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Tertiary phosphine adducts of alane and gallane

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Abstract

Thermally stable mono-tri-t-butylphosphine adducts of alane and gallane, $H_3MP^tBu_3$ (M = Al, **1**; M = Ga, **2**) and the gallane rich adducts of 1,2-bis(diisopropylphosphino)ethane and 1,2-bis(diphenylphosphino)ethane, $[(H_3Ga)_2\{(PR_2CH_2)_2\}]$ (R = ^{i}Pr, **3**; R = Ph, **4**), have been prepared from $LiMH_4$/HCl/phosphine; reactions involving H_3MNMe_3/P^tBu_3 also yield **1** and **2**, for the former *via* a mixed donor $^tBu_3PAl(H)_3NMe_3$ (**5**), which decomposes to **1** and NMe_3 at *ca.* 40°C; compounds **1** and **2**, and the previously reported alane analogue of **3**, *viz.* $[(H_3Al)_2\{(P^iPr_2CH_2)_2\}]$ (**6**) have been shown to be four coordinate (Al–P, 2.471(3) and 2.451(3) Å, **1** and **6**; Ga–P 2.444(6) Å, **2**). *Ab initio* calculations on relevant model systems, H_3GaPMe_3 (DZP level) and $H_3Al(PR_3)_2$ (R = H or Me; D95* level) are reported, Ga–P 2.550 Å, and Al–P 2.828 Å (R = H), 2.786 Å (R = Me).

1. Introduction

Unsolvated alane is polymeric, $(AlH_3)_\infty$, and can form volatile and hydrocarbon soluble 1:1 or 2:1 adducts with Lewis bases, *e.g.* dimeric $[\{H_2(\mu\text{-H})AlNMe_3\}_2]$ which has unsymmetrical hydride bridges, $H_3Al(NMe_3)_2$ [1,2] and related adducts [3], and H_3AlPCy_3, Cy = cyclohexyl [4]. Tertiary amine adducts have found applications in materials science as precursors for delivering aluminium metal to surfaces. These include electroplating aluminium [5], and conventional thermal and laser induced chemical vapour deposition (CVD) technology [6–8]. In the gas phase, $H_3Al(NMe_3)_2$ is in reversible equilibrium with monomeric H_3AlNMe_3 [9], with complete loss of amine yielding highly reactive AlH_3, and ultimately aluminium metal close to 100°C [6]. In addition to the useful vapour pressure of these adducts for CVD technology, the absence of metal–carbon bonds in the precursors results in metal deposits being devoid of deleterious carbonaceous material [7]. Moreover, the compounds are less air sensitive than trialkylaluminium compounds which have been used extensively in CVD technology [6,10].

Gallane exists as an unstable dimeric species, $[\{H_2(\mu\text{-H})Ga\}_2]$ [11], which also forms adducts with Lewis bases [1], albeit without formation of five coordinate bridging hydride species, unlike alane, and bis-Lewis base adducts are unstable. The bis-trimethyl amine adduct of gallane, for example, is stable only between −45.4 and −22.8°C, decomposing at higher temperatures to H_3GaNMe_3, and on to gallium metal at ambient temperature [12]. More thermally robust species are possible using stronger base tertiary amines, for example, in $H_3GaN(CH_2CH_2)_3CH$, dec. > 100°C [13], or trialkylphosphines [14–16]. These compounds have scope for application in CVD technology as sources of gallium metal. Interestingly, polydentate tertiary amines yield unstable adducts with gallane, yet form stable alane containing species [3,17]; the reverse applies to phosphine adducts of the two metal hydrides. Overall, the difference between alane and gallane is (i) a stronger tendency of aluminium to form "hyper"-valent structures compared to gallium [18] (gallane forms four coordinate species in the gas phase [19] and the solid [13,20], even with potentially polydentate ligands, *e.g.* in the gallane rich species

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$(H_3GaNMe_2CH_2)_2$ [13,16]), (ii) the frailty of Ga–H bonds [21], and (iii) the polarizing influence/back bonding participation of the d^{10} core for gallium.

