246. *Gallium Hydride Adducts of Trimethylphosphine and Triphenylphosphine.*

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The new compounds Me_3PGaH_3 and Me_3PGaD_3 have been prepared and shown by their gas-phase infrared spectra to be monomeric. The P–Ga stretching frequency has been identified at 326 cm.$^{-1}$. The absence of a 2 : 1 adduct, $(Me_3P)_2GaH_3$, was shown by tensiometric titration at $-21°$. Gas-phase displacement reactions indicate that trimethylamine and trimethylphosphine have similar donor strengths towards gallium hydride. The corresponding aluminium hydride adduct Me_3PAlH_3 could not be prepared directly, and trimethylphosphine does not displace trimethylamine from Me_3NAlH_3. The compound Ph_3PGaH_3 has been prepared but readily decomposes at room temperature. The equilibrium between trimethylamine, trimethylphosphine, and their adducts with gallium hydride in benzene solution has been investigated by n.m.r. spectroscopy.

The trimethylamine derivatives of gallium hydride and deuteride have recently been reported,[1,2] and the present Paper discusses the preparation, stability, and properties of

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[1] Greenwood, Storr, and Wallbridge, *Proc. Chem. Soc.*, 1962, 249.

[2] Greenwood, Storr, and Wallbridge, *Inorg. Chem.*, 1963, **2**, 1036.

the corresponding compounds with trimethylphosphine and triphenylphosphine. Trimethylphosphine-gallium hydride, m. p. 71°, was prepared by the reaction of lithium gallium hydride on equimolar amounts of trimethylphosphine and hydrogen chloride in diethyl ether.

$$LiGaH_4 + Me_3P + HCl \xrightarrow[0^\circ]{Et_2O} Me_3PGaH_3 + LiCl + H_2 \qquad (1)$$

The adduct was purified by sublimation. It decomposes slowly under vacuum but it is quite stable under nitrogen. Trimethylphosphine-gallium deuteride was prepared similarly from lithium gallium deuteride, trimethylphosphine, and deuterium chloride. The absence of the 2 : 1 adduct, bis(trimethylphosphine)-gallium hydride was shown by tensiometric titration of trimethylphosphine-gallium hydride with trimethylphosphine at −21°.

In order to determine which of the two ligands trimethylamine and trimethylphosphine is the stronger donor towards gallium hydride, the equilibrium (2) was investigated by

$$Me_3PGaH_3(s) + Me_3N(g) \rightleftharpoons Me_3NGaH_3(s) + Me_3P(g) \qquad (2)$$

infrared spectroscopy. The same equilibrium position was reached independently of whether trimethylamine was added to the trimethylphosphine adduct or trimethylphosphine was added to the trimethylamine adduct, and corresponded to approximately equal amounts of trimethylamine and trimethylphosphine in the gas phase. In contrast, it was found that trimethylphosphine did not displace trimethylamine from trimethylamine–aluminium hydride, Me_3NAlH_3, and the adduct trimethylphosphine-aluminium hydride could not be prepared directly, from lithium aluminium hydride, trimethylphosphine, and hydrogen chloride, since this reaction resulted in reduction to aluminium metal.

$$LiAlH_4 + Me_3P + HCl \xrightarrow{Et_2O} Me_3P + LiCl + Al + \tfrac{5}{2}H_2 \qquad (3)$$

These observations extend the information already available about the stability relationships among adducts of these ligands with Group III hydrides. It has been shown that trimethylphosphine is a stronger donor than trimethylamine towards borane.[3] However, both trimethylamine–borane [4] and trimethylphosphine–borane [5] are thermally more stable than the corresponding aluminium hydride and gallium hydride adducts, which decompose [2] below 100°. These stability relationships may be summarized as follows:

$$Me_3PBH_3 > Me_3PGaH_3 \gg Me_3PAlH_3$$

and

$$Me_3NBH_3 < Me_3PBH_3; \quad Me_3NAlH_3 \gg Me_3PAlH_3; \quad Me_3NGaH_3 \sim Me_3PGaH_3$$

