from the low temperature NMR spectrum. Attempts to sublime the product on a reasonable scale led to decrease in the purity of the product by a shift in the equilibrium shown in eq. 1 to the left with loss of trimethylaluminum. The above procedure is somewhat different than that originally described by Magnuson and Stucky [8,9], but gave rise to a product which had an identical NMR spectrum with two lines at 1.73 and 2.69 ppm above the methyl group of toluene (the toluene methyl peak is 2.31 ppm downfield from TMS) in a 4/1 ratio at low temperature.

Trimethylgallium was prepared by the exchange reaction between dimethylmercury and gallium metal with a trace of mercuric chloride present as a catalyst as described previously [13]. The product was fractionally distilled and the purity checked by examination of its NMR spectrum which gave a single sharp line, 1.48 ppm above cyclopentane (the cyclopentane peak is 1.50 ppm downfield from TMS).

Baker reagent grade cyclopentane and toluene used as solvents and reference were dried over Na/K.

The samples containing I were made from a stock solution prepared in toluene and stored in a dry box (N_2 atmosphere scavenged by NaK). All samples were capped in the dry box with a standard taper joint and stopcock. They were then transferred to a vacuum system, degassed, and sealed or had trimethyl-

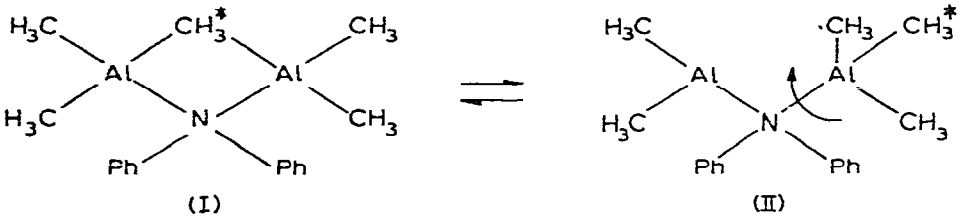
gallium added directly from a calibrated volume on the vacuum system and then sealed for use.

All NMR spectra were obtained using a Varian Associates A60-A spectrometer equipped with variable temperature probe and control unit. The temperatures were calibrated using a methanol sample before and after each kinetic measurement [14]. The life times were determined using a two site exchange program [15] or using a program specifically written for this problem [16].

Results and discussion

Life times for the bridge and terminal methyl groups in μ-methyl-μ-diphenylaminotetramethyldialuminum as a function of concentration at 290 K are given in Table 1. These data clearly show that the exchange reaction is independent of concentration. They also show that the exchange life time of the bridging group is 1/4 that of the terminal groups as expected from the two site exchange program, a fact which is also born out by independent estimate of the life times by use of the aproximation, $1/\tau = \pi(\nu_{1/2} - \nu_{1/2}^{\circ})$.

This behavior is consistent with the mechanism indicated in eq. 2 in which a single bridged species forms in the transition state followed by rotation of the



(2)

$Al(CH_3)_3$ moiety which effects exchange. This species then recloses to form I leading to equilibration of the bridge and terminal sites.

Complete dissociation can be ruled out unequivocally for two reasons. First, I does not undergo rapid exchange with the dimer bis(μ-diphenylamino)tetramethyldialuminum as indicated in Fig. 1 nor for that matter even with trimethyl-

TABLE 1

KINETIC PARAMETERS FOR THE INTRAMOLECULAR METHYL GROUP EXCHANGE IN μ-METHYL-μ-DIPHENYLAMINOTETRAMETHYLDIALUMINUM AT 290 K

Concentration (mol/kg toluene)	E_a [a,b] (calcd.) (kcal/mol)	$1/\tau_B$ (sec^{-1})	$1/\tau_T$ (sec^{-1})
0.048		45.1	11.3
0.074	14.6 ± 1	47.8	12.0
0.092	12.8 ± 0.5	51.2	12.8
0.120	14.2 ± 0.9	50.4	12.6
0.130	13.0 ± 0.7	48.6	12.2
0.173		46.9	11.7
	av. 13.6 ± 1	av. 48.3 ± 2.2	av. 12.1 ± 0.55

[a] E_a values were obtained from least squares fits of Arrhenius plots of ln $1/\tau$ vs. $1/T$ (K).
[b] $\Delta H^{\ddagger}$ 13.0 ± 0.6 kcal/mol, $\Delta S^{\ddagger}_{290K}$ −5.8 ± 3.6 e.u.

