Methyl Group Exchanges in Lewis Acid–Base Adducts of Group III Trimethyl Compounds[1]

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Abstract: Proton magnetic resonance spectra have been employed to measure the exchanges of methyl groups between distinct chemical sites in cyclopentane solutions of the following systems: $Al_2(CH_3)_6$–$Ga(CH_3)_3$, $Al_2(CH_3)_6$–$Zn(CH_3)_2$, $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot B$, and $Ga(CH_3)_3$–$Al(CH_3)_3 \cdot B$, where B is pyridine, 2,6-lutidine, tetrahydrofuran, diethyl ether, dimethyl sulfide, or a similar compound. In the slow-exchange range, variations in the relative concentrations of the exchanging components produce changes in the mean reciprocal exchange times which can be associated with an appropriate rate law for the exchange. In general, the kinetics do not follow a simple first-order dissociative or simple second-order associative rate law. In the $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot B$ systems, exchanges are observed to be much faster when B is a group VI element base than when it is a group V element base. A base-assisted associative exchange mechanism involving interaction of the second lone pair on the group VI atom with $Al_2(CH_3)_6$ is proposed.

The extensive literature dealing with nmr studies of exchange reactions of groups I, II, and III organometallics has recently been reviewed.[2,3] Although much valuable work has been reported, there are not yet any clearly established patterns of exchange, particularly for systems involving a role for coordinated bases. We report here new data for group III organometallic exchange systems which involve acid–base adducts, $MR_3 \cdot B$. Systems of this general type are particularly important because of the known, very marked effect of bases on the reactivities of the organometallics toward organic compounds such as ketones.

Matteson has recently put forth a new, more general approach to analyzing the nmr exchange data in $Al_2(CH_3)_6$–$M(CH_3)_3$ systems which resolves certain shortcomings in previous analyses of this and related systems.[4] We present here new nmr exchange data for $Al_2(CH_3)_6$–$Ga(CH_3)_3$ solutions, with the aim of clarifying certain points which remain uncertain.

Experimental Section

Materials and Procedures. Cyclopentane was shaken with Linde Type 4A Molecular Sieves, passed through a 1-m column of activated silica gel, and stored over sodium wire under an inert atmosphere.

Aluminum metal (99.99%, Alpha Chemicals, Inc.) was turned into rough shavings, with precautions to prevent contamination. Gallium metal (99.999%) was used as obtained from Indium Corporation of America. Zinc metal (20 mesh, Allied Chemical) was washed with dilute HCl, water, and acetone, then dried under an argon atmosphere.

Reagents used in forming adducts were purified by thorough drying and careful distillation, with subsequent storage in the inert atmosphere glove box.

Trimethylaluminum, trimethylgallium, and dimethylzinc were all prepared by adding about 6 g of the metal in a bomb tube to a quantity of $Hg(CH_3)_2$ sufficient to produce about 20 mmol of the desired organometallic. The tubes were then degassed and sealed under vacuum; the sealed bomb tubes were allowed to react for 5 days at approximately 90°. (*Caution!* $Hg(CH_3)_2$ is extremely toxic. Tubes are liable to rupture due to excessive gas pressure.) The tubes were then opened in the glove box and cyclopentane was added to prepare approximately 1 *M* stock solutions which were then filtered and stored.

Trimethylaluminum adducts of the various bases were prepared by mixing a stoichiometric amount of the base with a stock solution of trimethylaluminum. For the $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot B$ systems, it was necessary only to add the base to a predetermined excess of the trimethylaluminum stock solution. In preparing $Al(CH_3)_3 \cdot B$–$Ga(CH_3)_3$ mixtures, it is important that there be no excess base or $Al_2(CH_3)_6$ in the formation of the adduct. The adducts were formed with as closely stoichiometric amounts of the components as possible. Solvent was then removed under vacuum and the acid–base adduct purified by sublimation or distillation. All of the adducts prepared in this manner are sufficiently robust to withstand the mild conditions required for sublimation or short pathlength distillation without significant decomposition.

Samples for nmr study were prepared from stock solutions of accurately known molarity using gas-tight syringes. The relative concentrations of the components in the various mixtures were determined also by comparisons of relative areas in the nmr spectra of the samples at a temperature below the slow-exchange limit.

Measurements of nmr spectra were made on a Varian Model A-60A, A56-60, or HA-100 spectrometer. Samples were degassed and sealed under vacuum in nmr tubes.

The temperatures of the samples during the nmr spectral runs were determined by use of a methanol chemical shift calibration, by thermocouple measurements under conditions matching the actual sample running conditions as closely as possible. and by similar use of a calibrated thermistor. The relative temperatures over a range for a given sample are undoubtedly accurate to within about 1°, but there is some question about the absolute accuracy of the measurements in the temperature range below about −20°. The various methods employed yielded a range of values of about 3° in some cases.

The reciprocal mean lifetimes of the protons at the various sites in the exchanging systems were estimated from line-width results in the slow-exchange region. Under the conditions of slow exchange the resonances are broadened; the half-intensity line width is related to the mean lifetime $1/\tau_j$ by the expression

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

where Δ^0 is the measured half-intensity width in hertz for the *j*th component in the absence of exchange. This quantity can be obtained in some instances by examination of the line width for a single component alone in solution at a given temperature, *e.g.*, for $Ga(CH_3)_3$ or $Zn(CH_3)_2$. In other instances it is necessary to employ the value of $\Delta_{1/2}$ measured at a temperature below that at which exchange makes a significant contribution to the broadening.

The line-width broadening measurements give reasonably accurate exchange rate data provided there are no serious overlaps of absorptions, nor scalar couplings. It is possible that a ^{27}Al–C–^1H coupling makes a contribution to the proton line width in the slow-exchange limit for methyl groups bonded to aluminum.[5] Quadrupolar relaxation of the ^{27}Al nucleus should result

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[1] This research was supported by the National Science Foundation, under research Grant No. GP 6396X.