Triphenylphosphine-gallium hydride was prepared by the reaction of an excess of lithium gallium hydride on equimolar amounts of triphenylphosphine and hydrogen chloride in diethyl ether.

$$LiGaH_4 + Ph_3P + HCl \xrightarrow[-5^\circ]{Et_2O} Ph_3PGaH_3 + LiCl + H_2 \qquad (4)$$

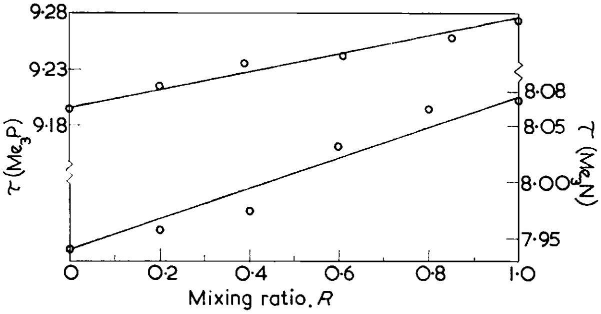
The adduct obtained from the ethereal solution was of low stability and decomposed under nitrogen at room temperature. By comparison, triphenylamine-gallium hydride and triphenylarsine-gallium hydride could not be isolated from this type of system; gallium metal was deposited from the ethereal solution even below room temperature.

Methyl proton magnetic resonance spectra in benzene have been used to determine the position of the equilibrium (5).

$$Me_3PGaH_3 + Me_3N \rightleftharpoons Me_3NGaH_3 + Me_3P \qquad (5)$$

[3] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164.
[4] Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780.
[5] Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

Preliminary measurements were made in order to determine the relation between the methyl proton chemical shift and composition for the two binary systems, " gallium hydride + trimethylamine " and " gallium hydride + trimethylphosphine." The binary mixtures were prepared by dissolving a known weight of adduct in benzene and then adding a known amount of the appropriate free ligand. The relationship is shown graphically in the Figure, where R is the molar ratio of gallium hydride to the total amount of free and complexed ligand, and τ is the methyl proton chemical shift in parts per million referred to benzene as 2·840 p.p.m. *i.e.*, τ (Me_4Si) = 10·000 p.p.m. It can be seen that, for both ligands, there is but little change in chemical shift on co-ordination, and this limits the precision with which concentrations can be measured from the graphs. Two mixtures corresponding to equilibrium (5) were prepared by adding an equimolar amount of the appropriate ligand to a known weight of adduct dissolved in benzene. In both mixtures, the methyl proton chemical shifts observed were 8·023 p.p.m. for trimethylamine and 9·223 p.p.m. for trimethylphosphine. The value of 8·023 p.p.m. on the graph of methyl proton chemical shift against the mixing ratio (R) of trimethylamine with its adduct corresponds to a mixing ratio of 0·62. Since $R = C/(L + C)$, where C and L denote respectively the molar amounts of complexed and uncomplexed ligand, then $(L/C) = (1/R) - 1$. Hence, in the equilibrium mixtures,



Proton chemical shifts for mixtures of trimethylamine with trimethylamine–gallium hydride and of trimethylphosphine with trimethylphosphine–gallium hydride.

$$[Me_3N]/[Me_3NGaH_3] = L/C = (1/0{\cdot}62) - 1 = 0{\cdot}61$$

Similarly, from the graph of methyl proton chemical shift against the mixing ratio of trimethylphosphine with its adduct, the mixing ratio corresponding to 9·223 p.p.m. is 0·36, which gives the value

$$[Me_3P]/[Me_3PGaH_3] = (1/0{\cdot}36) - 1 = 1{\cdot}78$$

for the equilibrium mixtures. The value of the equilibrium constant, K, in benzene solution for reaction (5) is therefore