Here we report the synthesis, structure and stability studies of some tertiary phosphine adducts of alane and gallane. This builds on our recent work on the synthesis, structure and stability of four and five coordinate alane [4] and four coordinate gallane [14] phosphine adducts, the first example of a mixed tertiary amine/phosphine adduct, $[\{Me_3N(H)_3Al\}_2\{(PMe_2CH_2)_2\}]$ [22], and theoretical studies on the model compounds H_3GaPH_3 [14], H_3AlPR_3 (R = H [4] or Me) and $Me_3PAl(H)_3NH_3$ [22]. Features of the present work include synthetic, thermal stability studies, and structural investigations on tri-t-butylphosphine and bis(diisopropylphosphino)ethane and 1,2-bis(diphenylphosphino)ethane adducts of alane and gallane, along with *ab initio* calculations on model compounds H_3GaPMe_3 and $H_3Al(PR_3)_2$ (R = H or Me).

2. Experimental section

Syntheses were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or nitrogen. Solvents were dried then freeze/thaw degassed prior to use. All reagents were obtained from Aldrich. Compound **6** [4], tri-t-butylphosphine and 1,2-bis(diisopropylphosphino)ethane [23] were prepared by variation of the literature procedures. ^1H NMR spectra were recorded on Bruker WM-250 or CXP-300 spectrometers in deuterated benzene, and referenced to the residual ^1H resonances of this solvent (δ 7.15 ppm). ^{13}C NMR spectra were recorded in the same solvent on a Bruker WM-250 spectrometer operating at 62.8 MHz using broad band proton decoupling or DEPT pulse sequences and were referenced to the ^{13}C resonances of the deuterated solvent (δ 128.00). ^{31}P and ^{27}Al NMR spectra (deuterated benzene solutions) were recorded on a Bruker CXP-300 spectrometer operating at 101.27 and 78.18 MHz, respectively, and were measured relative to external 1 M H_3PO_4 and 1 M $[Al(OH_2)_6]^{3+}$. Elemental analyses were performed by the Canadian Microanalytical Services Ltd. Melting points were determined in sealed glass capillaries under argon, and are uncorrected.

2.1. Synthesis of $H_3AlP^tBu_3$ (1)

Tri-t-butylphosphine (0.413 g, 2.04 mmol) and HCl in Et_2O (2.3 ml. 0.91 M) were added, in succession, to a solution of $LiAlH_4$ (0.2 g, 2.03 mmol) in OEt_2 (15 ml) at 0°C. The mixture was brought to room temperature and stirred for 4 h. The solution was then filtered, to remove a white precipitate, and the solvent was removed *in vacuo* to yield a fine white crystalline powder which was then recrystallized from OEt_2 to give long rod like crystals of the title compound; 0.45 g, yield 95%; m.p. 103–105°C, dec. > 180°C. ^1H NMR (250 MHz, C_6D_6): δ 1.22 (d, CH_3, J(H–P) 11.9 Hz). ^{13}C NMR (62.8 MHz, C_6D_6): δ 36.1 (s, C); 31.0 (s, CH_3). ^{31}P NMR (121.47 MHz, C_6D_6): δ 42.4 (*cf.* 62.3, free ligand). ^{27}Al NMR (78.18 MHz, C_6D_6): δ 121.8 (br). IR: ν(Al–H) 1786br cm^{-1}.

2.2. Synthesis of $H_3GaP^tBu_3$ (2)

Method A. Tri-t-butylphosphine (0.41 g, 2.04 mmol) and HCl in Et_2O (1.2 ml, 1.68 M) were added, in succession, to a solution of $LiGaH_4$ (3.7 ml, 0.55 M, 2.04 mmol) in Et_2O with stirring at 0°C. The mixture was brought to room temperature and stirred for 2 h. The resulting mixture was filtered to remove a white precipitate, and the filtrate was concentrated to yield colorless needles of the title compound; 0.54 g, yield 96%; m.p. 52°C, dec. > 115°C. ^1H NMR (250 MHz, C_6D_6): δ 4.25 (br s, GaH); 1.00 (d, CH_3). ^{13}C NMR (62.8 MHz, C_6D_6): δ 36.1 (d, CH); 31.3 (s, CH_3). ^{31}P NMR (121.47, C_6D_6): δ 50.8 (*cf.* 62.3, free ligand). IR: ν(Ga–H) 1835 cm^{-1}. Anal. Found C 51.31, H 10.01, P 11.43. Calc. C 52.55, H 10.95, P 11.31%.

Method B. To a solution of $H_3GaN(CH_3)_3$ (0.3 g, 2.27 mmol) in Et_2O was added 0.56 ml of tri-t-butylphosphine with stirring at 0°C. The solution was brought to room temperature and stirred for 2 h. The solution was then filtered and concentrated to give fine colorless needles of the title compound; 96% yield.