[2] J. P. Oliver, *Advan. Organometal. Chem.*, **8**, 167 (1970).

[3] N. S. Ham and T. Mole, *Progr. Nucl. Magn. Resonance Spectrosc.*, 4, 91 (1969).

[4] D. S. Matteson, *Inorg. Chem.*, **10**, 1555 (1971).

in effective decoupling of the two spins, but there may be a residuum which makes a contribution. In the absence of evidence that there is a significant contribution, we have simply assumed that there is none. Since the bridging and terminal line widths of $Al_2(CH_3)_6$ in cyclopentane at −70° are about 1.2 Hz, as compared with 0.70 Hz for $Ga(CH_3)_3$, the contributions from scalar coupling are evidently not large. We have elected to employ these low-temperature half-intensity line widths in eq 1, rather than the solvent line width employed in the earlier study,[7] on the grounds that whatever the contributions to the line width may be, aside from the coupling effects just mentioned, the exchange phenomenon adds to that line width.

The methyl group chemical shift τ values at room temperature in cyclopentane for all of the species studied are as follows: $Al_2(CH_3)_6$, 10.31; $Ga(CH_3)_3$, 9.99; $Zn(CH_3)_2$, 10.55; $Al(CH_3)_3 \cdot N(C_2H_5)_3$, 10.89; $Al(CH_3)_3 \cdot NC_5H_5$, 10.81; $Al(CH_3)_3 \cdot NC_5H_3(CH_3)_2$, 10.70; $Al(CH_3)_3 \cdot O(C_2H_5)_2$, 10.91; $Al(CH_3)_3 \cdot OC_4H_8$, 10.95; $Al(CH_3)_3 \cdot (CH_3)_3COCH(CH_3)_2$, 10.72; $Al(CH_3)_3 \cdot S(CH_3)_2$, 10.82; $Al(CH_3)_3 \cdot S[CH_2CH(CH_3)_2]_2$, 10.77; $Al(CH_3)_3 \cdot P(C_4H_9)_3$, 10.87.

Results and Discussion

The treatment of nmr data in terms of models for the mechanisms of exchange processes varies with the particular type of system studied; we therefore consider several types separately. For generality in the development which follows, we often employ the symbol R for the organic group bound to the metal, although in fact the present work is restricted to studies of methyl compounds.

(A) The $Al_2(CH_3)_6$–$Ga(CH_3)_3$ System. Since the first publication of an nmr study of methyl group exchange between $Al_2(CH_3)_6$ and $Ga(CH_3)_3$ or $In(CH_3)_3$ in cyclopentane and toluene,[7] other workers have reported additional data and offered alternative interpretations of the experimental results.[4,8]

There seems little question but that the bridge–terminal exchange and the exchange of methyl groups between the two different metals are both controlled by a dissociation of $Al_2(CH_3)_6$

$$Al_2(CH_3)_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Al(CH_3)_3 \tag{2}$$

$$Al(CH_3)_3 + Ga(CH_3)_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [AlGa(CH_3)_6] \tag{3}$$

In addition, however, we proposed a cage effect, operative in noninteracting solvents such as cyclopentane, which results in preferential recombination of $Al(CH_3)_3$ monomers. The cage effect, if operative, should result in a bridge–terminal exchange faster than the intermolecular exchange with $Ga(CH_3)_3$. Jeffery and Mole have contested the importance of this cage effect on the basis of new experimental results.[8] They also suggested that the simple mechanistic model could not account for some of the details of line-width dependence on concentrations.

We have reinvestigated the $Al_2(CH_3)_6$–$Ga(CH_3)_3$ system in cyclopentane and have made a few additional measurements in decalin. The results are shown in Tables I and II.

Table I. Reciprocal Mean Exchange Times (sec^{-1}) for $Al_2(CH_3)_6$–$Ga(CH_3)_3$ Mixtures in Cyclopentane at −52°

$[Ga(CH_3)_3]$, M	$[Al_2(CH_3)_6]$, M	$1/\tau_{br}$	$1/\tau_{Ga}$	$1/\tau_t$
0.316	0.223	7.2	7.1	7.2
0.167	0.110	5.5	3.5	4.1
0.070	0.042	4.5	2.1	3.2
0.363	0.106	4.8	1.7	3.8
0.115	0.225	6.0	8.2	4.8
0.554	0.296	7.2	5.6	6.3
0.194	0.104	4.6	1.6	3.3
0.604	0.193	8.2	3.0	6.3
0.609	0.140	5.1	1.9	6.0
0.030	0.225	6.3	[a]	5.0
0.233	0.232	7.0	7.2	5.8

[a] Broad.

Table II. Reciprocal Mean Exchange Times (sec^{-1}) for $Al_2(CH_3)_6$–$Ga(CH_3)_3$ Mixtures in Cyclopentane and Decalin at −50°

$[Ga(CH_3)_3]$, M	$[Al_2(CH_3)_6]$, M	$1/\tau_{br}$	$1/\tau_{Ga}$	$1/\tau_t$
		Cyclopentane		
0.363	0.106	10.4	3.8	7.0
0.121	0.035		2.1	5.3
0.115	0.225	9.5	15.4	7.6
		Decalin		
0.455	0.127	8.5	4.1	7.0
0.152	0.042	6.6	2.8	4.5