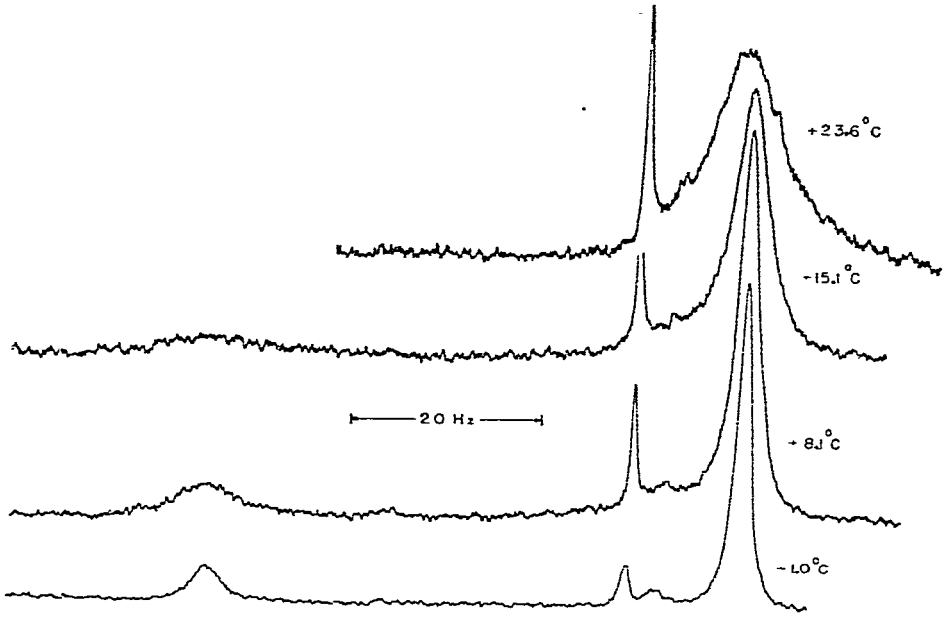


Fig. 1. The 60 MHz proton NMR spectrum of μ-methyl-μ-diphenylaminotetramethyldialuminum as a function of temperature in toluene solution.

aluminum or -gallium under the conditions used to study the bridge-terminal exchange. Second, the amount of bis(μ-diphenylamino)tetramethyldialuminum present as an impurity in the sample remains constant under the conditions used for kinetic measurement, and, in fact, does not change until the sample temperature is raised to ~100° C for an extended period. Then complete dissociation may occur with formation of free trimethylaluminum and bis(μ-diphenylamino)-tetramethyldialuminum. Under the latter conditions bis(μ-diphenylamino)tetramethyldialuminum builds up in the sample, suggesting that it is the thermodynamically stable product, but even then I does not undergo rapid intermolecular exchange with the trimethylaluminum present in the sample.

The temperature dependent spectrum of a sample of I is given in Fig. 1. A plot of the lifetimes as a function of temperature for five different samples is given in Fig. 2 and leads to an Arrhenius activation energy of 13.7 ± 0.5 kcal/mol. The enthalpy and entropy terms associated with this reaction were calculated to be $\Delta H^{\ddagger}$ —13.0 ± 0.6 kcal/mol and $\Delta S^{\ddagger}$ —5.8 ± 3.6 e.u. at 290 K. All values are from the least squares fit with standard deviations given as error limits.

The second system examined is more complex and involves the intermolecular transfer or equilibration of the alkyl groups on I with those on $Ga(CH_3)_3$. The qualitative behavior of this system can be seen on examination of Fig. 3 which shows the temperature dependence of a sample containing both compounds. At approximately 30° C, two broadened lines are observed which implies exchange is occurring between $Ga(CH_3)_3$ and I. As the temperature is lowered, the low field line sharpens. In addition, the broad, high field absorption sharpens and a new resonance appears further downfield. These lines can be identified with the

