^{1}H Nuclear Magnetic Resonance Studies of Exchange Reactions between Complexes $R_3M,M'R_3'$ and their Components. Part II.[1,2] Exchange between the Complex Trimethylphosphine–Trimethylborane and an Excess of Trimethylborane and between Trimethylphosphine–Trimethylalane and an Excess of Hexamethyldialuminium

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The reaction between the complex Me_3P,BMe_3 and an excess of trimethylborane in toluene or dichloromethane is first order in complex concentration, consistent with a dissociative mechanism. Data for the complex $Me_3P,AlMe_3$ and an excess of hexamethyldialuminium in toluene suggest a bimolecular reaction between complex and monomeric trimethylalane. Explicit n.m.r. line-shape equations are given for exchange between a singlet and a first-order doublet.

EXCHANGE of components between molecules of donor–acceptor complexes (DA) involving a Group V or VI donor (D) and a Group III acceptor (A) have been studied by n.m.r. methods. In some cases, rates have been derived from measurements of peak widths, but in others, where there is overlap between exchange-broadened peaks or where there are complications from spin–spin coupling, comparison of full experimental and calculated line-shapes has been necessary. The reaction between the complexes Me_3N,BMe_3 and an excess of trimethylborane is first order in complex

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[1] Ref. 2 should be regarded as Part I of this series.

[2] K. J. Alford, E. O. Bishop, P. R. Carey, and J. D. Smith, *J. Chem. Soc.* (*A*), 1971, 2574.

[3] A. H. Cowley and J. L. Mills, *J. Amer. Chem. Soc.*, 1969, **91**, 2911.

concentration,[3] suggesting that dissociation of the complex is rate determining. A similar dissociative

$$DA \xrightarrow[\text{slow}]{k_1} D + A;\ D + A^* \xrightarrow[\text{fast}]{k_{-1}} DA^* \quad (1)$$

$$\tau_{(DA)} = k_1^{-1};\ \tau(A) = k_1^{-1}[A]/[DA]$$

mechanism has been proposed[4] for exchange between the complexes $D,AlMe_3$ ($D = Et_3N$ or Bu_3P) and an excess of hexamethyldialuminium, but bimolecular mechanisms are suggested when D = pyridine (py), Me_2S, and Bu^tPr^iO. Dissociation of the complex seems to be rate determining for exchange between $D,GaMe_3$ and trimethylgallane ($D = Me_3N$, Me_2HN, or Me_3P) and for exchange between $D,InMe_3$ and trimethylindium ($D = Me_3N$ or Me_2HN), but bimolecular displacements are indicated for exchange between $D,GaMe_3$ and trimethylgallane ($D = MeH_2N$, H_3N, py, or Me_2O) and between $MeH_2N,InMe_3$ and trimethylindium.[5]

In this paper, we describe the exchange reactions between Me_3P,BMe_3 and trimethylborane and between $Me_3P,AlMe_3$ and hexamethyldialuminium. For both these reactions, the n.m.r. signal due to protons of the complexed acceptor $M'Me_3$ is a doublet, and the signal due to the free acceptor is a singlet. Under fast-exchange conditions the doublet and singlet coalesce to a single peak. The singlet from uncomplexed hexamethyldialuminium is partly broadened by bridge-terminal exchange.[6,7] This is considerably faster than the exchange reaction with the complex $Me_3P,AlMe_3$, but the broadening must be allowed for in deriving kinetic parameters by comparison of experimental and calculated spectra. We have therefore used line-shape equations for exchange between a singlet and a first-order doublet which include the possibility of different transverse relaxation times T_2 for each site.

EXPERIMENTAL

The preparation of samples, using vacuum-line techniques, has been described.[2] No precipitates formed in solutions in dichloromethane; it seems that the complex Me_3P,BMe_3 reacts with the solvent much less readily than does trimethylphosphine. For samples with an excess of trimethylborane, b.p. -22 °C, it was necessary to make an allowance for material in the vapour phase. This was estimated in two ways which gave values in close agreement. First, vapour pressures of solutions of Me_3P,BMe_3 and BMe_3 in toluene were measured for the range of concentrations and temperatures used in the kinetic experiments. Secondly, the relative areas of the n.m.r. peaks due to the methyl protons of trimethylborane and trimethylphenylsilane, b.p. 171 °C, assumed to be non-volatile, were found by integration for an appropriate series of concentrations and temperatures. Typically, *ca.* 10% of the trimethylborane distilled into an n.m.r. tube was in the vapour at -10 °C. The concentration of uncomplexed trimethylphosphine was assumed to be small in all samples, for reasons given in ref. 2.

