36. *Trimethylgallium. Part III.*[1] *Reaction with Diphenylphosphine and -arsine.*

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Dimeric products, exemplified by $(Me_2Ga{\cdot}PPh_2)_2$, have been obtained by reactions between trimethyl-aluminium, -gallium, and -indium, and diphenyl-amine, -phosphine, and -arsine. The order of reactivity, indicated by reaction temperatures, is $N < P < As$ in reaction with trimethylgallium, but the reverse order is observed with trimethylaluminium. The gallium compound mentioned was also prepared from diphenylphosphinosodium and dimethylgallium chloride in tetrahydrofuran–ether.

In Part II [1] of this series some reactions between trimethylgallium and donor molecules containing reactive hydrogen were described. During that work, the reaction with dimethylphosphine was investigated; it was found to be very slow and to result in the formation of some brown tarry matter. In contrast the dimethylamine complex,[2] $Me_3Ga,NHMe_2$, begins to decompose to methane and a dimer $(Me_2Ga{\cdot}NMe_2)_2$ at ~115°, the reaction being complete after about an hour at 180°.

We now find that the trimethylgallium adduct with diphenylamine begins to eliminate methane in the range 120—140°. Further heating causes little change in the rate of methane formation until about 200°, where extensive decomposition occurs. On the other hand, the diphenylphosphine complex, $Me_3Ga,PHPh_2$, loses methane smoothly at

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[1] Part II, Coates and Hayter, *J.*, 1953, 2519.

[2] Coates, *J.*, 1951, 2003.

90—110° with quantitative formation of the dimer $(Me_2Ga\cdot PPh_2)_2$. Diphenylarsine is even more reactive towards trimethylgallium, since methane is formed as the reactants melt and the formation of a dimer $(Me_2Ga\cdot AsPh_2)_2$ is quantitative after a few minutes at 30°.

The corresponding trimethylaluminium complexes, $Me_3Al,N(P,As)HPh_2$, all eliminate methane with formation of dimeric products, $[Me_2Al\cdot N(P,As)Ph_2]_2$, but the order of decomposition temperatures (N, 60—80°; P, 140—160°; As, 150—170°) is the reverse of that observed for the gallium complexes.

The reaction between trimethylindium and diphenylarsine takes a very similar course to that between trimethylgallium and diphenylarsine, methane elimination being rapid below 0°, giving the dimer $(Me_2In\cdot AsPh_2)_2$.

The formation of dimeric products in all these reactions is worth noting, since similar compounds, in which an acceptor atom of Group III is bound to one donor atom of Group V, are sometimes monomeric [$Me_2B{:}NMe_2$,[3] $Ph_2B\cdot P(C_6H_4Me\text{-}m)_2$, and $Ph_2B\cdot AsPh_2$ [4]], sometimes trimeric [$(Me_2B\cdot PMe_2)_3$,[5] $(Me_2Al\cdot PMe_2)_3$,[6] $(Cl_2Al\cdot PEt_2)_3$ [7]], but much more commonly dimeric [8] [$(Ph_2B\cdot NH_2)_2$,[4] $(Me_2Al\cdot NMe_2)_2$,[6] $(Me_2Ga\cdot NMe_2)_2$,[2] $(Me_2In\cdot NMe_2)_2$ [9]]. There appears to be no general rule which may be used to predict the degree of association of these compounds, though it seems that monomeric compounds exist in that condition only when the donor or acceptor atom can achieve co-ordination saturation by double bonding either to each other (as in $Me_2B{:}NMe_2$ [3]) or by partial double bonding to suitable groups, for example, between boron and phenyl in $Ph_2B\cdot PEt_2$.[4] Certain instances have been reported in which acceptor atoms are bound to more than one donor atom and association is prevented sterically, *e.g.*, $Al(NPr^i{}_2)_3$ [10] and $Al(NPh_2)_3$.[11]

In particular, there seems to be little to indicate the extent of association when association does take place. That co-ordination saturation is most commonly achieved by the formation of dimers, shown to consist of four-membered rings whenever physical evidence has been available, rather than by the formation of trimers, tetramers, or polymers is presumably because the favouring of smaller molecules on entropy grounds outweighs the valency-angle strain implied in four-membered rings. Gillespie [12] has shown that valency-angle deformation from 109° to 90° or less occurs much more readily with elements of the second or third period than with first-period elements; consequently we might expect that compounds $R_2M\cdot DR'_2$ (M = Al, Ga, In, Tl; D = P, As, Sb) would be dimeric; the only exceptions to this rule appear to be the compounds $(Me_2Al\cdot PMe_2)_3$ [6] and $(Cl_2Al\cdot PEt_2)_3$.[7]