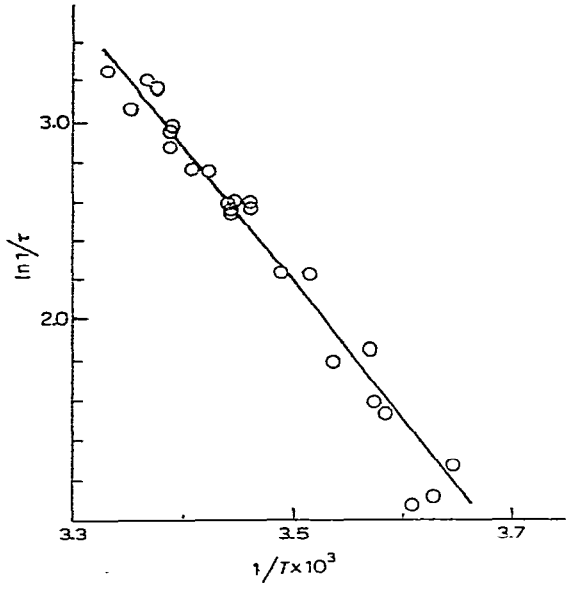


Fig. 2. The least squares Arrhenius activation plots for the intramolecular bridge-terminal methyl group exchange in μ-methyl-μ-diphenylaminotetramethyldialuminum (ln $1/\tau$ terminal vs. $1/T \times 10^3$ for 5 samples; $E_a = 13.7 \pm 0.45$ kcal/mol.

bridging methyl group, trimethylgallium, and the terminal methyl groups going from low to highfield.

The lifetimes for a series of samples are collected in Table 2. The concentration

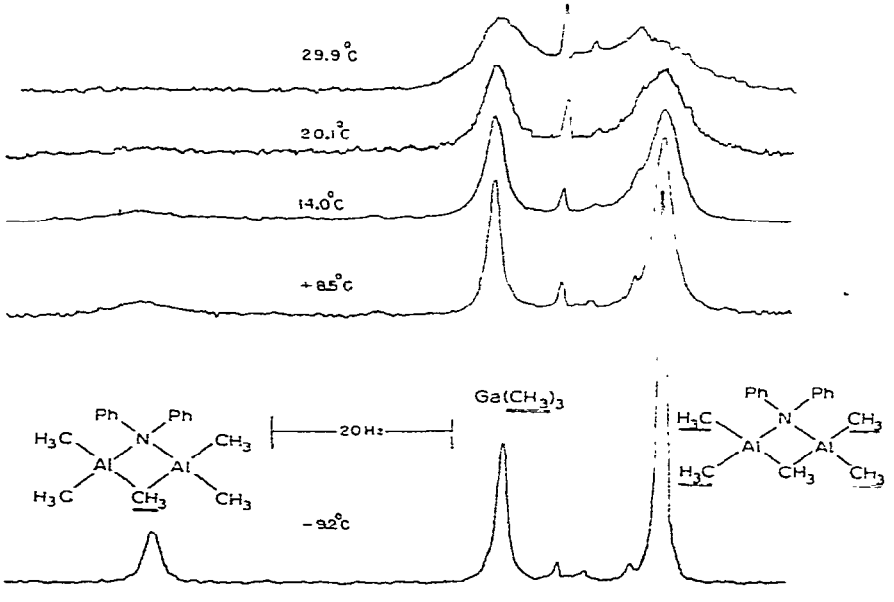


Fig. 3. The 60 MHz proton NMR spectrum of a mixture of μ-methyl-μ-diphenylaminotetramethyldialuminum and trimethylgallium as a function of temperature in toluene solution.