Jeffery and Mole have rightly pointed out that comparisons of low-temperature exchange data obtained in different laboratories are likely to reflect large uncertainties in measurement of the correct temperature. To avoid this problem, we restrict our considerations to data obtained in a single solvent and for samples at a temperature within a short time interval. Following Matteson's development, we have

$$1/\tau_{Ga} = 2Qk_1[Al_2(CH_3)_6]/[Ga(CH_3)_3] \tag{4}$$

$$1/\tau_{br} = k_1[2/3 + Q/3] \tag{5}$$

$$1/\tau_t = k_1[1/3 + 2Q/3] \tag{6}$$

$$Q = [Ga(CH_3)_3]/\{[Ga(CH_3)_3] + a[Al_2(CH_3)_6]^{1/2}\} \tag{7}$$

where $a = (12k_1/k_2)(k_1/k_{-1})^{1/2}$. Using the data for $1/\tau_{Ga}$ in Table I one can find a best value for a. The scatter in the values of a is quite large, but a value of about 0.4 is obtained from graphical solutions of the simultaneous equations. Using this value, the $1/\tau_{Ga}$ values lead to a value for k_1 of 5.3 sec^{-1}, with a sample standard deviation of 1.8 sec^{-1}. The same value of a leads to values of k_1 of 6.8 sec^{-1} from the $1/\tau_t$ data, standard deviation 1.8 sec^{-1}, and 7.0 sec^{-1} from the $1/\tau_{br}$ data, standard deviation 1.5 sec^{-1}. Values of k_1 were calculated also from the $Al_2(CH_3)_6$ line widths assuming that $\Delta_{1/2}^0$ is 0.70 Hz rather than the 1.2 Hz employed in arriving at the results shown in Table I. The smaller assumed value for $\Delta_{1/2}^0$ results in k_1 values of 8.7 and 8.9 sec^{-1} based on terminal and bridging line width data, respectively, with the same sample standard deviations as given above.

Because the experimental determination of the line widths is inherently not very accurate, and because it is not possible to vary the concentrations over more

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(5) J. P. Oliver and C. A. Wilkie, *J. Amer. Chem. Soc.*, **89**, 163 (1967), and E. S. Gore and H. S. Gutowsky, *J. Phys. Chem.*, 73, 2515 (1969), report a ^{27}Al–^1H coupling constant of 6.3 Hz in $Al(CH_3)_4^-$. Even in this highly symmetric ion, however, the scalar interaction is largely decoupled *via* ^{27}Al quadrupolar relaxation in less polar solvents where ion pairing predominates.[6]

(6) K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, **88**, 4134 (1966).

(7) K. C. Williams and T. L. Brown, *ibid.*, **88**, 5460 (1966).

(8) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **22**, 1129 (1969).

than a limited range and still obtain meaningful lineshape results, the equations from which a is calculated are not very well conditioned. This means that a could be somewhat smaller or larger without much increase in the standard deviations. For example, assuming $a = 1.0$ leads to an estimated k_1 from the $1/\tau_{\mathrm{Ga}}$ data of 6.7 sec^{-1}, with a standard deviation of 2.1 sec^{-1}. Assuming $a = 0$ leads to an estimated k_1 of 4.2 sec^{-1}, with a standard deviation of 2.6 sec^{-1}. Similar changes occur in the k_1 values calculated from the $Al_2(CH_3)_6$ line-width data as a is varied.

From these results we can conclude only that the value chosen for a is approximately correct. Most important, the values computed for k_1 from the line widths of the three observed lines are approximately the same. Even when $\Delta_{1/2}^0$ for the $Al_2(CH_3)_6$ lines is assumed to be as small as for $Ga(CH_3)_3$, k_1 values calculated from the $Al_2(CH_3)_6$ line widths are less than twice those based on the $Ga(CH_3)_3$ line widths. These comparative results indicate that there cannot be an appreciable cage effect operative in this system. They also indicate quite clearly that the more complex kinetic scheme invoked by Jeffery and Mole is not required to explain the concentration dependences observed in the data.

The data in Table II show a comparative study of the line widths of a few solutions in cyclopentane and decalin. The latter solvent was chosen because it possesses a much higher macroscopic viscosity than cyclopentane. Studies of the cage effect as a function of solvent in free-radical reactions provide some indication that cage recombination is favored in the more viscous solvent.[9,10] There is no indication of such an effect in the line-shape results, further evidence that a cage effect is not important in the exchange processes.

The a term which is important in determining the value for Q is in all probability not independent of temperature. Since this is so, the observation of $1/\tau$ for a single solution as a function of temperature will not in general lead to a correct value for the Arrhenius energy for the dissociative step. In the case of trimethylaluminum, however, the nmr results lead to an apparent enthalpy of activation for the forward step in eq 2 which is consistent with thermochemical estimates of the dissociation energy for the dimer.[11]

A few experiments were carried out on cyclopentane solutions of $Al_2(CH_3)_6$ and $Zn(CH_3)_2$. With minor alterations in the coefficients to allow for the differing numbers of methyl groups per molecule, the rate expressions 4–7 should apply for these systems as well. Because the chemical shifts of the $Zn(CH_3)_2$ and $Al_2(CH_3)_6$ absorptions differ by only 0.1 ppm, it was necessary to observe the spectra with an HA 100 instrument. The results indicate that there is little difference in the apparent rates of exchange in this system as compared with $Ga(CH_3)_3$. One expects that the exchange of methyl groups between $Al(CH_3)_3$ and $Zn(CH_3)_2$ should be slower than the exchange with $Ga(CH_3)_3$ and that the difference should appear as an apparently slower exchange in the $Zn(CH_3)_2$ line. On the other hand, as we have already seen, it is difficult to specify the value of a with accuracy from the experimental results. This parameter could vary over a wide range without markedly affecting the lineshape data. An uncertainty of a few degrees in the relative temperatures measured on two different instruments adds to the difficulties of making an accurate comparison.

