

Table III are slightly modified from the experimental values based on the isotope ratios obtained from our disilane spectrum.

We used the values for 1,2-H₂Si₂D₄ instead of those for 1,1-H₂Si₂D₄, since this sample was of a higher purity. The 1,1-H₂Si₂D₄ contained about 15% Si₂D₆H. When the intensities of Si₂D₆H were removed from those of 1,1-H₂Si₂D₄, the mass spectra of both H₂Si₂D₄ isomers were similar.

The mass spectra of disilane and disilane-*d*₆ were obtained with butane as an internal standard. These experiments demonstrated that the relative intensity of the parent peak for disilane compared to disilane-*d*₆ was 1.05 at equal pressures. We have calculated relative quantities with the assumption that the most intense *m/e* values have the same intensities at equal pressure.

(4) **Decomposition Reactions of SiH₄-SiD₄ Mixtures.**—The silent electrical discharge and direct photolysis of equimolar mixtures of silane and silane-*d*₄ were examined in a mercury-free vacuum system.

Silane and silane-*d*₄ were prepared by the reduction of silicon tetrachloride with lithium aluminum hydride and lithium aluminum deuteride. The infrared spectrum of the silane-*d*₄ demonstrated that only a very small amount of silane-*d*₃⁹ was present. Mass spectra of the silanes demonstrated that no disilanes were present.

The electric discharge apparatus was similar to that described by Spanier and MacDiarmid⁹ with a transformer potential of 5000 V. A polymer was deposited by the discharge decomposition of silane and the polymer was converted to a mirror by the electric discharge in the presence of hydrogen. All of the discharge reactions were carried out in the tube coated with this silicon mirror.

The xenon lamp (1470 Å) used in the direct photolysis experiments was similar in design to that described by Okabe¹⁰ except that the lithium fluoride window was sealed as described by Bass¹¹ in order to prevent decomposition of the sealant. The lamp intensity was of the order of 2 × 10¹⁵ quanta/sec. However, a mirror was deposited on the LiF window which greatly reduced the effective lamp intensity. The rapid decomposition on the mirror made it impossible to obtain quantum yields.

In the electric discharge reactions, the ratio of mixed silanes (SiH₃D, SiH₂D₂, SiHD₃) produced to disilanes formed was less than 1:8. In the photolysis experiments, the mixed silanes were not observed. The total silane decomposition in each experiment was of the order of 2–4%.

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(9) J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956).

(10) H. Okabe, *J. Opt. Soc. Am.*, **54**, 478 (1964).

(11) A. M. Bass, *Appl. Opt.*, **5**, 1967 (1966).

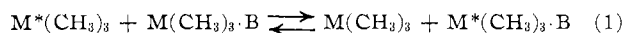
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Nuclear Magnetic Resonance Studies on Exchange Reactions of Group III Alkyl Derivatives. IV. Trimethylgallium-Trimethylphosphine

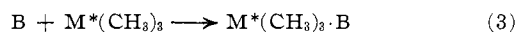
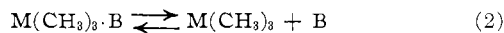
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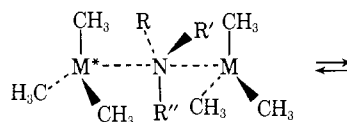
Earlier papers in this series have investigated group exchange reactions of the type^{3–5} shown in eq 1



where M = M* = Ga or In and B = trimethylamine (I), dimethylamine (II), monomethylamine (III), or ammonia (IV). For both the gallium and indium systems a dissociative process (shown in eq 2 and 3) is followed when the base is I or II. When the base is



III or IV, the bimolecular process shown in eq 4 becomes lower in energy and is preferred. Because of the



nature of the transition state in eq 4, it is reasonably easy to see why, when R, R', and R'' are all methyl groups, the exchange proceeds by the dissociation mechanism. The transition state in eq 4 is simply too sterically hindered. Only as two methyl groups are replaced by hydrogen atoms does the bimolecular process become energetically favored.

Contrary to this, when the amine adducts of trimethylgallium and trimethylindium are present with excess base, base exchange is postulated to proceed through a bimolecular process in all cases. For these systems the central atom in the transition state is the larger group III atom, and the transition state is able to form even with the fully methylated derivatives. Cowley and Mills have observed that base exchange with the trimethylboron-trimethylamine adduct does proceed through unimolecular dissociation of the adduct,⁶ implying steric crowding for the hypothetical bimolecular transition state.

Considering the manner in which steric interactions influence the mechanism of reaction, it was of interest to study Ga(CH₃)₃ exchange with the Ga(CH₃)₃·P(CH₃)₃ adduct to see whether the phosphorus atom was large enough to accommodate bimolecular exchange for the fully methylated derivative.