For samples containing hexamethyldialuminium, n.m.r. tubes were sealed directly on to the vacuum line, which was equipped with mercury float valves and greaseless. Each new set of tubes was dried with hexamethyldialuminium vapour before use. No correction for hexamethyldialuminium in the vapour phase was necessary,[8] and the concentration of uncomplexed trimethylphosphine, found from the dissociation constant of the complex $Me_3P,AlMe_3$,[9] was negligible.

N.m.r. spectra were recorded on Varian HA100 or A60 spectrometers. The temperature of each sample was checked using a standard methanol sample, and all spectra of a series were recorded on the same day.

RESULTS

Line Envelope for Singlet–Doublet Exchange.—Let the singlet site be A and the first-order doublet sites be B and C, which are equally populated. Consider the exchange of spin-1/2 nuclei between sites A and B, and, with equal probability, between sites A and C, equations (2)—(4) are applicable [where p_j = fractional population, ω_j =

$$p_B = p_C = \tfrac{1}{2}p_{(DA)} \quad (2)$$

$$\tau_B = \tau_C = \tau_{(DA)} \quad (3)$$

$$\omega_B, \omega_C = \omega_{(DA)} \pm \tfrac{1}{2}J \quad (4)$$

unperturbed resonant frequency (in angular units, rad s^{-1}), τ_j = mean lifetime, and $T_{2(j)}$ = transverse relaxation time, each for nuclei in the jth site (j = A, B, or C) and DA is the molecular species giving the doublet of component spacing J (rad s^{-1})]. Quantities F_j may be defined by equation (5), where ω_1 is the angular frequency of the field H_1.

$$F_j = \tau_j^{-1} + T_{2(j)}^{-1} - \mathrm{i}(\omega_j - \omega_1) \quad (j = \mathrm{A, B, or\ C}) \quad (5)$$

McConnell's method[10] gives equations (6)—(8) for the rate of change of site magnetizations M_A, M_B, and M_C, where M_0p_j are their unperturbed values in the presence of the field H_0 alone. Under slow passage conditions,

$$(\mathrm{d}M_A/\mathrm{d}t) + F_AM_A = -\mathrm{i}\gamma H_1M_0p_A + \tau_B^{-1}(M_B + M_C) \quad (6)$$

$$(\mathrm{d}M_B/\mathrm{d}t) + F_BM_B = -\mathrm{i}\gamma H_1M_0p_B + \tfrac{1}{2}\tau_A^{-1}M_A \quad (7)$$

$$(\mathrm{d}M_C/\mathrm{d}t) + F_CM_C = -\mathrm{i}\gamma H_1M_0p_B + \tfrac{1}{2}\tau_A^{-1}M_A \quad (8)$$

the time differentials may be equated to zero, giving three coupled linear equations in M_A, M_B, and M_C. The solutions are (9) and (10). M_B and M_C are related simply ($F_BM_B = F_CM_C$), but need not be known separately. The above complex expressions contain both the in- and out-of-phase components of the magnetization. From the

$$M_A = \frac{\mathrm{i}\gamma H_1M_0[p_AF_BF_C + p_B\tau_B^{-1}(F_B + F_C)]}{\tfrac{1}{2}\tau_A^{-1}\tau_B^{-1}(F_B + F_C) - F_AF_BF_C} \quad (9)$$

$$M_B + M_C = \tau_B(\mathrm{i}\gamma H_1M_0p_A + F_AM_A) \quad (10)$$

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[4] T. L. Brown and L. L. Murrell, *J. Amer. Chem. Soc.*, 1972, **94**, 378.

[5] J. P. Oliver, *Adv. Organometallic Chem.*, 1970, **8**, 167.

[6] K. C. Williams and T. L. Brown, *J. Amer. Chem. Soc.*, 1966, **88**, 5460.

[7] E. A. Jeffery and T. Mole, *Austral. J. Chem.*, 1969, **22**, 1129.

[8] M. B. Smith, *J. Organometallic Chem.*, 1972, **46**, 31.