2.3. Synthesis of $[(H_3Ga)_2\{(P^iPr_2CH_2)_2\}]$ (3)

Method A. 1,2-Bis(diisopropylphosphino)ethane (0.47 g, 1.8 mmol) and HCl in Et_2O (4.0 ml, 0.91 M, 3.6 mmol) were added, in succession, to a Et_2O solution of $LiGaH_4$ (6.5 ml, 0.55 M, 3.6 mmol) with stirring at 0°C. The mixture was brought to room temperature and stirred for 2 h. The solution was filtered to remove a white precipitate, and the solvent was removed *in vacuo* to yield a crystalline white powder; 0.54 g, yield 74%; dec. > 130°C. ^1H NMR (250 MHz, C_6D_6): δ 4.61 (br s, GaH); 2.73 (d, 4H, CH_2); 2.41 (m, 4H, CH); 1.93 (m, 24H, CH_3). ^{13}C NMR (62.8 MHz, C_6D_6): δ 22.4 (s, CH); 18.1 (s, CH_2); 17.4 (s, CH_3). ^{31}P NMR (121.47 MHz, C_6D_6): δ 12.4 (*cf.* 9.4, free ligand). IR: ν(Ga–H) 1810br cm^{-1}.

Method B. To a solution of $H_3GaN(CH_3)_3$ (0.47 g, 3.6 mmol) in Et_2O was added an ethereal solution of 1,2-bis(diisopropylphosphino)ethane (0.5 ml, 1.8 mmol) with stirring at room temperature. The reaction mixture was stirred for 2 h. The solvent was removed *in vacuo* to give a white micro-crystalline powder; 74% yield.

2.4. Synthesis of $[(H_3Ga)_2\{(Ph_2PCH_2)_2\}]$ (4)

To a slurry of 1,2-bis(diphenylphosphino)ethane (0.5 g, 1.24 mmol) in Et_2O was added 4.6 ml of $LiGaH_4$ (0.55 M, 2.48 mmol) in Et_2O and 2.7 ml of HCl in Et_2O (0.91 M, 2.48 mmol) with stirring at 0°C. The solution was stirred for 2 h in an ice bath. After warming to room temperature, the solution was filtered to remove a white precipitate, and the solvent was removed *in vacuo* to give a white micro-crystalline powder; 0.53 g, yield 78%; dec. 87°C. ^{1}H NMR (250 MHz, C_6D_6): δ 6.69 (m, 20H, $CH_{aromatic}$); 4.45 (br s, GaH); 2.24 (s, 4H, CH_2). ^{13}C NMR (62.8 MHz, C_6D_6): δ 132.9 (t, $CH_{aromatic}$); 131.8 (d, $C_{aromatic}$); 130.5 (s, $CH_{aromatic}$); 129.2 (d, $CH_{aromatic}$); 21.8 (d, CH_2). ^{31}P NMR (121.47 MHz, C_6D_6): δ −7.3 (*cf.* −12.3 free ligand). IR: ν(Ga–H) 1800 cm^{-1}.

2.5. Synthesis of $^tBu_3PAl(H)_3NMe_3$ (5)

Tri-t-butylphosphine (0.413 g, 2.04 mmol) was added to a solution of H_3AlNMe_3 (0.2 g, 2.04 mmol) in OEt_2 (15 ml) at 0°C. The mixture was brought to room temperature and stirred for 2 h. Concentration *in vacuo* (*ca.* 5 ml) gave a white precipitate which was collected and dried *in vacuo*; 0.51 g, yield 90%; m.p. 61 − 64°C, dec. > 150°C. ^{1}H NMR (250 MHz, C_6D_6): δ 1.25 (d, 27H, PCH_3, J(H–P) = 10.0 Hz); 2.04 (s, 9H, NCH_3); 3.97 (br s, AlH). IR: ν(Al–H) 1760 br cm^{-1}.

2.6. Structure determinations

Suitable prismatic crystals of **1**, **2** and **6** were grown from OEt_2 at −30°C. Unique diffractometer data sets were measured using Enraf-Nonius CAD4 diffractometers. Reflections with $I > 2.5\sigma(I)$ were considered "observed" and used in the full matrix least squares refinement, minimizing $\Sigma_w \Delta^2$ after solution of the structure by direct methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x,y,z,U_{iso})_H$ were constrained at estimated values (see below) except for non-methyl hydrogens in **6** which were refined in x,y,z,U_{iso}. Conventional residuals on $[F]$ at convergence are quoted, R,R' $[(\Sigma_w \| F_o | - | F_o \|^2 / \Sigma_w | F_o |^2)^{1/2}]$. No extensive, significant extinction effects were found and the data were uncorrected for absorption. Neutral-atom complex scattering factors were employed [24]; computation used the SHELX [25] and XTAL [26] program system implemented on a SUN SPARC/Station 2. Crystal data, atom coordinates, and molecular core geometries are given in Tables 1–3 and Figs. 1 and 2.