$$[Me_3NGaH_3][Me_3P]/[Me_3PGaH_3][Me_3N] = 1{\cdot}78/0{\cdot}61 = 2{\cdot}94$$

The positions of the hydridic proton resonances in Me_3PGaH_3 and Me_3NGaH_3 have been located in saturated benzene solutions at $\tau = 5{\cdot}94$ and 5·54 p.p.m., respectively. These values are at much lower field strengths than those found for the resonances of hydrogen bound to transition metals[6] (τ = 15—35 p.p.m.), but are comparable with recent results quoted for various hydride derivatives of germanium and tin.[7] The resonance bands of the two gallium hydride adducts were broad and of low intensity, and the expected quartet (^{71}Ga: I = 3/2, abundance 39·8%; ^{69}Ga: I = 3/2, abundance 60·2%) could not be resolved because of nuclear quadrupole broadening. The position of

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[6] Wilkinson, " Advances in the Chemistry of the Coordination Compounds," Macmillan Co., New York, 1961, p. 50.

[7] Potter, Pratt, and Wilkinson, *J.*, 1964, 524.

the Al–H proton resonance was very difficult to detect even in saturated solutions of trimethylamine–aluminium hydride in benzene. The expected sextet (^{27}Al: I = 5/2, abundance 100%) was a very weak, broad line centred at 6·09 p.p.m., a value close to that recently quoted [8] for the hydridic proton resonance (6·04 p.p.m.) in Me_3NAlH_2Me.

The gas-phase infrared absorptions at room temperature of trimethylphosphine–gallium hydride and deuteride are weak in comparison with those of the corresponding trimethylamine adducts [1] because of the lower vapour pressure of the trimethylphosphine complexes. The only bands observed in addition to those arising from the co-ordinated ligand, trimethylphosphine, were the Ga–H stretch at 1846 cm.$^{-1}$, the antisymmetric Ga–H deformation at 750 cm.$^{-1}$, and the symmetric Ga–H deformation at 704 cm.$^{-1}$ In the deuteride these bands were shifted by a factor of 1/1·39 and occurred at 1326, 538, and 508 cm.$^{-1}$, respectively. Weaker absorptions, due to the methyl groups, were observed at 2984 cm.$^{-1}$ (antisym. C–H stretch), 2925 cm.$^{-1}$ (sym. C–H stretch), 1445 cm.$^{-1}$, 1432 cm.$^{-1}$ (antisym. C–H deformations), 950 cm.$^{-1}$, and 940 cm.$^{-1}$ (CH_3 rocking modes).

Infrared results for Me_3P, Me_3PGaH_3, and Me_3PGaD_3 in benzene.

Me_3P ν (cm.$^{-1}$)	Me_3PGaH_3 ν (cm.$^{-1}$)	Me_3PGaD_3 ν (cm.$^{-1}$)	ν(Ga–H)/ν(Ga–D)	Assignment
2950s	2945w			antisym. C–H stretch
2890s	2886w			
2812m				sym. C–H stretch
1958w	1959w			
	1831s	1314s	$1·39_3$	antisym. Ga–H stretch
	1807s			sym. Ga–H stretch
1434s	1434sh	1425sh		antisym. C–H deformation
1426s	1422m	1412m		
1393sh	1395sh			
1304w				sym. C–H deformation
1294m	1293m	1285m		
1277m				
1115w	1100w			
945sh	961sh	960m		CH_3 rock
938s	949s	950m		
	846w	745w		
	752s	540s	$1·39_2$	antisym. Ga–H deformation
		503s		sym. Ga–H deformation
	467m	339w	$1·37_7$	$P–Ga\equiv H_3$ rock
	326m			P–Ga stretch

Intensity: w = weak, m = medium, s = strong, sh = shoulder.