(B) $AlR_3 \cdot B$–MR_n Exchanges. The exchange reactions in this class are characterized by the necessity that there be a cleavage of the carbon–metal bond for exchange to occur. There is the *a priori* possibility that exchange might occur by the direct attack of MR_n upon the adduct, $AlR_3 \cdot B$.

$$MR_n + AlR_3 \cdot B \rightleftharpoons (BAlMR_{3+n}) \qquad (8)$$

An exchange process of this type would lead to simple second-order kinetics. In the class of compounds under consideration, in which exchange involves transfer of a methyl group from one metal to another, this does not seem a likely pathway for exchange.

An alternative involves dissociation of the acid–base adduct, followed by formation of an intermediate in which exchange might occur. The rate expressions appropriate to the nmr data for this pathway can be obtained following the approach taken by Matteson.[4] We have the following two exchange equilibria to consider

$$AlR_3 \cdot B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AlR_3 + B \qquad (9)$$

$$AlR_3 + MR_n \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (AlMR_{3+n}) \qquad (10)$$

Following Matteson, let Q be the fraction of alkyl groups in AlR_3 which have come from the MR_n. Then the rate at which methyl groups transfer from the MR_n site is given by

$$-\mathrm{d}[(CH_3)^{M}]/\mathrm{d}t = 3Qk_{-1}[AlR_3][B] \qquad (11)$$

$$= 3Qk_1[AlR_3 \cdot B] \qquad (12)$$

where $[(CH_3)^M]$ refers to the total concentration of methyl groups bound to M in MR_n, *i.e.*, $[(CH_3)^M] = n[MR_n]$.

$$-\mathrm{d}[(CH_3)^{Al}]/\mathrm{d}t = (1/2)(1 - Q)k_2[AlR_3][MR_n] \qquad (13)$$

Since the two rates must be equal

$$6Qk_{-1}[AlR_3][B] = (1 - Q)k_2[AlR_3][MR_n] \qquad (14)$$

$$Q = k_2[MR_n]/(k_2[MR_n] + 6k_{-1}[B]) \qquad (15)$$

The concentration of B is obtainable from the equilibrium condition for eq (9)

$$[B] = (k_1/k_{-1})^{1/2}[AlR_3 \cdot B]^{1/2} \qquad (16)$$

$$Q = \frac{[MR_n]}{[MR_n] + 6k_{-1}/k_2(k_1/k_{-1})^{1/2}[AlR_3 \cdot B]^{1/2}} \qquad (17)$$

We have also that

$$1/\tau_{\mathrm{M}} = \frac{-\mathrm{d}[(CH_3)^{M}]}{[(CH_3)^{M}]\mathrm{d}t} = \frac{3Qk_1[AlR_3 \cdot B]}{n[MR_n]} \qquad (18)$$

$$1/\tau_{\mathrm{Al \cdot B}} = \frac{-\mathrm{d}[(CH_3)^{Al}]}{[(CH_3)^{Al}]\mathrm{d}t} = Qk_1 \qquad (19)$$

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[9] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 544.

[10] O. Dobis, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 278 (1968).

[11] J. N. Hay, P. G. Hooper, and J. C. Robb, *J. Organometal. Chem.*, **28**, 193 (1971).

In determining a value for Q, it is convenient to treat $6k_{-1}/k_2(k_1/k_{-1})^{1/2}$ as a constant.

The particular type of kinetic data obtained from the effects of concentration variations on the nmr line shapes depends on the relative magnitudes of the various rate constants, particularly on the ratio k_{-1}/k_2, assuming k_{-2} is large. When k_1 is rate controlling (k_2 large), the fraction Q approaches one, and the reaction becomes first order in $AlR_3 \cdot B$, zero order in MR_n. On the other hand, when k_{-1} is much larger than k_2, the equilibrium dissociation of $AlR_3 \cdot R$ is established before exchange occurs, and the reaction becomes half order in adduct and first order in MR_n. In the general case neither extreme prevails, and the reaction kinetics exhibit complex behavior.

To test these relationships, we have studied the exchanges of $Al(CH_3)_3 \cdot B$ adducts with trimethylgallium. A few additional experiments were carried out with $Zn(CH_3)_2$ as the MR_n component. The results are summarized in Table III.

Table III. Reciprocal Mean Exchange Times for $Al(CH_3)_3 \cdot B + MR_n$ Systems in Cyclopentane

$[Al(CH_3)_3 \cdot B]$	$[MR_n]$	$1/\tau_{Al}$	$1/\tau_M$
$Al(CH_3)_3 \cdot NC_5H_3(CH_3)_2 + Ga(CH_3)_3$ at −40°			
0.554	0.716	10.0	9.0
0.230	0.242	9.2	10.9
0.202	0.692	11.6	5.1
0.699	0.249	7.5	19.8
$Al(CH_3)_3 \cdot NC_5H_5 + Ga(CH_3)_3$ at 47.5°			
0.497	0.489	13.0	14.6
0.204	0.201	8.0	8.2
0.125	0.123	5.8	5.3
0.136	0.541	15.9	5.0
0.474	0.172	5.1	14.9
$Al(CH_3)_3 \cdot O(C_2H_5)_2 + Ga(CH_3)_3$ at −17.5°			
0.526	0.468	8.0	9.4
0.194	0.139	5.1	5.7
0.183	0.450	9.9	4.2
0.492	0.162	5.0	14.3
$Al(CH_3)_3 \cdot P(C_4H_9)_3 + Zn(CH_3)_2$ at +8°			
0.512	0.771	7.1	9.2
0.161	0.240	3.7	5.9
0.247	0.707	6.1	3.3
0.555	0.247	4.0	18.9