A preliminary report postulated that this exchange might proceed *via* a bimolecular pathway or through the bimolecular and unimolecular processes simultaneously.³ The more detailed kinetic and activation energy studies undertaken here, however, clearly point toward a dissociation pathway equivalent to that for trimethylamine.

Experimental Section

All materials were prepared by methods reported earlier.³ Methylene chloride was used as solvent after refluxing over

(1) Recipient of a NASA traineeship for 1968–1969.

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(3) J. B. De Roos and J. P. Oliver, *Inorg. Chem.*, **4**, 1741 (1965).

(4) J. B. De Roos and J. P. Oliver, *J. Am. Chem. Soc.*, **89**, 3970 (1967).

(5) K. L. Henold and J. P. Oliver, *Inorg. Chem.*, **7**, 950 (1968).

(6) A. H. Cowley and J. L. Mills, *J. Am. Chem. Soc.*, **91**, 2911 (1969).

barium oxide. Samples were prepared by standard high-vacuum techniques and stored at -196° prior to use.

The concentrations in moles per liter of solvent were determined by integration of the low-temperature nonexchange spectra by comparing the intensity of the methylene chloride peak to the peaks of the interacting species. This has proved to be a more consistent method than the previously used method of pressure-volume measurements.

Nmr measurements were made on a Varian A-60A spectrometer equipped with a V-6040 temperature controller. Temperatures were determined by the method of Van Geet using the internal chemical shift of methanol⁷ {i.e., $T = 406.0 - 0.551|\Delta\nu| - 63.4(10^{-2}\Delta\nu)^2$ }. The pmr spectrum of the region of interest consists of three lines. One of these is caused by the protons on the free $\text{Ga}(\text{CH}_3)_3$. The other two arise from the $\text{Ga}(\text{CH}_3)_3$ protons in the adduct, split by the ^{31}P nucleus ($I = 1/2$); $J_{^{31}\text{P}-\text{H}} = 8.25$ cps. Lifetimes were determined by using the McConnell equations for exchange between nonequivalent sites⁸ modified for three sites, with the assumption that no exchange occurs between two adduct molecules. The calculated spectra were fitted to the experimental by a method of iteration over the lifetimes. This method has been described in detail elsewhere.⁹ An example of the fit between the calculated and experimental spectra is shown in Figure 1.

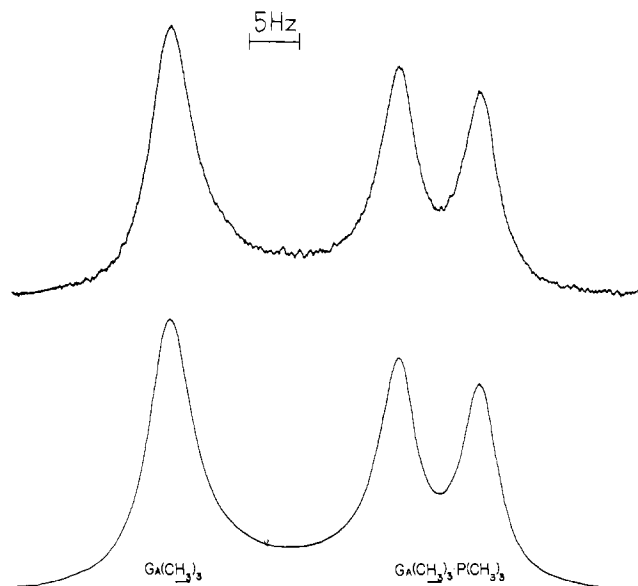


Figure 1.—The observed (top) and calculated (bottom) spectra of the $\text{Ga}(\text{CH}_3)_3-(\text{CH}_3)_3\text{Ga}\cdot\text{P}(\text{CH}_3)_3$ system at 251°K .

Results and Discussion

Results of a concentration dependence study on the $\text{Ga}(\text{CH}_3)_3-\text{Ga}(\text{CH}_3)_3\cdot\text{P}(\text{CH}_3)_3$ system are given in Table I. Detailed kinetic studies worked out earlier^{4,5} show that for a dissociation mechanism the lifetime of the $\text{Ga}(\text{CH}_3)_3$ protons (τ_A) is related to the concentration by the relationship

$$1/\tau_A = k \frac{[\text{Ga}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3]}{[\text{Ga}(\text{CH}_3)_3]} \quad (5)$$

The lifetimes of the adduct protons are independent of

$$1/\tau_{AB} = k \quad (6)$$

TABLE I
KINETIC PARAMETERS FOR THE
 $\text{Ga}(\text{CH}_3)_3-(\text{CH}_3)_3\text{Ga}\cdot\text{P}(\text{CH}_3)_3$ SYSTEM^a