More complete infrared results were obtained from benzene solutions; the results, together with the assignment of bands, are listed in the Table. The figures for trimethylphosphine in benzene are essentially the same as those already reported for the gas-phase spectrum of this compound.[9] Bands in the $P–C_3$ stretching region could not be investigated because of interference by the solvent. The symmetric and antisymmetric Ga–H stretches are now partly resolved at 1807 and 1831 cm.$^{-1}$, and the $P–GaH_3$ rock and P–Ga stretch are located at 467 and 326 cm.$^{-1}$, respectively. These spectra are very similar to those obtained from the corresponding trimethylamine adducts.[1,2] The value of the P–Ga stretching frequency calculated from the N–Ga stretching frequency in trimethylamine–gallium hydride simply on the basis of a change in mass is 364 cm.$^{-1}$; the observed value (326 cm.$^{-1}$) is somewhat lower than this, implying a smaller force constant for the P–Ga bond.

DISCUSSION

The position of equilibrium (2), which may be established in the gas phase through the unstable, mixed compound $(Me_3N)(Me_3P)GaH_3$, suggests a close similarity in the donor strengths of trimethylamine and trimethylphosphine towards gallium hydride. However,

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[8] Peters, Bartocha, and Bilbo, *Canad. J. Chem.*, 1963, **41**, 1051.
[9] Halmann, *Spectrochim. Acta*, 1960, **16**, 405.

the position of the equilibrium is also likely to be that favouring formation of the least volatile component, and, although the vapour pressures of the two solids cannot be measured accurately at room temperature because of slow decomposition under vacuum, trimethylphosphine-gallium hydride is known to be slightly less volatile than the amine adduct under the above conditions. Nevertheless, the existence of this equilibrium contrasts with the behaviour of the majority of Group III acceptors, which show a stability order N > P in their compounds with the trimethyl derivatives of Group V donor atoms.[10] This observation, together with our inability to prepare trimethylphosphine–aluminium hydride, the reports of the instability of other phosphine–aluminium hydrides,[11,12] and the absence of an analogous ligand displacement equilibrium involving trimethylamine-aluminium hydride and trimethylphosphine, suggests that some factor other than pure σ-bonding is involved in the stabilization of the P–Ga bond. Stone, in reporting [3] that the displacement reaction

$$Me_3NBH_3(s) + Me_3P(g) \rightleftharpoons Me_3PBH_3(s) + Me_3N(g)$$

proceeded to the right to the extent of 80%, suggested that the three B–H orbitals contribute to the formation of a pseudo-p_π orbital which overlaps with a vacant phosphorus $3d$ orbital to supplement the P–B σ-bond. However, the present results show that a similar mechanism does not stabilize the P–Al bond, and is therefore even less likely to influence the P–Ga bond. Probably back-donation from filled gallium $3d$ orbitals to vacant phosphorus $3d$ orbitals occurs, though the low order of the overlap integral calculated for $d_\pi - d_\pi$ bonding in this case [13] indicates that such interaction is probably weak. Furthermore, the absence of a 2 : 1 adduct, bis(trimethylphosphine)-gallium hydride, at low temperature, is difficult to explain, unless the requirement of a $d_\pi - d_\pi$ component in the P–Ga bonds is taken as essential for their stability; the competition of the two ligands would minimize the $d_\pi - d_\pi$ interaction and lead to instability of the 2 : 1 complex.

The methyl proton n.m.r. results indicate that only 40% of displacement of trimethylamine by trimethylphosphine from trimethylamine–gallium hydride occurs in benzene solution, whereas for the gas-phase displacement the figure is 50%. The discrepancy probably arises from the volatility effect mentioned previously; accordingly, the n.m.r. results are considered more reliable in assessing the relative donor strengths. It must be noted, however, that the ranges of methyl proton chemical shifts are quite small for both ligands, consequently the error in determining K is considerable, although each chemical shift could be measured to within $\pm 0{\cdot}005$ p.p.m.