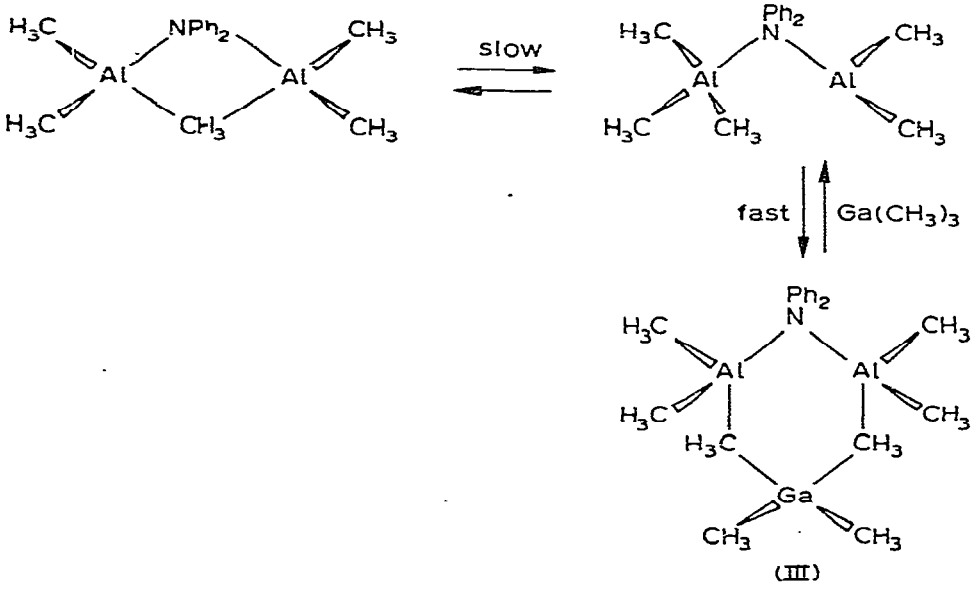
TABLE 2

THE LIFE TIMES OF TRIMETHYLGALLIUM, AND OF THE BRIDGE AND TERMINAL GROUPS IN μ-METHYL-μ-DIPHENYLALMINOTETRAMETHYLDIALUMINUM AS A FUNCTION OF CONCENTRATION AND TEMPERATURE

$[Ga(CH_3)_3]$ [a]	$[\mu\text{-}CH_3\text{-}\mu\text{-}NPh_2Al_2(CH_3)_4]$ [a]	$\frac{[Ga(CH_3)_3]}{[I]}$	T (°C)	$1/\tau_B$ (sec^{-1})	$1/\tau_T$ (sec^{-1})	$1/\tau_{Ga}$ (sec^{-1})
		Concentration dependence				
0.18	0.13	1.41	18.7	84.1	17.3	3.4
0.20	0.14	1.38	18.7	81.6	17.5	3.5
0.13	0.25	0.52	18.7	85.5	18.9	12.0
0.88	1.13	0.78	18.7	85.6	19.9	7.5
1.70	0.63	2.67	18.7	85.0	18.0	1.6
0.24	0.75	0.33	18.7	85.2	17.8	13.1
		Temperature dependence				
0.089	0.15	0.61	14.0	43.5	10.4	3.6
			16.5	64.3	14.1	5.9
			19.8	91.9	20.5	6.8
			22.6	115.8	25.3	10.0
			26.4	145.2	31.9	15.2
0.22	0.10	2.15	20.1	91.3	21.4	2.4
			30.2	208.2	44.3	6.6
			32.2	220.4	45.5	8.8
			37.3	325.3	70.7	16.7
			38.6	350.9	70.3	19.6

[a] Concentrations are in mol/l and were determined from the integration of solvent and compound peak areas at low temperature (−75°C) in toluene solvent. [b] The activation parameters determined for a least squares fit ot the data are E_a 20.7 ± 0.8 kcal/mol; $\Delta H^{\ddagger}$ 20.1 ± 0.8 kcal/mol; $\Delta S^{\ddagger}$ +16 ± 4.2 e.u. [c] Ratio of concentations of $Ga(CH_3)_3$ to $\mu\text{-}CH_3\text{-}\mu\text{-}NPh_2Al_2(CH_3)_4$.

dependence of the lifetimes is shown in Fig. 4, in which the reciprocal lifetimes of the methyl groups on gallium are plotted vs. the ratios of aluminum/gallium compounds. This plot shows that the reaction is zero order in trimethylgallium and first order in I. This behavior is consistent with a rate-determining bridge opening as indicated in eq. 3.



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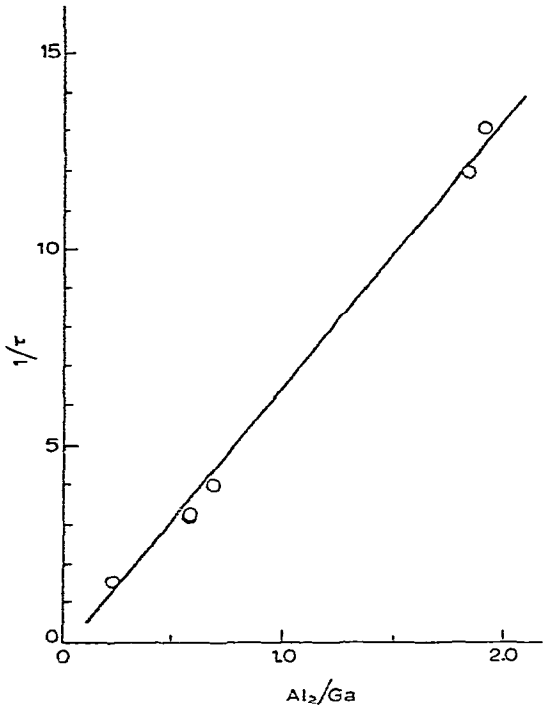