$[\text{Ga}(\text{CH}_3)_3], M$	$[\text{Ga}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3], M$	$1/\tau_A, \text{sec}^{-1}$	$1/\tau_{AB}, \text{sec}^{-1}$	$[\text{Ga}(\text{CH}_3)_3]/\tau_A[\text{Ga}(\text{CH}_3)_3 \cdot \text{P}(\text{CH}_3)_3], \text{sec}^{-1}$
0.307	0.199	6.48	10.0	10.0
0.236	0.294	15.78	12.7	12.6
0.121	0.126	13.13	12.3	12.6
0.197	0.394	27.70	13.8	13.9
0.315	0.598	25.17	13.7	13.3

^a Average $k = 12.5 \pm 1.5 \text{ sec}^{-1}$ at 251°K .

concentration and for a bimolecular process $1/\tau_A$ and $1/\tau_{AB}$ are proportional to the concentrations of the adduct and free acid, respectively. The agreement between the values in columns 4 and 5 of Table I clearly demonstrate the validity of the dissociative mechanism described in eq 5 and 6.

The activation energy obtained from a least-squares fit of the Arrhenius plot of $\ln(1/\tau_A)$ vs. $1/T$ shown in Figure 2 gives a value of $16.9 \pm 0.5 \text{ kcal/mol}$ which

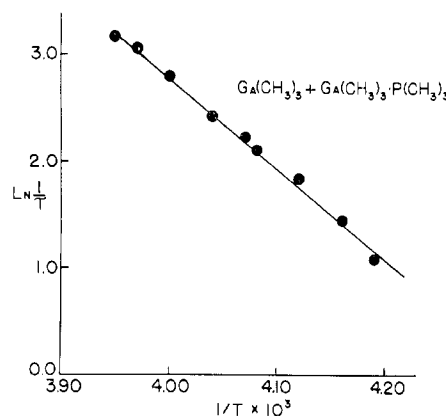


Figure 2.—The Arrhenius activation energy for the $\text{Ga}(\text{CH}_3)_3-(\text{CH}_3)_3\text{Ga}\cdot\text{P}(\text{CH}_3)_3$ system ($E = 16.9 \pm 0.5 \text{ kcal/mol}$).

is in reasonable agreement with the reported gas-phase dissociation energy of 18.0 kcal/mol .¹⁰ It is in even better agreement if one considers the studies of Hendrickson and Eyman which indicate that the solution-phase dissociation energies of alkylaluminum adducts are slightly lower than the gas-phase values.¹¹ The calculated entropy of activation, $+12 \text{ eu}$ (251°K), is also consistent with a dissociative mechanism.

The degree of steric crowding involved in the hypothetical bimolecular transition state even with the larger phosphorus atom can be more easily understood if one considers the crystal structure of the dioxonate of trimethylaluminum.¹² This structure revealed that instead of the expected tetrahedral coordination around the aluminum atom with the base molecule occupying the fourth site, the trimethylaluminum moiety retains a nearly planar configuration between the methyl groups

(7) A. L. Van Geet, Abstracts, 10th Experimental Nmr Conference, Pittsburgh, Pa., 1969.

(8) H. M. McConnell, *J. Chem. Phys.*, **23**, 430 (1955).

(9) K. L. Henold, J. Soulati, and J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 3171 (1969).

(10) G. E. Coates, *J. Chem. Soc.*, 2003 (1951).

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

(12) J. L. Atwood and G. O. Stucky, *J. Am. Chem. Soc.*, **89**, 5362 (1967).

and the aluminum atom. If the gallium-phosphine system is analogous to this, nine methyl groups would be reasonably close to each other in the transition

state illustrated in eq 4. Since this is not energetically favorable, the reaction proceeds through the dissociative mechanism.

Correspondence

Solid-State Behavior of Some Cobalt(II) Complexes Containing Trimethylamine N-Oxide

Sir:

Recently¹ we reported the preparation and study of several $\text{Co}(\text{TMNO})_2\text{X}_2$ (TMNO = trimethylamine N-oxide; X = halide, NCS) complexes. While the solution behavior of these complexes, alone and in the presence of added base, was easily interpreted by assuming a constant coordination number of 4 for the cobalt(II) ion, the solid-state data defied such interpretation. Definite differences between solid and solution electronic spectra were noted (Figures 1 and 2), and attempts to calculate values of λ' using solid-state moments (Table I) and solution-state spectrochemical data¹ gave completely unreliable results. Thus the use of a tetrahedral (or pseudotetrahedral) model for the crystalline compounds was discarded, although nothing definite was then formulated regarding their structures.