We were, therefore, not surprised that all the aluminium, gallium, and indium compounds prepared in the course of the present work were dimers. However, the question arises whether monomers could exist. Dipole-moment studies on phosphino- and arsinodiarylboranes [4] indicate that phosphorus and arsenic have weak (if any) π-donor character towards boron, this being attributed to unfavourable relations between the sizes of the boron 2*p*- and the phosphorus or arsenic atomic orbitals. With larger acceptor atoms the size factor improves and, although we have no evidence about the nature of the gallium–phosphorus bond, we think we have obtained (diphenylphosphino)dimethylgallium, $Me_2Ga\cdot PPh_2$, in a monomeric state. We were not able to study this compound in detail since it very readily transforms itself into the dimer.

Both the dimers $(Me_2Al\cdot PPh_2)_2$ and $(Me_2Al\cdot AsPh_2)_2$ absorb trimethylamine, which can be recovered quantitatively from the phosphino-compound by evacuation at 65—75°.

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[3] Becher and Goubeau, *Z. anorg. Chem.*, 1952, **268**, 133.

[4] Coates and Livingstone, *J.*, 1961, 1000.

[5] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

[6] Davidson and Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316.

[7] Fritz and Trenczek, *Z. anorg. Chem.*, 1962, **313**, 236.

[8] Stone, *Chem. Rev.*, 1958, **58**, 101.

[9] Coates and Whitcombe, *J.*, 1956, 3351.

[10] Ruff, *J. Amer. Chem. Soc.*, 1961, **83**, 2835.

[11] Longi, Mazzanti, and Bernadini, *Gazzetta*, 1960, **90**, 180.

[12] Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

In contrast, the dimethylphosphino-trimer, $(Me_2Al{\cdot}PMe_2)_3$, does not react with trimethylamine, though the dimers $(Me_2Al{\cdot}SMe)_2$ [6] and $(Me_2Ga{\cdot}SMe)_2$ [1] react rapidly and reversibly: $(Me_2Ga{\cdot}SMe)_2 + 2NMe_3 \rightleftharpoons 2MeS{\cdot}GaMe_2,NMe_3$.

While this work was in progress the reaction between diphenylphosphine and diethylzinc was described.[13] The product, $[(Ph_2P)_2Zn]_x$, was described as insoluble in ether, benzene, dioxan, and tetrahydrofuran; it is presumably polymeric. More recently the dimers $(Et_2Al{\cdot}PPh_2)_2$, from diphenylphosphine and triethylaluminium, and $(Et_2Al{\cdot}PEt_2)_2$, from diethylaluminium chloride and diethylphosphinolithium, have been prepared.[14] These results make the trimeric compounds $(Me_2Al{\cdot}PMe_2)_3$ and $(Cl_2Al{\cdot}PEt_2)_3$ still more anomalous.

EXPERIMENTAL

Most of the compounds prepared in this work were readily hydrolyzed or oxidized in the air, and were manipulated in a nitrogen atmosphere. Aluminium compounds were analyzed for metal and for hydrolyzable methyl content. Gallium and indium compounds, which evolve methane slowly and incompletely on reaction with acid, were analyzed for metal and for phosphorus or arsenic. After combustion by the oxygen-flask method, a solution of known volume was prepared, a part being used for determination of metal, the remainder for phosphorus. Difficulty has been experienced in the analysis of gallium compounds by the oxygen-flask method, owing to incomplete solution of the oxide,[15] but we overcame this by the use of aqueous sodium hypobromite. Phosphorus was determined, after destruction of the excess of hypobromite, by the quinoline molybdate method.[16]

Determination of arsenic by oxygen-flask combustion is difficult,[15,17] but decomposition by chloric acid [18] was effective. Arsenic was then determined by the quinoline molybdate method, and metal could be determined in another aliquot part.