The data for the 2,6-lutidine $[NC_5H_3(CH_3)_2]$ system can be analyzed in terms of eq 11–13 to yield a value for k_1 of 19 sec^{-1} based on the $Ga(CH_3)_3$ line widths, and 14 sec^{-1} based on the $Al(CH_3)_3 \cdot NC_5H_3(CH_3)_2$ line widths. The fraction Q varies in the range from 0.55 to about 0.8. The data for the closely related pyridine system fits the assumption that a dissociative equilibrium of the pyridine adduct is established before exchange occurs. The appropriate expressions for the reciprocal exchange times in this case are

$$1/\tau_M = k_2(k_1/k_{-1})^{1/2}[AlR_3 \cdot B]^{1/2} \tag{20}$$

$$1/\tau_{Al} = k_2(k_1/k_{-1})^{1/2}([MR_n]/[AlR_3 \cdot B]^{1/2}) \tag{21}$$

Further support for this interpretation of the pyridine adduct data comes from the observation that methyl group exchange in the system $Al(CH_3)_3 \cdot NC_5H_5 + Zn(CH_3)_2$, also in cyclopentane, is markedly slower; comparable line broadening occurs at about 25° higher temperature than for the $Ga(CH_3)_3$ system, despite the fact that the internal chemical shift separation between the two exchange sites is smaller for the zinc system. This suggests that the $Al(CH_3)_3$–$Zn(CH_3)_2$ exchange, measured by k_2, is slower than the $Al(CH_3)_3$–$Ga(CH_3)_3$ exchange, which is to be expected.

The data for the $Al(CH_3)_3 \cdot O(C_2H_5)_2$ do not fit the limiting case of a preequilibrium precisely, but the correspondence is sufficiently close to suggest that the recombination is faster than $Al(CH_3)_3$–$Ga(CH_3)_3$ exchange.

The data for the $Al(CH_3)_3 \cdot P(C_4H_9)_3$–$Zn(CH_3)_2$ system were fitted using eq 11–13 to yield values for k_1 at 8° of 7.0 sec^{-1} based on the $Zn(CH_3)_2$ line width, and 6.0 sec^{-1} based on the adduct line width. The fraction Q for the solutions studied ranged from 0.77 to 0.93. The choice of $Zn(CH_3)_2$ as the second Lewis acid in this case was dictated by the fact that the equilibrium

$$Al(CH_3)_3 \cdot P(C_4H_9)_3 + Ga(CH_3)_3 = Ga(CH_3)_3 \cdot P(C_4H_9)_3 + Al(CH_3)_3 \tag{22}$$

was found to lie far to the right. Had the equilibrium not been disadvantageous, the exchange with $Ga(CH_3)_3$ would presumably have been observed to occur at lower temperature, as in the pyridine systems. Thus, it appears that for the four adduct systems studied, the relative rates of adduct dissociation are in the order $NC_5H_3(CH_3)_2 > O(C_2H_5)_2 > P(C_4H_9)_3 > NC_5H_5$. The observed heats of dissociation of the $Al(CH_3)_3$ adducts of these bases in hexane are −19.9, −20.2, −22.1, and −27.5 kcal/mole, respectively.[12] The relative rates of dissociation are thus in the expected inverse order of adduct stability.

Apparent Arrhenius activation energies for these exchanges were calculated from observations of the temperature dependences of the line widths. The apparent activation energies in all cases were considerably less than the enthalpies of dissociation of the adducts. An Arrhenius energy comparable to the enthalpy of dissociation of the adduct is to be expected only when the dissociation is rate controlling. This limiting condition is not met in any of the systems listed in Table III. At the opposite extreme, in the limiting condition of a rapid preequilibrium, the apparent Arrhenius energy should equal half the dissociation energy of the adduct plus generally much smaller activation energy for the forward step in eq 10. The apparent Arrhenius energy for the $Al(CH_3)_3 \cdot NC_5H_5$–$Ga(CH_3)_3$ exchange was determined to be about 15 kcal/mol on the basis of line-width measurements at various temperatures, at both sites. This value is consistent with a dissociation energy for the adduct of about 27 kcal/mol, and a small—perhaps 2–6 kcal/mol—activation energy for $Al(CH_3)_3$–$Ga(CH_3)_3$ exchange.

(C) $AlR_3 \cdot B$–Al_2R_6 Systems. The $Al(CH_3)_3 \cdot N(C_2H_5)_3 + Al_2(CH_3)_6$ system represents an apparently straightforward example of an exchange controlled by a first-order dissociative process. The line width of the adduct resonance (Table IV) is essentially independent of the reactant concentrations; the $Al_2(CH_3)_6$ line width (due to both the terminal and bridging methyl protons) varies with the concentration ratio $Al(CH_3)_3 \cdot B/Al_2$-

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(12) C. H. Hendrickson, D. Duffy, and D. P. Eyman, *Inorg. Chem.*, 7, 1047 (1968).

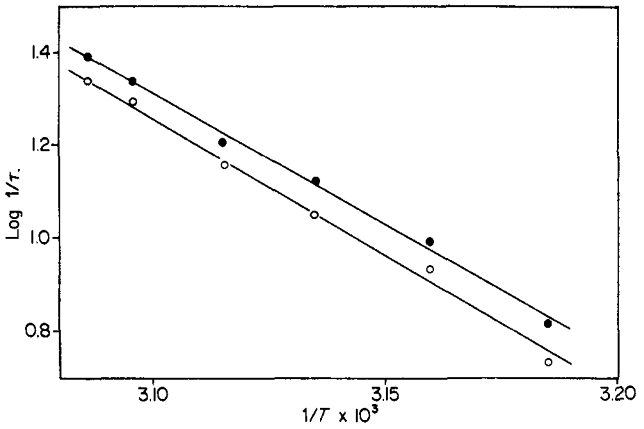

Figure 1. Temperature dependences of $1/\tau$ for the methyl resonances in $Al_2(CH_3)_6$, 0.23 *M*, and $Al(CH_3)_3 \cdot N(C_2H_5)_3$, 0.39 *M*, in cyclopentane: ●, dimer data; ○, adduct data. Both sets of data yield the same Arrhenius energy, 27 kcal/mol. The vertical separation of the two lines is precisely equal to the log ratio of total concentrations of the two sites.