Invariant hydrogen atom positions were calculated in idealized positions at a distance of 1.0 Å from the parent carbon atom with temperature factors at *ca.* 1.25 × U_{ii}(average) of the attached carbon atom. The structure of **1** was initially solved in $Pna2_1$ and transformed to the higher symmetry space group *Pcmn* with 50% disorder across a mirror plane for one of the ^{t}Bu groups. Attempts at refinement in $Pna2_1$ gave no significant improvement in the disorder model; compound **2** was found to be isostructural with **1**. Lists of U_{ij} values, hydrogen atom parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Database Centre.

TABLE 1. Non-hydrogen atom coordinates for $H_3MP^tBu_3$, M = Al (**1**), M = Ga (**2**)

Atom	x	y	z
Compound 1			
Al	0.5803(5)	0.2500	0.2100(2)
P	0.4139(2)	0.2500	0.3517(1)
C(1)	0.560(1)	0.2500	0.4539(6)
C(2)	0.2789(8)	0.1372(4)	0.3536(5)
C(11) [a]	0.477(2)	0.207(1)	0.5441(6)
C(12)	0.667(1)	0.1628(7)	0.4483(7)
C(21)	0.387(1)	0.0468(4)	0.3453(6)
C(22)	0.177(1)	0.1248(7)	0.4387(9)
C(23)	0.174(1)	0.1369(7)	0.2657(8)
Compound 2			
Ga	0.5783(5)	0.2500	0.2093(2)
P	0.4151(8)	0.2500	0.3506(3)
C(1)	0.566(4)	0.2500	0.451(1)
C(2)	0.284(2)	0.135(1)	0.355(1)
C(11) [a]	0.473(4)	0.202(3)	0.543(2)
C(12)	0.684(3)	0.158(2)	0.438(2)
C(21)	0.392(3)	0.046(1)	0.347(1)
C(22)	0.176(3)	0.122(2)	0.431(2)
C(23)	0.167(4)	0.134(2)	0.272(2)

[a] Population parameter 0.5.

2.7. Theoretical structures

Ab initio molecular orbital calculations have been carried out on $H_3Al(PR_3)_2$, R = H or Me, (and PH_3 and PMe_3) using GAUSSIAN 90 [27] on IBM RISC 6000 and Sun SPARC/station 2 computers. Structures were

TABLE 2. Non-hydrogen atom coordinates for $[(H_3Al)_2\{(P^iPr_2CH_2)_2\}]$ (**6**)

Atom	x	y	z
Al	0.2094(3)	−0.0319(5)	0.3210(2)
P	0.2073(2)	0.0570(3)	0.5047(2)
C(1)	0.0580(7)	0.013(1)	0.5480(6)
C(11)	0.2339(9)	0.271(1)	0.5243(8)
C(12)	0.3692(9)	0.318(1)	0.5098(9)
C(13)	0.125(1)	0.364(1)	0.450(1)
C(21)	0.3383(8)	−0.043(1)	0.6085(7)
C(22)	0.348(1)	0.009(2)	0.7251(7)
C(23)	0.328(1)	−0.221(1)	0.5960(9)
H(1)	0.119(9)	0.07(1)	0.246(7)
H(2)	0.136(9)	−0.19(1)	0.302(8)
H(3)	0.35(1)	−0.04(1)	0.313(8)