Metals were determined by a modification of a method [19] based on EDTA, in which the back-titration was carried out with 0·01M-zinc acetate at a pH 4·5—5 with Xylenol Orange as indicator. The pH of an aliquot part was adjusted with standard sodium hydroxide to the end-point of the B.D.H. " 4·5 " indicator; other portions were then brought to this pH without the use of indicator by adding the same amount of alkali, and a known amount of 0·01M-EDTA was added followed by a few drops of indicator and then *ca.* 0·1 g. of hexamethylenetetramine (as buffer). The solution was warmed to 40—50° and the excess of EDTA titrated with zinc acetate. End-points were sharp except during the determination of aluminium in the presence of arsenic. The diphenylarsinodimethylaluminium dimer was analyzed gravimetrically by the oxine method. Molecular weights were determined cryoscopically in 1—3·5 wt. % solution.

Reactions of Trimethylgallium.—(*a*) *Diphenylamine.* Trimethylgallium (204 c.c. at S.T.P) was condensed on diphenylamine (1·4927 g., 1 mol.). When the trimethylgallium melted a solid adduct was formed, which itself melted at ~60°, and evolved methane slowly at 120—140°. As the temperature was raised to 200° the rate of evolution of methane increased a little, but extensive decomposition prevented the isolation of any pure product.

(*b*) *Diphenylphosphine.* Trimethylgallium (255 c.c. at S.T.P.) was condensed on diphenylphosphine (2·08 g., 0·98 mol.) in a flask fitted with a stopcock and a spherical joint. Overnight the mixture crystallized. When the solid adduct was heated, it did not melt but evolved methane in the range 90—110°. After 20 min. at this temperature the methane (240 c.c. at S.T P., 96% theor., identified by infrared spectrum) was collected by Töpler pump, after separation from the small excess of trimethylgallium. The *diphenylphosphinodimethylgallium dimer* crystallized from benzene and had m. p. 194° (Found: Ga, 24·5; P, 10·8%; *M*, cryoscopic in benzene, 577, 580, 577, 555. $C_{28}H_{32}Ga_2P_2$ requires Ga, 24·5; P, 10·9%; *M*, 570).

The same compound was prepared in 87% yield by addition of diphenylphosphinosodium (1 mol.) in tetrahydrofuran (200 c.c.) to dimethylgallium chloride (5·8 g., from trimethylgallium and gallium chloride) in diethyl ether (100 c.c.). The supernatant liquid was decanted

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[13] Issleib and Fröhlich, *Chem. Ber.*, 1962, **95**, 375.

[14] Issleib and Deylig, *Z. Naturforsch.*, 1962, **17**b, 198.

[15] Belcher and Macdonald, *Talanta*, 1958, **1**, 409.

[16] Belcher and Macdonald, *Talanta*, 1958, **1**, 185.

[17] Macdonald, *Analyst*, 1961, **86**, 3.

[18] Mayer and Koch, *Z. analyt. Chem.*, 1957, **158**, 434; Tuckerman, Hodecker, Southworth, and Fleischer, *Analyt. Chim. Acta*, 1959, **21**, 463.

[19] Kinnunen and Wennerstrand, *Chem. Analyst*, 1957, **46**, 93.

from the precipitated salt, solvent removed under reduced pressure, and the colourless solid product recrystallized from benzene. When solvent was removed by flash distillation, a liquid product was obtained which was distilled at 125—150° (bath-temperature)/$\sim 10^{-3}$ mm. This liquid generally solidified to a dimer (identical in infrared spectrum with material prepared from trimethylgallium and diphenylphosphine), sometimes rapidly but rather slowly in some instances in which the presence of impurity was suspected. The dimer melts at 194° only if heated rapidly to 180° and more slowly above that temperature; if it is heated slowly it softens above 100°, possibly owing to the formation of some monomer. In an attempted sublimation of solid dimer at 150—160°, only about 10% evaporated; this condensed as liquid which solidified within 10 min.; the residue was extensively decomposed on attempted distillation at higher temperature.

Though the dimer is easily hydrolyzed by atmospheric moisture, with formation of dimethylgallium hydroxide and diphenylphosphine (and its oxide), the methyl groups could not be hydrolyzed quantitatively to methane. When the dimer had been heated for 5½ hr. with 50% aqueous sulphuric acid, only 87% of the theoretical amount of methane was evolved.

Dimethylgallium chloride–diethyl ether complex, $Me_2GaCl(OEt_2)$, does not appear to have been described previously. It was prepared both by reaction of gallium chloride with trimethylgallium in ether, and on addition of methyl-lithium (2 mol.) to gallium chloride in ether; it has b. p. 160° (bath)/0·1 mm. (Found: Ga, 33·2. $C_6H_{16}ClGaO$ requires Ga, 33·3%). It is quantitatively hydrolyzed (to hydrochloric acid) by water, but no methyl groups are detached from the gallium.