[9] C. H. Henrickson, D. Duffy, and D. P. Eyman, *Inorg. Chem.*, 1968, **7**, 1047.

[10] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.

original formulation of the Bloch equations, the line envelope $L(\omega_1)$ of the absorption mode signal requires the imaginary part (Im) (11). Defining $T_j = \tau_j^{-1} + T_{2(j)}^{-1}$

$$L(\omega_1) = \mathrm{Im}(M_A) + \mathrm{Im}(M_B + M_C) \qquad (11)$$

and $W_j = \omega_j - \omega_1$, then equations (12) and (13) may be obtained.

$$\mathrm{Im}(M_A) = \gamma H_1 M_0 (QX + PY)/(X^2 + Y^2) \qquad (12)$$

$$\mathrm{Im}(M_B + M_C) = \frac{\tau_B \gamma H_1 M_0}{X^2 + Y^2}\Big[X(T_A Q - W_A P + p_A X) + Y(T_A P + W_A Q + p_A Y)\Big] \qquad (13)$$

where

$$P = p_A(W_B T_C + W_C T_B) + p_B \tau_B^{-1}(W_B + W_C)$$

$$Q = p_A(T_B T_C - W_B W_C) + p_B \tau_B^{-1}(T_B + T_C)$$

$$X = \tfrac{1}{2}\tau_A^{-1}\tau_B^{-1}(T_B + T_C) + T_C(W_A W_B - T_A T_B) + W_C(W_A T_B + W_B T_A)$$

$$Y = \tfrac{1}{2}\tau_A^{-1}\tau_B^{-1}(W_B + W_C) - T_C(W_A T_B + W_B T_A) + W_C(W_A W_B - T_A T_B)$$

The Trimethylphosphine–Trimethylborane System.—At −40 °C, the spectrum of Me_3P,BMe_3, with an excess of trimethylborane in toluene [Figure 1(*a*)], showed a singlet (I) (1·38 p.p.m. upfield from *Me*Ph, attributed to uncomplexed trimethylborane), and doublets[2] (II) (1·72 p.p.m., attributed to Me_3P,BMe_3) and (III) (1·96 p.p.m., $Me_3P,B\mathit{Me}_3$). As the temperature was raised, the resonances (I) and (III) broadened and finally collapsed to a narrow singlet at a position given by the weighted mean of the chemical shifts for the uncomplexed and complexed trimethylborane. This shows that the reaction (14) between complex and trimethylborane is fast on the n.m.r. time-scale at +30 °C and slow at −40 °C. The

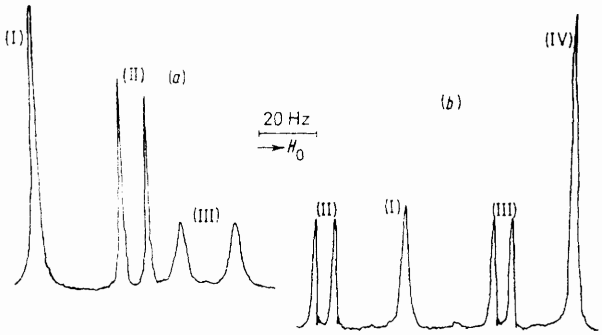


FIGURE 1 100 HMz ¹H N.m.r. spectra of trimethylphosphine with an excess of (*a*) trimethylborane at −40 °C and (*b*) hexamethyldialuminium at −60 °C. For notation see text

$$Me_3P,BMe_3 + {}^*BMe_3 \rightleftharpoons Me_3P,{}^*BMe_3 + BMe_3 \qquad (14)$$

doublet (II) was unaffected by the exchange process and remained sharp at all temperatures, although its chemical shift changed. Kinetic parameters may be derived from the remainder of the spectrum. In toluene at −40 °C, signals (I) and (III) appeared on either side of signal (II), so at higher temperatures some of the spectrum of interest was lost beneath the doublet (II). In most cases, however, the unobscured part of the spectrum was sufficient to permit line-shape analysis. Spectra of solutions in dichloromethane at −40 °C showed doublet (II) (4·24 p.p.m. upfield from $C\mathit{H}_2Cl_2$) at lower field than singlet (I) (4·63 p.p.m.) or doublet (III) (5·59 p.p.m.). At no temperature, therefore, was the exchange-broadened region obscured.