$(CH_3)_6$. Further evidence that dissociation of the complex is rate determining comes from the fact that the Arrhenius energy for the reaction, based on the temperature dependence of both the adduct and dimer lines, Figure 1, is 27 kcal/mol. This corresponds very well to the gas-phase dissociation energy of 26.5 kcal/mol for $Al(CH_3)_3 \cdot N(C_2H_5)_3$. The results are consistent with the following kinetic scheme.

Table IV. Reciprocal Mean Exchange Times for $Al(CH_3)_3 \cdot B + Al_2(CH_3)_6$ Systems in Cyclopentane

$[Al_2(CH_3)_6]$	$[Al(CH_3)_3 \cdot B]$	$1/\tau_{Al_2}$		$1/\tau_{Al \cdot B}$
$Al_2(CH_3)_6 + Al(CH_3)_3 \cdot NC_5H_5$ at 47.5°				
0.24	0.66	14.1		11.7
0.12	0.34	10.9		9.7
0.08	0.22	9.4		7.7
0.22	0.20	7.9		15.6
0.21	0.11	6.0		14.6
0.07	0.50	14.6		6.2
0.04	0.34	24		6.7
$Al_2(CH_3)_6 + Al(CH_3)_3 \cdot N(C_2H_5)_3$ at 41°				
0.23	0.39	5.4		6.5
0.11	0.20	5.4		7.0
0.06	0.11	6.2		7.2
0.24	0.22	2.6		6.4
0.24	0.13	1.3		7.0
0.12	0.44	10.6		6.6
0.047	0.39	22.4		6.5
$Al_2(CH_3)_6 + Al(CH_3)_3 \cdot S(CH_3)_2$ at −93°				
		Bridge	Terminal	
0.28	0.56	15	*a*	*a*
0.14	0.28	7.4	6.9	6.7
0.09	0.20	4.4	5.0	5.7
0.28	0.20	4.4	5.0	12
0.14	0.56	13	13	8.5
$Al_2(CH_3)_6 + Al(CH_3)_3 \cdot S[CH_2CH(CH_3)_2]_2$ at −97°				
0.46	0.71	4.3	4.2	9.6
0.17	0.23	7.2	5.6	7.5
0.41	0.24	2.0	1.5	8.5
0.17	0.60	5.9	6.2	7.2
$Al_2(CH_3)_6 + Al(CH_3)_3 \cdot OC_4H_8$ at −63°				
0.081	0.17	14.6	13.7	11.7
0.05	0.13	8.5	7.9	6.1
$Al_2(CH_3)_6 + Al(CH_3)_3 \cdot O[C(CH_3)_3][CH(CH_3)_2]$ at −70°				
0.36	0.60	13.3		
0.11	0.16	3.7		
0.06	0.10	1.5		
0.33	0.24	4.0		
0.14	0.66	12.8		

[a] Broad

$$AlR_3 \cdot B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AlR_3 + B \tag{23}$$

$$Al_2\overset{*}{R}_6 \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} 2Al\overset{*}{R}_3 \tag{24}$$

$$B + Al\overset{*}{R}_3 \xrightarrow{k_2} Al\overset{*}{R}_3 \cdot B \tag{25}$$

$$B + Al_2\overset{*}{R}_6 \xrightarrow{k_3} Al\overset{*}{R}_3 \cdot B + Al\overset{*}{R}_3 \tag{26}$$

The data require that the dissociation of $AlR_3 \cdot B$ is rate determining, which means that reaction of B, either with monomer produced in the dissociation of the dimer or with the dimer itself, is fast with respect to recombination of B and an AlR_3 originating from the adduct. The $Al(CH_3)_3 \cdot N(C_2H_5)_3$ + $Ga(CH_3)_3$ system was not studied in detail, but examination of line-width data for a few solutions in the slow-exchange region in cyclopentane gave $1/\tau$ values at both the adduct and $Ga(CH_3)_3$ sites identical with those obtained for the adduct–$Al_2(CH_3)_6$ solutions. However, exchange in the $Ga(CH_3)_3$ *must* involve a step such as that shown in eq 10. The data therefore suggest that in the triethylamine system the recombination is slow relative to formation of the intermediate $GaAl(CH_3)_6$. If this were not true, *i.e.*, if the fraction *Q* in eq 17 were not effectively one, then the exchange in the $Ga(CH_3)_3$-containing system would appear to be slower than in the $Al_2(CH_3)_6$.

A similar, but less easily understood, situation arises in connection with the $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot NC_5H_5$ exchange. The data listed in Table IV are clearly not consistent with a rate-determining dissociation as the reaction pathway. The data can be fitted reasonably well to a preequilibrium model, just as for the $Al(CH_3)_3 \cdot NC_5H_5$–$Ga(CH_3)_3$ system. However, in the preequilibrium model the rate-determining step is the second-stage exchange, which is very different for these two systems. In the one case it involves an exchange of methyl groups between the group III metals, eq 10; in the other it involves merely base transfer, as in eq 15 and 26. That these two different types of process should occur at such closely similar rates, as required by the observation that the kinetic data for the two systems are virtually the same (Tables I and II), is perplexing.

An alternative explanation in this case, consistent with what is known about related exchange systems, is that the complex kinetics for the pyridine adduct systems arises from the contribution of a bimolecular process concurrent with an otherwise rate-determining dissociative process. As we have already shown,[13] the exchange $Ga(CH_3)_3 \cdot NC_5H_5$ + $Ga(CH_3)_3$ is cleanly bimolecular. By contrast, the $Ga(CH_3)_3 \cdot N(CH_3)_3$ + $Ga(CH_3)_3$ exchange is first-order dissociative.[14] It is not unreasonable, then, that exchanges involving $Al(CH_3)_3 \cdot NC_5H_5$ might be intermediate in character,[15]

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(13) T. L. Brown, *Accounts Chem. Res.*, 1, 23 (1968).