(*c*) *Diphenylarsine.* Trimethylgallium (232·5 c.c. at S.T.P.) was condensed on diphenylarsine (2·279 g., 0·95 mol.). Methane (216 c.c. at S.T.P., 98%) was evolved as the reactants melted and warmed spontaneously to about 30°. The solid product, crystallized from benzene–hexane, had m. p. 160—170° (Found: C, 50·4; H, 4·9; As, 22·3; Ga, 21·1%; *M*, cryoscopic in benzene, 668, 651, 655. $C_{28}H_{32}As_2Ga_2$ requires C, 51·1; H, 4·9; As, 22·8; Ga, 21·2%; *M*, 658). All preparations of *diphenylarsinodimethylgallium dimer* melted over about the same temperature range, even after further recrystallization, and this may have been due to some dissociation to monomer. This dimer is rather less sensitive to moisture than its phosphorus analogue.

Diphenylarsinodimethylindium Dimer.—This was prepared by the method used for its gallium analogue, but the solid *dimer*, which was very soluble in benzene, was crystallized from hexane; it had m. p. 192—195° (decomp.) (Found: As, 19·8; In, 30·2%; *M*, cryoscopic in benzene, 747, 832, 802, 806. $C_{28}H_{32}As_2In_2$ requires As, 20·0; In, 30·7%; *M*, 748). No methane was formed when the dimer came into contact with water, and methane evolution was slow and incomplete even after 5½ hr. with a sulphuric acid–water–2-methoxyethanol mixture.

Reactions of Trimethylaluminium.—(*a*) *Diphenylamine.* When trimethylaluminium is condensed on diphenylamine (1 mol.), and the mixture allowed to come to room temperature, an exothermic reaction occurs with formation of the adduct, m. p. ~60°. The molten adduct evolves methane at 60—80°, giving *diphenylaminodimethylaluminium dimer*, which was recrystallized from hexane (Found: Al, 11·95; Me, 13·2%; *M*, cryoscopic in benzene 490, 467, 475. $C_{28}H_{32}Al_2N_2$ requires Al, 12·0; Me, 13·3%; *M*, 450). This softens at about 130° and evolves methane between 160° and 170°; this reaction will be described separately. Though vigorously hydrolyzed by water, it reacts only slowly with air, becoming red, then brown, and finally an intense blue-black. Similar colour changes are observed when benzene solutions are exposed to air; though the colour changes occur within a few minutes in solution, insoluble matter is not formed until after about an hour's exposure.

(*b*) *Diphenylphosphine.* A mixture of trimethylaluminium (3·32 g.) and diphenylphosphine (8·91 g.) evolved methane at 140°—160°, forming hexagonal crystals of *diphenylphosphinodimethylaluminium dimer* which were purified by sublimation at 160°/$\sim 10^{-3}$ mm.; the crystals (1 g.), m. p. 230°, were collected after 12 hours' sublimation (Found: Al, 10·95; Me, 12·9%; *M*, 489, 507, 493. $C_{28}H_{32}Al_2N_2$ requires Al, 11·1; Me, 12·4%; *M*, 484). The compound inflamed in air and was vigorously hydrolyzed by water. Moderately soluble in benzene, from which it may be recrystallized, it is only sparingly soluble in ether.

Though an equimolar mixture of diphenylphosphine and trimethylgallium crystallized overnight to the 1 : 1 adduct, rhombic crystals of a complex $Me_3Al,PHPh_2$ were deposited only after the reactant mixture has been kept for about five months.

(*c*) *Diphenylarsine.* The arsine (2·75 g.) was mixed with a slight excess of trimethylaluminium (1·04 g.), and the excess of the latter removed by evacuation at room temperature. The adduct melted in the range 90—100° and evolved methane at 150—170°, forming *diphenylarsinodimethylaluminium dimer*, which, recrystallized from benzene, had m. p. 184—185·5° (Found: Al, 9·4; hydrolyzable methyl, 9·8%; *M*, cryoscopic in benzene, 570, 606, 586. $C_{28}H_{32}Al_2As_2$ requires Al, 9·4; hydrolyzable methyl, 10·5%; *M*, 572). Like its phosphorus analogue it inflames in air and is vigorously hydrolyzed by water.

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