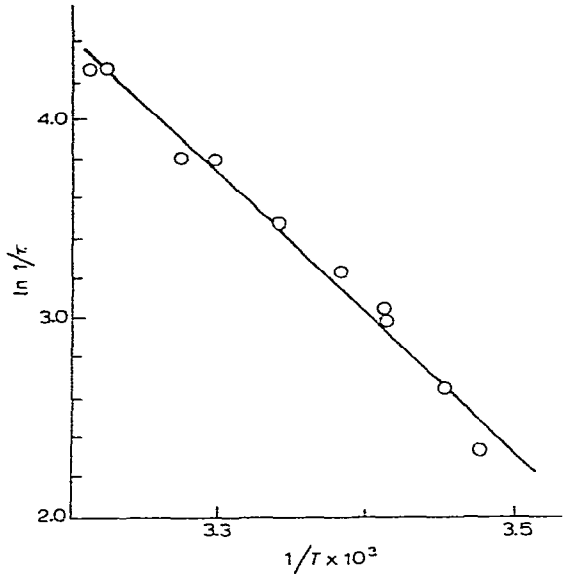


Fig. 4. The reciprocal lifetime, $1/\tau$, of trimethylgallium plotted vs. the ratio of the concentration of trimethylgallium to μ-methyl-μ-diphenylaminotetramethyldialuminum at 18.7°C.

Fig. 5. The least squares Arrhenius activation plot for the intermolecular exchange between $Ga(CH_3)_3$ and μ-methyl-μ-diphenylaminotetramethyldialuminum (ln $1/\tau$ terminal vs. $1/T \times 10^3$ for 2 samples: E_a = 20.7 ± 0.8 kcal/mol).

To account for this first order behavior, the rate of intermolecular exchange must be governed by formation of an activated species involving only I.

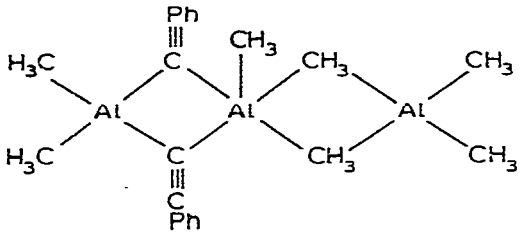
The Arrhenius activation energy for this process was determined to be 20.7 ± 0.8 kcal/mole from the plot shown in Fig. 5 and the enthalpy and entropy of activation for this process are $\Delta H^{\ddagger}$ 20.0 ± 0.8 kcal/mole and $\Delta S^{\ddagger}$ +16 ± 4 e.u. at 290 K. The activation energy is substantially higher than that observed for the simple bridge-terminal exchange and clearly indicate that the intermolecular process requires a more energetic molecule of I in the transition state than required for bridge-terminal group exchange, further the large positive entropy suggests that some form of disorder occurs with formation of activated species.

This substantial change in the activation parameters may arise as a result of the introduction of a new group into the system which requires much greater distortion of the molecule of I before reaction can occur. Using our model this would correspond to breaking an Al—C bridge bond followed by rapid rotation for the bridge terminal exchange without appreciable bending of the Al—N—Al angle. While in the intermolecular exchange substantial distortion would be required in order to permit entrance of the $Ga(CH_3)_3$ molecule as indicated in III with some unfavorable interactions occurring between the phenyl and methyl groups. This would lead to the substantially higher activation energy observed.

This activated complex once formed must then react in a fast step with trimethylgallium. Further, this step also must occur with trimethylgallium essentially for every fully activated molecule of I which indicates that the $Ga(CH_3)_3$ undergoes many more collisions per second with the dimer than exchange of methyl groups.