(14) J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, 4, 1741 (1965).

(15) J. B. DeRoos and J. P. Oliver, *J. Amer. Chem. Soc.*, 89, 3970 (1967).

containing contributions from both the dissociative and bimolecular pathways. This interpretation of the data, however, requires that the contribution from the bimolecular pathway be of comparable importance for $Ga(CH_3)_3$ and $Al_2(CH_3)_6$. It does not seem reasonable that this should be the case, since methyl groups must be transferred between metals in the one instance, and only a simple base transfer is involved in the other. An additional difficulty with this view is that if the bimolecular pathway is to provide an *additional* route for exchanges, the total exchange rate should be faster than if the first-order step alone were involved. However, the overall exchange rate in the pyridine systems seems to be slightly slower than for the triethylamine adducts, consistent with the observation that the enthalpy of dissociation of the pyridine adduct is 1 kcal/mol larger. Thus, although data exemplified by the entries in Table III and IV for the pyridine adducts can be fitted reasonably well to a two-term rate law, we are not inclined to favor this interpretation.

Still a third system involving a comparison of two different acids with a given adduct is the $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot P(C_4H_9)_3$ system. The kinetics of this system were not investigated in detail, but the spectra in the slow-exchange region in cyclopentane ($\sim -10°$) indicate that the exchange is slightly faster than in the $Al(CH_3)_3 \cdot P(C_4H_9)_3$–$Zn(CH_3)_2$ system. Dilution of the sample by a factor of 3 does not materially change the line widths. Presumably in this case the dissociation of the adduct is rate determining.

The data for the three remaining systems listed in Table IV are different from the data for the group V base adducts both in terms of the temperature range in which exchange occurs and in terms of the concentration dependences. The $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot OC_4H_8$ (OC_4H_8 is tetrahydrofuran) system could not be studied in much detail because of the limited solubility of the adduct in cyclopentane. Nevertheless, comparisons of a few spectra for this pair of components with analogous data for $Ga(CH_3)_3$–$Al(CH_3)_3 \cdot OC_4H_8$ mixtures showed that comparable exchange broadening occurs in the latter system at about 40° higher temperature. Since in the $GaCH_3$–$Al_2(CH_3)_6$ comparisons involving group V bases the spectra show comparable broadening at about the same temperatures, it would appear that there is an additional low-energy pathway for base exchange available in the $Al(CH_3)_3 \cdot OC_4H_8$–$Al_2(CH_3)_6$ system.

The exchanges involving both the $S(CH_3)_2$ and $(CH_3)_3COCH(CH_3)_2$ adducts follow bimolecular kinetics. The small chemical shift separation of only 4 Hz between the terminal methyl resonances of the dimer and the adduct methyl resonances in the case of the latter complex limited useful line-width observations to just the bridging methyl line. It is important to note that the exchanges occurring below $-50°$ are occurring in the slow-exchange region for bridge–terminal methyl group exchange in the dimer. Thus the dimer dissociation cannot be rate limiting. On the other hand, since bridge and terminal line widths increase from exchange to the same extent, rupture of the dimer bonding does occur during exchange.

It is possible to conceive *a priori* that the exchange pathway for these systems might be just as described by eq 23–26. The exchanges seem too rapid for this to be reasonable, however, considering the heats of dissociation of the adducts. For example, the enthalpies of dissociation of the $Al(CH_3)_3 \cdot S(CH_3)_2$ and $Al(CH_3)_3 \cdot OC_4H_8$ adducts are 16.7 and 22.9 kcal/mol, respectively.[12,16] Secondly, the fact that the concentration dependence suggests a bimolecular reaction pathway is consistent with neither a rate-limiting dissociation of adduct nor a preequilibrium involving adduct dissociation. We propose that the exchange in these group VI base adduct systems involves a bimolecular interaction of $Al_2(CH_3)_6$ with $Al(CH_3)_3 \cdot B$.

$$Al(CH_3)_3 \cdot B + Al_2(\overset{*}{C}H_3)_6 \overset{k_2}{\rightleftharpoons} [Al_3(CH_3)_9 \cdot B] \rightleftharpoons Al(\overset{*}{C}H_3)_3 \cdot B + Al_2(CH_3)_3(\overset{*}{C}H_3)_3 \quad (27)$$

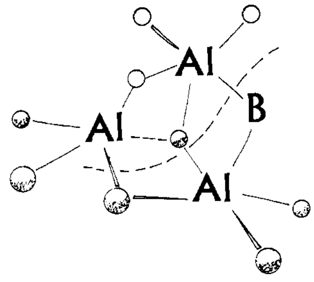
With formation of the intermediate as rate-determining step, the reciprocal mean exchange times at the two sites are of the form

$$1/\tau_{Al \cdot B} \sim k_2[Al_2(CH_3)_6]$$

$$1/\tau_{Al_2} \sim k_2[Al(CH_3)_3 \cdot B]$$

The precise form of the coefficient in the exchange expression depends on whether the exchange involves only simple base transfer from one $Al(CH_3)_3$ moiety alone, or also an exchange of methyl groups between aluminum centers. The data do not permit a judgement on this question.

We term the relatively facile exchange exhibited by these systems as "base-assisted." Since a bimolecular pathway is not observed in the case of the group V base adducts, it is likely that the existence of second basic site, in addition to that required for adduct formation, is required. The second site might be an unshared electron pair, as in the group VI bases. The intermediate might be pictured as I, in which the dotted line represents a possible mode of decomposition leading to methyl group transfer between dimer and adduct.