While the electronic spectra of these complexes are quite different from those in pseudooctahedral cases, such as $\text{Co}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$,² they do compare quite favorably with those of several complexes (such as $[\text{Co}(\text{Me}_6\text{tren})\text{Br}]\text{Br}$,³ $\text{Co}(\text{Et}_4\text{dien})\text{Cl}_2$,⁴ $\text{Co}(\text{Me}_5\text{dien})\text{Cl}_2$,⁵ and $[\text{Co}((\text{C}_6\text{H}_5)_2\text{CH}_2\text{AsO})_4(\text{ClO}_4)]\text{ClO}_4$ ⁶) known from X-ray studies to contain pentacoordinated cobalt(II). Thus it seems that these crystalline $\text{Co}(\text{TMNO})_2\text{X}_2$ complexes do not contain four- but rather five-coordinate cobalt(II).

The achievement of pentacoordination in these complexes requires that some type of ligand bridging be occurring, thereby reducing the molecular symmetry to a rather low level. Thus these complexes will be best described as having either distorted trigonal-bipyramidal or distorted square-pyramidal structures. While it

has been noted that the pattern of allowed electronic transitions for pentacoordinate cobalt(II) complexes is relatively independent of structure,^{3a,4a,7} these compounds do not possess the characteristics needed for stabilizing a square-pyramidal structure⁸ and thus are probably more closely trigonal bipyramidal in nature.

Using the idealized C_{3v} symmetry point group^{3a} for these complexes, the assignments for the electronic transitions can be made as follows: ν_2 , ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{E}(\text{F})$; ν_3 , ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{E}(\text{F})$; ν_4 , ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{A}_2(\text{P})$; ν_5 , ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{E}(\text{P})$. An alternative set of assignments, in which the ν_3 band would be assigned as a spin-forbidden transition (in D_{3h} symmetry),⁹ does not appear feasible if the widths of the spin-allowed and spin-forbidden bands are compared (Figure 2). The general positions of the main transitions and the magnetic moments vary in the anticipated way. The strengths of the ligand fields in these complexes (as determined by the transition energies) appear to be greater than those of the $\text{Co}(\text{Et}_4\text{dien})\text{X}_2$ ^{4a} and $\text{Co}(\text{Me}_5\text{dien})\text{X}_2$ ^{5a} complexes and approximately equal to those of the $[\text{Co}(\text{Me}_6\text{tren})\text{X}]\text{X}$ ^{3b} complexes. These findings are consistent with the high donor strength for TMNO found in four-coordinated cobalt(II) complexes.¹

Determination of the identity of the bridging ligands is complicated by the fact that the metal ions, anions, and amine oxides¹⁰ are all capable of such behavior. Metal-metal interaction appears unlikely, however, in light of the high magnetic moments recorded for the complexes (Table I). While it is apparent from the electronic spectra that the three halide complexes (and probably the thiocyanate complex) have the same structure, it is unfortunate that no physical method other than X-ray diffraction (or possibly nuclear quadrupole resonance) can definitively ascertain the nature of the bridging species in the halide complexes.

(7) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).

(8) Furlani states that a square-pyramidal structure can possibly be stabilized if any one or a combination of the following factors is present: (a) a ligand system (such as a pentadentate Schiff's base) which imposes the geometry upon the metal ion; (b) a weak, often electrostatic, interaction between a square-planar complex and a fifth ligand, as found in some palladium(II) complexes; and (c) the loss of stabilizing π bonding if the five-coordinate species were to distort from square-pyramidal geometry. These cobalt complexes possess none of the above qualities, and in addition the presence of unidentate, electronegative ligands is a factor which favors trigonal-bipyramidal coordination of metal ions.⁷

(9) J. S. Woods, *Inorg. Chem.*, **7**, 852 (1968).

(10) Thus pyridine N-oxide ($\text{C}_5\text{H}_5\text{NO}$) has been shown^{11,12} to act as a bridge between the two copper atoms in dimeric $[\text{Cu}(\text{C}_5\text{H}_5\text{NO})\text{Cl}_2]_2$.

(11) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(12) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

(1) D. W. Herlocker and R. S. Drago, *Inorg. Chem.*, **7**, 1479 (1968).

(2) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

(3) (a) M. Ciampolini and I. Bertini, *J. Chem. Soc., A*, 2241 (1968); (b) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (c) M. Ciampolini, N. Nardi, and G. P. Spononi, *Coord. Chem. Rev.*, **1**, 222 (1968); (d) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, **6**, 955 (1967); Mestren = $\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$.

(4) (a) Z. Dori and H. B. Gray, *ibid.*, **7**, 889 (1968); (b) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966); (c) Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, **6**, 483 (1967); Et₄dien = $\text{HN}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_3)_2]$.

(5) (a) M. Ciampolini and G. P. Spononi, *ibid.*, **5**, 45 (1966); (b) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965); Me₅dien = $\text{CH}_3\text{N}[\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$.

(6) (a) J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, **207**, 72 (1965); (b) P. Pauling, G. B. Robertson, and G. A. Rodley, *ibid.*, **207**, 73 (1965).