Spectra of samples at −40 °C showed that the resonance (III) from complexed BMe_3 was broader than that from the uncomplexed BMe_3 (I). This was accommodated in the line-shape analysis by applying a finite spin–spin relaxation time T_2 to resonance (III), as in the previous study.[3] The variation of T_2 over the small temperature range used in the kinetic experiments was small, and the previous constant value was used.

A computer program was written to give a least-squares fit between experimental and theoretical curves by iterative convergence. Three variables were used: (i) the chemical shift of complexed trimethylborane from the solvent peak; (ii) the chemical shift of uncomplexed trimethylborane from the solvent peak; and (iii) the mean lifetime of the complex, $\tau_{(DA)}$. Starting values of (i) and (ii) were found from graphs of chemical shifts of complexed and free BMe_3 against temperature. An initial value for $\tau_{(DA)}$ was found from a non-iterative version of the program, by matching spectra by eye. Table 1 lists values of $\tau_{(DA)}^{-1}$ over a range of temperature for a single sample in toluene, and for another sample in dichloromethane. Compositions at the lower end of the temperature range are given in this Table and small corrections were made at higher temperatures as described above. Values of $\tau_{(DA)}^{-1}$ found at constant temperature for samples of varying composition are given in Table 2.

TABLE 1

Variation of lifetime of complex with temperature for the system trimethylphosphine–trimethylborane

100 MHz Spectra: $[Me_3P,BMe_3]$ 0·168M; $[BMe_3]$ (excess) 0·254M; in toluene

t/°C	−2·5	−6	−8	−10	−18	−21·5	−27
$\tau_{(DA)}^{-1}/s^{-1}$	231	135	143	75	43	27	11

60 MHz Spectra: $[Me_3P,BMe_3]$ 0·114M; $[BMe_3]$ (excess) 0·049M; in dichloromethane

t/°C	+1	−4	−6	−8	−10	−12	−14	−16	−18
$\tau_{(DA)}^{-1}/s^{-1}$	111	49·3	40·6	35·5	27·0	23·1	18·4	14·3	10·1

TABLE 2

Lifetime of complex at various concentrations for the system trimethylphosphine–trimethylborane

100 MHz Spectra in toluene at −9 °C

$[BMe_3]$ (excess)/M	0·119	0·254	0·203	0·536	0·675
$[Me_3P,BMe_3]$/M	0·248	0·168	0·153	0·431	0·665
$\tau_{(DA)}^{-1}/s^{-1}$ [a]	100	95	105	98	115

60 MHz Spectra in dichloromethane at +1 °C

$[BMe_3]$ (excess)/M	0·049	0·135	0·181	0·228
$[Me_3P,BMe_3]$/M	0·114	0·087	0·116	0·195
$\tau_{(DA)}^{-1}/s^{-1}$ [b]	111	94	112	124

[a] Mean, 103 s⁻¹; a plot of $\tau_{(A)}^{-1}$ against [DA]/[A] had a gradient of 100 s⁻¹. [b] Mean, 110 s⁻¹; a plot of $\tau_{(A)}^{-1}$ against [DA]/[A] had a gradient of 108 s⁻¹.

The Trimethylphosphine–Trimethylalane System.—At −60 °C, the spectrum of $Me_3P,AlMe_3$, with an excess of hexamethyldialuminium in toluene [Figure 1(*b*)] showed two singlets (I) (2·07 p.p.m. upfield from *Me*Ph) and (IV) (2·64 p.p.m.), attributed to the bridge and terminal methyl groups of hexamethyldialuminium,[6,7] and two doublets, (II) [1·75 p.p.m., ^{2}J(PCH) −6·8 Hz, from *Me*$_3$P,AlMe$_3$] and (III) [2·45 p.p.m., ^{3}J(PAlCH) ±6·75 Hz, from Me$_3$P,-Al*Me*$_3$]. As the temperature was raised to −30 °C, singlets (I) and (IV) moved together close to the doublet (III), which remained sharp. At still higher temperatures, all the peaks except doublet (II) coalesced to a single line at the weighted mean position of (I), (III), and (IV). Spectra of hexamethyldialuminium alone in toluene[6] show that peaks (I) and (IV) merge to a single resonance above about −30 °C and that little asymmetry is detectable above *ca.* −20 °C. Spectra recorded above −20 °C were thus analysed in terms of singlet–doublet exchange to give kinetic parameters for reaction (15).