I

The concentration-dependence data for the $Al_2(CH_3)_6$–$Al(CH_3)_3 \cdot S[CH_2CH(CH_3)_2]_2$ exchange do not appear to follow simple bimolecular kinetics. It may be that this adduct has a particularly low enthalpy of dissociation, and that a dissociative pathway makes a significant contribution to the exchange. In any case, the onset of exchange broadening at a very low temperature indicates that the exchange is quite facile and probably of the base-assisted variety.

The temperature dependences of the line shapes were ascertained for a number of these systems to provide approximate values for the apparent Arrhenius energies. These are (kcal/mol): 11 ± 3 for Al-

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(16) C. H. Hendrickson and D. P. Eyman, *Inorg. Chem.*, 6, 1461 (1967).

$(CH_3)_3 \cdot OC_4H_8$, 8.5 ± 1 for $Al(CH_3)_3 \cdot (CH_3)_3COCH(CH_3)_2$, 6.9 ± 2 for $Al(CH_3)_3 \cdot S(CH_3)_2$, and 5.8 ± 2 for $Al(CH_3)_3 \cdot S[CH_2CH(CH_3)_2]_2$. These values are consistent with the bimolecular pathway proposed; the calculated entropies of activation in all cases are on the order of −12 eu.

It is likely that the intermediate in a base-assisted exchange process of the type described is important in determining the rates of reaction of certain substrates with $Al(CH_3)_3$. For example, Ashby and coworkers have shown that the reaction of trimethylaluminum with benzophenone is very strongly influenced by the presence of excess trimethylaluminum.[17] Whereas the reaction of the adduct by itself to form the alkoxide, eq 28, requires 24 hr at reflux for completion, in the

$$(CH_3)_3AlOC(C_6H_5)_2 \longrightarrow (CH_3)_2AlOC(CH_3)(C_6H_5)_2 \qquad (28)$$

presence of excess $Al_2(CH_3)_6$ the reaction proceeds very much more rapidly. Formation of the alkoxide requires the transfer of a methyl group from the metal to the carbonyl carbon. It is reasonable to suppose that this might occur much more readily in an intermediate analogous to I than in the simple adduct by itself. The kinetic data reported for the benzophenone system[17] have been interpreted in terms of an interaction between the $(CH_3)_3AlOC(C_6H_5)_2$ and monomeric $Al(CH_3)_3$, rather than with the dimer as depicted in I. This is quite consistent with our suggestion, since the methyl group transfer is more likely to occur upon interaction of the adduct with the more strongly acidic monomer. Complex formation with $Al_2(CH_3)_6$ has, however, been suggeted in another system.[18]

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(17) E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Amer. Chem. Soc.*, **90**, 5179 (1968).

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Nuclear Magnetic Resonance Studies of Methylatobis(dimethylglyoximato)cobalt(III) Adducts[1]

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Abstract: Reaction of bases with dimeric methylatobis(dimethylglyoximato)cobalt(III) in CH_2Cl_2 or C_6H_5Br solution leads to adducts: $[CH_3Co(DH)_2]_2 + 2L \rightleftarrows 2CH_3Co(DH)_2L$. Adduct formation is essentially complete, as evidenced by the proton nmr spectra at temperatures in the slow-exchange region, for L = $N(CH_3)_3$, CH_3CN, C_5H_5N, $P(OCH_3)_3$, $P(C_6H_5)_3$, $(CH_3)_2SO$, and $S(CH_3)_2$. The equilibrium was observed to be incomplete for diphenyl sulfoxide. Coordination isomerism is observed for dimethyl sulfoxide; the ratio of oxygen to sulfur coordination at −25° is 3.7. Addition of aquomethylatobis(dimethylglyoximato)cobalt(III) to d_6-DMSO containing some CH_2Cl_2 results in displacement of H_2O. The reciprocal mean-exchange time of protons between the water and the OHO bridges is estimated from the line shapes to be on the order of 10 and 50 sec^{-1} at 5 and 25°, respectively. Detailed line-shape studies at various temperatures yield Arrhenius activation energies for dissociation of the $P(OCH_3)_3$ and $P(C_6H_5)_3$ complexes of 23 and 21 kcal/mol, respectively, with an estimated uncertainty of about 3 kcal/mol.

In an earlier communication[2] we reported some observations on the ligand-exchange behavior of complexes of methylatobis(dimethylglyoximato)cobalt(III), $CH_3Co(DH)_2$ (also referred to as methylcobaloxime[3]). We report here some further details of the observations regarding ligand exchanges. In the contribution which follows[4] we describe detailed studies of the ligand-free forms of $RCo(DH)_2$ compounds, which are dimeric.

The $[CH_3Co(DH)_2]_2$ dimer is readily disrupted in solution by a variety of bases to form adducts $CH_3Co(DH)_2L$, where L may be an amine, sulfide, phosphite, phosphine, isonitrile, or other base.[5] The adducts vary considerably in the strength of the cobalt–ligand bond, as evidenced by the rates of dissociation of the ligand L, measured using nmr techniques.[2]

Attention has been drawn to the similarity of the cobalt–carbon bond in the alkylcobaloximes to that in methylcobalamin and coenzyme B_{12}.[3,6,7] The behavior of the metal center in the methylcobaloxime with respect to ligation in the position trans to the methyl group is of interest because of its possible relevance to binding of the vitamin to substrates. There is, of course, a great difference in the degree of steric hindrance toward coordination in the two systems. The electronic environments of the cobalt in the two systems may, however, be quite similar,[7] and thus they might be expected to exhibit the same preferential binding of certain ligand types. Comparison of the results reported in this work with the relatively slight evidence regarding coordination to methyl-

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