This fact, i.e., the independence of the rate on $Ga(CH_3)_3$, is therefore a consequence of the "high concentration" of $Ga(CH_3)_3$ relative to the activated complex, the lifetime of the activated complex, and the collision frequency between the activated complex and the $Ga(CH_3)_3$. In order to observe the concentration dependence on $Ga(CH_3)_3$, the concentration of $Ga(CH_3)_3$ would have to be decreased so that the reaction would become controlled by the collision of an activated complex with $Ga(CH_3)_3$ instead of the formation of the activated complex as observed in this case.

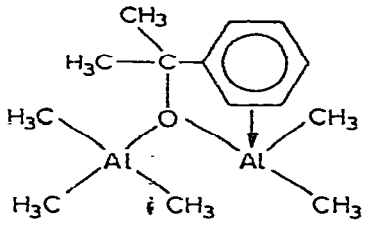
This behavior has been reported in the exchange of bis(μ-phenylethynyl)tetramethyldialuminum [5] with trimethylaluminum in which the concentration of the $Al(CH_3)_3$ monomer is low and is governed by the monomer—dimer equilibrium for this species with the rate-determining step the formation of a bimolecular transition state such as that indicated in IV with a 5-coordinate aluminum atom as suggested by Ham et al. [5].



(IV)

Data for the activation parameters for a number of systems have been collected and compared in Table 3. The systems appear to follow a reasonable trend with processes which involve complete dissociation either prior to or during the rate-determining step having substantial positive entropy, those processes in which the activated complex involves only a single bridged species have entropy terms near zero or slightly negative, while the reactions with a bimolecular rate-determining step have a substantial negative entropy of activation.

The final point to be made here is that the rate of both intra- and inter-molecular exchange in strongly bridged systems appears to depend very significantly on the substituents present on the bridging group. Jeffery and Mole [7] have reported that intramolecular exchange occurs in the series of oxy-bridged compounds; $\{[\mu\text{-}(CH_3)_3CO]\text{-}\mu\text{-}CH_3\}$-, $\{[\mu\text{-}Ph(CH_3)_2CO]\text{-}\mu\text{-}CH_3\}$-, and $\{[\mu\text{-}Ph_2(CH_3)\text{-}CO]\text{-}\mu\text{-}CH_3\}\text{-}Al_2(CH_3)_4$; with the rate of bridge terminal exchange increasing due



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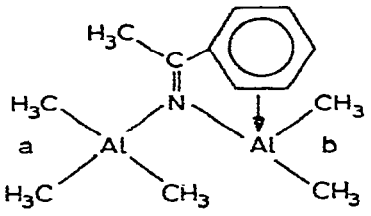
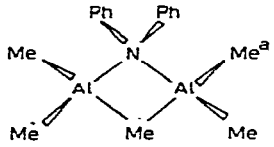
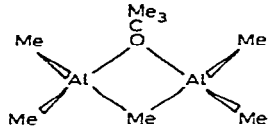
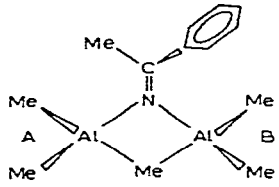
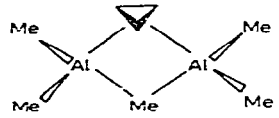
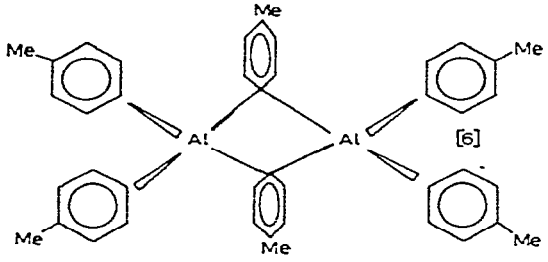
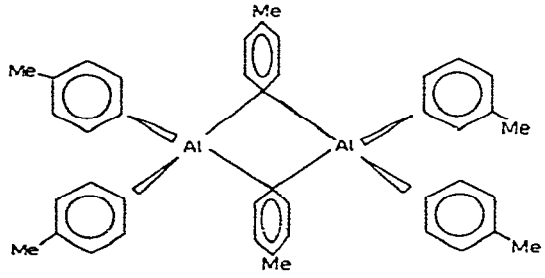
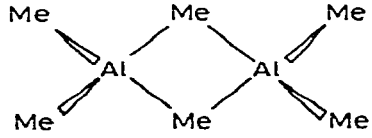