A noteworthy feature of the n.m.r. investigation is the occurrence of methyl proton resonance signals in both adducts at fields higher than those for the free ligands. This is perhaps surprising, since the decrease in electron density at the donor atom resulting from adduct formation would be expected to reduce the electron density at the methyl protons and so move the resonance to lower field. Evidently, other factors are more important in this particular case. With boron trifluoride–ether mixtures,[14] the methyl proton chemical shift moves to lower field on adduct formation as expected, but the reverse effect is again encountered in studies of trialkylaluminium–amine equilibria.[15]

The relative stabilities of the adducts of gallium hydride with the triphenyl derivatives of nitrogen, phosphorus, and arsenic follow the expected sequence since the nitrogen lone-pair is delocalized over the phenyl rings thus reducing the donor capacity of triphenylamine, and triphenylarsine is always a weaker donor than triphenylphosphine. Any influence of possible $d_\pi - d_\pi$ overlap between donor and acceptor also gives the same

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[10] Coates, *J.*, 1951, 2003.
[11] Wiberg, May, and Nöth, *Z. Naturforsch.*, 1955, **10**b, 239.
[12] Burg and Mödritzer, *J. Inorg. Nuclear Chem.*, 1960, **13**, 318.
[13] Perkins, private communication.
[14] Craig and Richards, *Trans. Faraday Soc.*, 1963, **59**, 1962.
[15] Mole, *Chem. and Ind.*, 1964, 281.

sequence since the absence of available *d*-orbitals on nitrogen rules out such bonding in the case of triphenylamine–gallium hydride, and only weak $d_\pi - d_\pi$ interaction is likely in triphenylarsine–gallium hydride because of the disparity in size between the arsenic and gallium *d*-orbitals; conditions are more favourable however in the case of triphenylphosphine–gallium hydride, and the P–Ga $d_\pi - d_\pi$ interaction may be extended by overlap of phosphorus *d*-orbitals with the π-electron clouds of the phenyl groups.

EXPERIMENTAL

Materials were handled in a conventional high-vacuum line or in a glove box under an atmosphere of oxygen-free, dry nitrogen. All solvents, after preliminary desiccation, were dried over lithium aluminium hydride or lithium hydride and redistilled before use. Gas volumes quoted below are at S.T.P.

Lithium gallium hydride, lithium gallium deuteride, trimethylamine–gallium hydride, and deuterium chloride were prepared as previously described.[2] Trimethylamine–aluminium hydride was obtained by the method of Ruff and Hawthorne.[16] Trimethylphosphine was prepared by the action of methylmagnesium iodide on phosphorus trichloride in dry diethyl ether.[17] It was isolated as its silver iodide complex, which was dried and then heated *in vacuo* to yield trimethylphosphine. The last traces of moisture were removed from the product by passing it several times over phosphorus pentoxide. The purity of the trimethylphosphine was checked by its infrared spectrum.[9]

Trimethylphosphine–Gallium Hydride.—Prepared by condensing equimolar amounts of trimethylphosphine and hydrogen chloride (45·8 ml., 2·05 mmoles) into a 500-ml. break-seal flask containing an excess of lithium gallium hydride (0·2 g., 2·48 mmoles) in diethyl ether (50 ml.). The flask was then sealed, warmed to 0°, and shaken for 6 hr. The volume of hydrogen evolved was then measured by using a Töpler pump (Found: 46·1 ml.; calc. 45·9 ml.). After the removal of solvent at $-78°$, the product was sublimed under dynamic vacuum from a bath at room temperature into a trap cooled to $-78°$ where it formed white, granular crystals, m. p. 70·5—71°, vapour pressure approximately 1 mm./22° (Found: Ga, 46·8; hydrolysable H, 2·0; P, 21·7. Me_3PGaH_3 requires Ga, 46·8; hydrolysable H, 2·0; P, 20·8%). The *gallium trideuteride derivative*, Me_3PGaD_3, was prepared similarly from lithium gallium deuteride (0·415 g., 4·90 mmole) and equimolar amounts of trimethylphosphine and deuterium chloride (101·3 ml., 4·52 mmoles). The deuterium evolved was measured (Found: 100·0 ml.; calc. 101·3 ml.).