$$\mathrm{Me_3P,Al^{*}Me_3 + Me_2AlMe_2AlMe_2 \rightleftharpoons Me_3P,AlMe_3 + [Me_2AlMe_2AlMe_2]^{*}} \quad (15)$$

Initial results at 60 MHz (Table 3) were obtained with the iterative program described above. This was less satisfactory than for the trimethylborane system, as the spectra were rather featureless. Quite small error functions could be obtained from computed solutions which smoothed out line-shape features and grossly overestimated the exchange rate. Later results at 100 MHz (Tables 3 and 4 and Figure 2), which are considered more reliable, were obtained by best visual fit using a non-iterative program. The singlet and doublet sites have similar chemical shifts in the temperature range of interest and so these must be found to greater accuracy than in the trimethylphosphine–trimethylborane system to obtain lifetimes $\tau_{(DA)}$ of comparable accuracy. We have therefore given values of the shift between singlet and doublet (Δν), obtained from our line-shapes, in Tables 3 and 4. A parallel variation in Δν was found from spectra at −60 °C, where the chemical shifts were directly measurable, and this provided a check on data at higher temperatures. For example, the second sample in Table 4 gave a spectrum at −10 °C in which the resonance of the uncomplexed hexamethyldialuminium was reduced to a slight inflexion on one peak of the doublet. This was very sensitive to small errors in temperature measurement and phase balance. In this case the spectrum at −60 °C suggests that our value of Δν at −10 °C is too large and that the value for $\tau_{(DA)}$ is therefore too small.

TABLE 3

Variation of lifetime of complex with temperature for the system trimethylphosphine–trimethylalane

60 MHz Spectra: [Me$_3$P,AlMe$_3$] 0·186M; [Me$_6$Al$_2$] 0·073M

t/°C	0	−2	−5	−10	−15
$\tau_{(DA)}^{-1}$/s^{-1}	20·8	20·2	12·9	9·1	4·6
Δν/Hz	7·7	8·1	6·0	5·4	2·1

100 MHz Spectra: [Me$_3$P,AlMe$_3$] 0·186M; [Me$_6$Al$_2$] 0·073M

t/°C	+1·5	−5	−8	−10	−14	−15	−20
$\tau_{(DA)}^{-1}$/s^{-1}	18·2	18 ± 2 [a]	10·0	8·0	5·0	4·0	2·6
Δν/Hz	10·6	10·5 ± 1·5	8·8	9·1	7·5	7·5	6·3

[a] Parameters from this spectrum were less accurate than those from the others.

TABLE 4

Lifetimes of complex and acceptor at various concentrations for the system trimethylphosphine–trimethylalane

		At −10 °C [a]			At −14 °C [b]			At −60 °C [c]
[Me$_3$P,AlMe$_3$] M	[Me$_6$Al$_2$] (excess) M	$\tau_{(DA)}^{-1}$ s^{-1}	$\tau_{(A2)}^{-1}$ [c] s^{-1}	Δν [d] Hz	$\tau_{(DA)}^{-1}$ s^{-1}	$\tau_{(A2)}^{-1}$ [c] s^{-1}	Δν [d] Hz	Δν [d] Hz
0·225	0·337	15·4	5·1	12·1	10·5	3·5	11·2	−5·5
0·198	0·056	10·0	17·8	11·0	5·0	8·9	8·0	−9·7
0·186	0·073	8·0	10·2	9·1	5·0	6·4	7·3	−9·5
0·075	0·049	7·7	5·9	7·6	4·0	3·1	5·7	−12·2
0·095	0·159	12·5	3·7	8·2	7·7	2·3	7·5	−9·5

[a] Calculated with $T_{2(DA)}$ 0·27 s; $T_{2(A2)}$ 0·094 s. Spectra at 100 MHz. [b] Calculated with $T_{2(DA)}$ 0·27 s; $T_{2(A2)}$ 0·087 s. Spectra at 100 MHz. [c] $\tau_{(A2)}^{-1} = \tau_{(DA)}^{-1}$ [DA]/2[A$_2$]. [d] Δν Positive indicates signal from complexed AlMe$_3$ at higher field.