(VI)

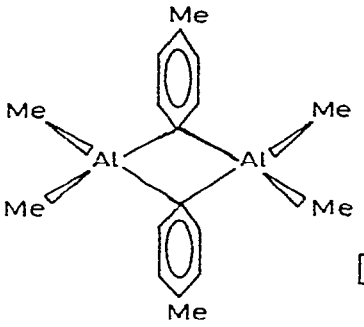
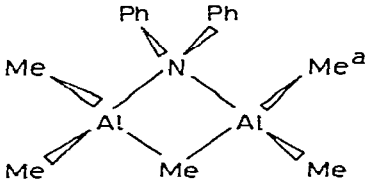
TABLE 3

KINETIC PARAMETERS FOR EXCHANGE REACTIONS OF BRIDGED ALUMINUM DERIVATIVES

	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
Intramolecular bridge terminal exchange reactions			
	13.7 ± 0.5	13.0 ± 0.6	—5.8 ± 3.6 (290 K)
 [7]	~20 ± 3		
 [7]	12.7 ± 2.0 for A methyls ~20 for B methyls		
 [4]	15.8 ± 0.7	15.1	—7.6
 [6]	9.7 ± 1.0	9.2	—9 (225 K)
	8.0 ± 1	7.6	—13 (225 K)
 [6]	13.6 ± 1 16.3 ± 0.6	13.0 15.8	+9 (toluene) (225 K) +16 (cyclo-pentane) (225 K)

(Table continued)

TABLE 3 (continued)

	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
Intramolecular bridge terminal exchange reactions			
 + Al_2Me_6 [6]	11.1 ± 1.0	10.6	−11 (225 K)
 + $GaMe_3$	20.7 ± 0.8	20.1 ± 0.8	+16 ± 4.2 (290 K)

[a] This work.

to an "assisted bridge opening" as illustrated in V and VI. For the fully methylated compound or with other nonaromatic R groups, they observed very high activation energies or no exchange on the NMR time scale between these strongly bridged species and added $Al_2(CH_3)_6$. The same process of assisted bridge opening was used to account for the differences in bridge-terminal exchange in $[\mu\text{-N=C(CH}_3)\text{Ph}]\text{-}\mu\text{-CH}_3\text{Al}_2(\text{CH}_3)_4$ in which the two kinds of terminal methyl groups shown in VI were found to exchange at different rates. No studies have been reported in which this compound was permitted to exchange with other species so it is not clear what effect this difference in exchange rate may have on intermolecular processes.

In our system, I cannot have this assistance in the manner prescribed by Jeffery and Mole [7], since the geometry places the aromatic groups away from the aluminum atoms as shown by the X-ray structure [8,9]. Further, we observed rapid intermolecular exchange which leads to the suggestion that the transition state may require substantial distortion of the $\text{Al—E(R}_n\text{)—Al}$ system, and any bulky alkyl group simply hinders the opening of this bridge sufficiently to accommodate the incoming species. Thus, for our system, we observe that bridge terminal interchange proceeds with a relatively low activation energy while in the sterically more hindered systems such as those described by Jeffery and Mole [7], the reaction is slower. The fact that two types of exchange processes occur in the $(\mu\text{-N=CPhCH}_3)\text{-}\mu\text{-CH}_3\text{Al}_2(\text{CH}_3)_4$ system does suggest some additional influence such as that proposed by Jeffery and Mole [7].

Some of the intermolecular exchange processes in which one bridging group

is either nitrogen or oxygen have been shown to proceed without complete dissociation of the dimeric species, but the exact mechanism and factors which control the rates of reaction are still somewhat unclear. Certainly the steric requirements for formation of the complex proposed are substantially greater than those for simple bridge terminal exchange and may well account for the failure to observe this process in some of the systems which have been described.

In the systems studied with only Al—C—Al bridged, the factors which seem to govern the rate and mechanism of bridge terminal exchange and of intermolecular alkyl exchange may be the same with weakly bridged systems such as trimethylaluminum proceeding through a dissociative process and those systems with stronger bridging groups proceeding through a partial bridge opening as proposed for the tolyl- [6] and cyclopropyl-aluminum [4] systems or through a bimolecular process as proposed for the phenylethynyl bridged system [5]. There, however, have not been a sufficient number and variety of these systems examined to permit a conclusive statement to be made.

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