Preparation of trimethylphosphine–aluminium hydride was attempted in a similar reaction with lithium aluminium hydride. The volume of hydrogen generated after 40 hr. of shaking suggested that the reaction had proceeded beyond the stage indicated by the equation

$$LiAlH_4 + Me_3P + HCl \xrightarrow{Et_2O} (Me_3PAlH_3) + LiCl + H_2$$

The excess of hydrogen was probably generated by decomposition of the aluminium hydride to aluminium metal. The solid left after removal of solvent and lithium chloride showed no infrared absorption attributable to Al–H or P–Al vibrations.

Triphenylphosphine–Gallium Hydride.—Prepared by condensing hydrogen chloride (262·0 ml., 11·7 mmoles) into a vessel of the type previously described containing triphenylphosphine (3·08 g., 11·7 mmoles) and lithium gallium hydride (0·94 g., 11·7 mmoles) in diethyl ether (50 ml.). A stoicheiometric amount of hydrogen was evolved (Found, 256 ml.; calc., 262 ml.) after 2 hr. of shaking at $-5°$. The filtrate from the reaction mixture was sealed in a glass ampoule and left for several weeks at $-5°$. A colourless, crystalline product separated from the solution. This product showed infrared absorptions characteristic of Ga–H (1880 cm.$^{-1}$) and P–Ga (365 cm.$^{-1}$) bonds.

Tensiometric Titration.—The procedure and apparatus used have been described elsewhere.[2] Trimethylphosphine (277·6 ml., 12·39 mmoles) was condensed on to trimethylphosphine–gallium hydride (0·234 g., 1·54 mmoles), and the titration carried out at $-21°$. A graph showing the variation of pressure with the molar ratio of trimethylphosphine to trimethylphosphine–gallium hydride gave no indication of interaction between these two components to form higher adducts.

[16] Ruff and Hawthorne, *J. Amer. Chem. Soc.*, 1960, **82**, 2141.

[17] Mann, Wells, and Purdie, *J.*, 1938, 702.

Displacement Reactions.—Trimethylamine (24·9 ml., 1·1 mmoles) was condensed on to trimethylphosphine–gallium hydride (0·165 g., 1·1 mmoles) in a 100-ml. flask, and the mixture was allowed to reach room temperature. Infrared spectra of the gas above the solid phase, obtained at regular intervals, were used to determine the position of the equilibrium by comparison of the intensities of selected absorption bands with those in the spectra of the pure donor molecules at known pressures. Finally, the amount of gas above the solid phase was measured (Found: 25·3 ml.; calc., 24·9 ml.).

A similar procedure was used to investigate the equilibrium involving trimethylphosphine (23·8 ml., 1·06 mmoles) and trimethylamine–gallium hydride (0·14 g., 1·06 mmoles). The amount of gas remaining above the solid phase after equilibration was found to be 24·0 ml. (calc. 23·8 ml.).

When trimethylphosphine (16·5 ml., 0·74 mmole) was condensed on to trimethylamine–aluminium hydride (0·066 g., 0·74 mmole), no displacement of trimethylamine was observed at room temperature.

Analytical Methods.—The samples were analysed for gallium and hydrolysable hydrogen as previously described.[2] Phosphorus was determined by oxidation of the sample in a sealed tube at 180° with concentrated nitric acid, followed by precipitation of the phosphorus as phosphomolybdate.

Spectra.—Infrared spectra for qualitative identification of the compounds were recorded on Perkin-Elmer Infracord model 137 instruments with sodium chloride (4000—670 cm.$^{-1}$) and potassium bromide (800—400 cm.$^{-1}$) optics. Definitive spectra were recorded on a Perkin-Elmer S.P. 125 grating infrared spectrometer (4000—400 cm.$^{-1}$), and a Grubb–Parsons DM4 spectrometer (450—200 cm.$^{-1}$) with cæsium iodide optics.

Proton nuclear magnetic resonance spectra were recorded at 60 Mc/sec. with an A.E.I. RS2 spectrometer.

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