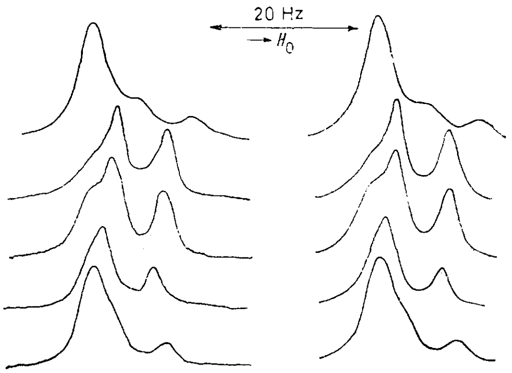


FIGURE 2 100 MHz ^{1}H N.m.r. spectra of samples at −14 °C with various trimethylphosphine : trimethylalane ratios. Left-hand side, experimental; right-hand side, calculated spectra. The samples are in the same sequence as in Table 4

The singlet from hexamethyldialuminium above −20 °C was appreciably broader than that from trimethylborane, due to a combination of T_2 processes and bridge-terminal exchange. The whole of the broadening was allowed for in the line-shape analysis in an apparent $T_{2(A)}$ term, estimated for each temperature from our spectra of toluene solutions of hexamethyldialuminium.

DISCUSSION

For the trimethylphosphine–trimethylborane system, mechanism (1) accounts for the experimental results. Thus, from Table 2, the lifetime of the complex, $\tau_{(DA)}$, shows little variation over a four-fold variation in concentration of DA and a five-fold variation in concentration of uncomplexed acceptor A, as required if the dissociation of the complex is the rate-determining step. Similar results were obtained from solutions in toluene and dichloromethane. Arrhenius activation energies E_a and thermodynamic activation parameters were found from the data of Table 1, using the equations $\Delta H^{\ddagger} = E_a - RT$ and $\log \tau_{(DA)}^{-1} = \log \boldsymbol{k}T/\boldsymbol{h} + (\Delta S^{\ddagger}/2{\cdot}3R) - (\Delta H^{\ddagger}/2{\cdot}3RT)$. Values for solutions in toluene

($E_a = 67 \pm 6$ kJ mol^{-1}, $\Delta H^\ddagger = 65 \pm 6$ kJ mol^{-1}, $\Delta S^\ddagger = +39 \pm 20$ J K^{-1} mol^{-1}) are similar to those found in studies of the exchange reaction with an excess of trimethylphosphine.[2] The activation enthalpy is similar to the gas-phase enthalpy of dissociation (69 kJ mol^{-1})[11] for the complex Me_3P,BMe_3, confirming that dissociation of the complex is the common slow step, whichever component is in excess. Activation parameters for solutions in dichloromethane ($E_a = 66 \pm 5$ kJ mol^{-1}, $\Delta H^\ddagger = 64 \pm 6$ kJ mol^{-1}, $\Delta S^\ddagger = +27 \pm 20$ J K^{-1} mol^{-1}) are not distinguishable from those in toluene, within the estimated limits of experimental error.

The trimethylphosphine–trimethylalane system is more complicated. Here the concentration of acceptor A is very small, at room temperatures or below, compared with that of the dimer A_2. The following mechanisms may be considered and expressions for life-times $\tau_{(DA)}$ and $\tau_{(A_2)}$ derived by the method of Matteson.[12]

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A;\ DA \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} D + A \qquad (16)$$

$$\tau_{(A_2)} = k_1^{-1} + 2[A_2]/k_2[DA];\ \tau_{(DA)} = k_2^{-1} + [DA]/2k_1[A_2]$$

$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A;\ A + DA^* \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} DA + A^* \qquad (17)$$

$$\tau_{(A_2)} = k_1^{-1} + 2[A_2]^{\frac{1}{2}}/k_3(k_1/k_{-1})^{\frac{1}{2}}[DA];\ \tau_{(DA)} = 1/k_3(k_1/k_{-1})^{\frac{1}{2}}[A_2]^{\frac{1}{2}} + [DA]/2k_1[A_2]$$

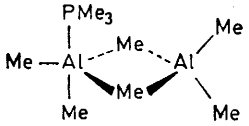
$$A_2 + DA^* \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_2A^*D \rightleftharpoons AA^* + DA \qquad (18)$$

$$\tau_{(A_2)} = 3/k_4[DA];\ \tau_{(DA)} = 3/2k_4[A_2]$$

The rate constant k_1 at −14 °C may be estimated[6,7] as 2—5×10^3 s^{-1}. Putting $k_1^{-1} = 0$, mechanism (16) becomes equivalent to mechanism (1) discussed above for the Me_3P,BMe_3 system. Clearly, this mechanism is inappropriate for the $Me_3P,AlMe_3$ system as Table 4 shows that $\tau_{(DA)}$ is not independent of concentration of acceptor A_2. Further, the energy of activation E_a for the exchange reaction, derived by plotting log $\tau_{(DA)}^{-1}$ against $1/T$, is 62 ± 10 kJ mol^{-1}, which is considerably less than 88 kJ mol^{-1}, the heat of dissociation of the complex $Me_3P,AlMe_3$. However, this last value was found from solutions in hexane; the heat of dissociation in toluene may be less, since there is some evidence for strong solvation of monomeric trialkylalanes by aromatic hydrocarbons.[13]

The data of Table 4 for −14 °C define a line $\tau_{(A_2)} = (0{\cdot}106 \pm 0{\cdot}011)[A]^{\frac{1}{2}}/[DA] + (0{\cdot}001 \pm 0{\cdot}029)$ and so fit well with mechanism (17). Plots of $\tau_{(DA)}$ against $1/[A_2]^{\frac{1}{2}}$ are also approximately linear. The enthalpy of dissociation ΔH_{diss} of hexamethyldialuminium in toluene has been given[13] as $65{\cdot}4 \pm 5{\cdot}9$ kJ mol^{-1} and we estimate * the equilibrium constant $K_c = k_1/k_{-1}$ as $2{\cdot}3 \times 10^{-8}$M at −14 °C. With the data of Tables 3 and 4 we find the rate constant k_3 at −14 °C is $1{\cdot}2 \times 10^5$ l mol^{-1} s^{-1}. The activation enthalpy for the bimolecular reaction in mechanism (17), given by $E_a - RT - \frac{1}{2}\Delta H_{diss}$, is 23 ± 6 kJ mol^{-1}, and the corresponding activation entropy $\Delta S^\ddagger$ is -57 ± 25 J K^{-1} mol^{-1}. Our data do not cover a sufficiently large range of concentrations of uncomplexed hexamethyldialuminium to rule out unequivocally the possibility of concurrent unimolecular and bimolecular reactions [mechanisms (16) and (18)]. Mechanism (18) alone is certainly insufficient to account for the results since a plot of $\tau_{(DA)}$ against $1/[A_2]$ does not pass through the origin.

Exchange between trimethylphosphine–trimethylgallane and an excess of trimethylgallane involves rate-determining dissociation of complex rather than bimolecular displacement of one trimethylgallane molecule by another.[5] This is attributed to crowding in the presumed bimolecular transition state $Me_3P(GaMe_3)_2$. A similar rationalization may be applied to exchange between the complex Me_3P,BMe_3 and an excess of trimethylborane, but it will not account for the bimolecular displacements observed for the complexes $Me_3P,AlMe_3$, py,$AlMe_3$, or py,$GaMe_3$,[14] each with an excess of acceptor. The bonds between the acceptors and trimethylphosphine or pyridine are strong, and phosphorus, unlike oxygen,[4] has only one lone-pair available for co-ordination. One possibility is that methyl-group exchange between complexed and uncomplexed trimethylalane does not involve breaking of the Al–P bond at all,[15] and that the transition state for the bimolecular step of mechanism (17) is as below,



similar to that suggested for exchange between the complexes PhMeO,$AlMe_3$ and PhMeO,$AlMe_2X$ (X = Cl, Br, or Ph). Five-co-ordinate aluminium is known in a number of crystalline compounds.[16] The failure of trimethyl-borane and -gallane to show mechanism (17) is then related to the failure of these molecules to dimerize.

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* In aliphatic hydrocarbons,[8] $\ln K_c = 14{\cdot}744 - (9\,762{\cdot}5/T)$. The equilibrium concentration of $AlMe_3$ at − 50° C is eight times as great in toluene as in cyclopentane solution of the same molarity.[13] We assume K_c(toluene) = 64 K_c (C_5H_{10}) at − 50 °C and $K_x = K_c \times$ (molar volume of solvent).

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