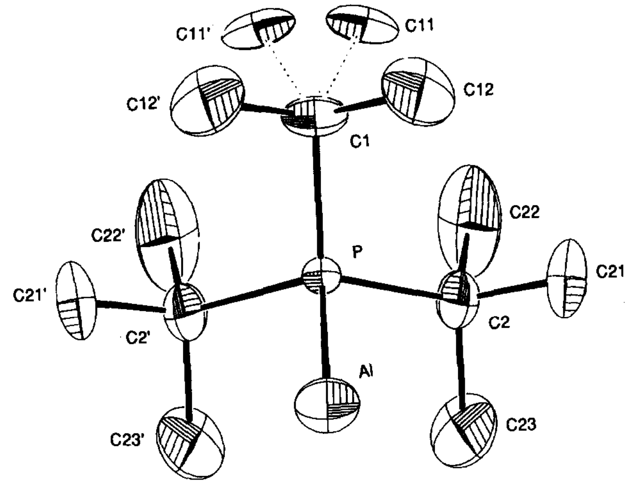


Fig. 1. Molecular projection of $H_3MP^tBu_3$, M = Al, **1**, showing the labelling scheme; thermal ellipsoids are drawn at the 20% probability level. Selected bond distances (Å) and angles (°) are as follows; values in parentheses are for isostructural $H_3MP^tBu_3$, M = Ga, **2**: M–P, 2.471(3), 2.444(6); P–C1, 1.906(8), 1.91(2); P–C2, 1.899(6), 1.90(2); Al–P–C1, 108.4(3), 107.2(8); Al–P–C2, 109.2(2), 109.3(5); Cl–P–C2, 110.3(2), 109.6(7); C2–P–C2', 109.5(3), 111.8(7).

computed using the D95* basis set, H_3GaPMe_3 excepted (DZP level), and are devoid of zero point energy corrections. Structures were constrained to have C_{3v} (mono-phosphine adducts) and D_{3h} symmetry (bis-phosphine adducts). Computed structures and molecular core geometries are given in Table 4, together with computed structures for related alane and gallane molecules.

3. Results and discussion

3.1. Synthesis and properties

Scheme 1 summarises the synthetic details for the new compounds **1–5**. All preparations were carried out in diethyl ether at *ca.* 0°C and yields were in the range 74–96%. Compound characterization was carried out using IR and ^1H, ^{13}C, ^{31}P and ^{27}Al solution NMR spectroscopy, where appropriate, and X-ray diffraction studies for compounds **1** and **2** (see structural commentary). Only compound **2** gave satisfactory microanalysis. As noted previously for alane/phosphine adducts [4], microanalyses were invariably a few percent low in carbon.

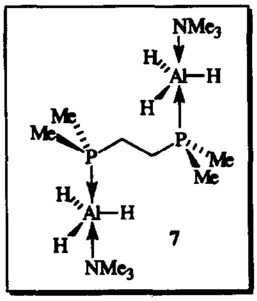
Noteworthy diagnostic spectroscopic data include (i) ν(Al–H) at 1786 and 1760 cm^{-1}, **1** and **5**, respectively, are typically lower than ν(Ga–H), 1835, 1810, and 1800 cm^{-1}, **2–4**, and with no discernible difference between ν(Al–H) for four coordinate (**1**) and five coordinate alane species (**5**), and previously reported compound **6**, and related compounds [4]); (ii) characteristic broad hydride ^1H NMR resonance for both alane and gallane derivatives are close to 4.5 ppm, except for **1** for which the hydride resonance was not detected; (iii) ^{31}P NMR on compounds **3**, **4**, **6** and the related polymeric species $H_3Al\{(P^iPr_2CH_2)_2\}$ (**7**) have chemical shifts close to those of the free phosphine ligands, *viz.* 12.4 ppm (**3**), *cf.* 9.4 ppm; −7.3 ppm (**4**), *cf.* −12.4 ppm; 10.2 (**6**); 9.6 ppm (**5**), *cf.* 9.4 ppm, whereas for compounds **1** and **2** there is a large upfield shift of 19.9 ppm and 11.5 ppm, respectively: a similar shift has been noted for the

TABLE 3. Summary of X-ray diffraction data for $H_3MP^tBu_3$, M = Al (**1**), M = Ga (**2**) and $[(H_3Al)_2\{(P^iPr_2CH_2)_2\}]$ (**6**)

	1	**2**	**6**
Formula	$C_{12}H_{30}PAl$	$C_{12}H_{30}PGa$	$C_{14}H_{38}P_2Al_2$
Mol. wt.	232.3	275.1	322.4
Space group	*Pcmn* (No. 62)	*Pcmn* (No. 62)	$P2_1/c$ (No. 14)
a (Å)	8.122(2)	8.117(5)	10.672(2)
b (Å)	13.745(1)	13.713(2)	8.409(3)
c (Å)	14.603(2)	14.530(3)	12.676(2)
β (°)	90.0	90.0	104.73(2)
V (Å³)	1630.2	1617.3	1100.0
Z	4	4	2
D(calcd.) (g cm^{-3})	0.95	1.13	0.98
F(000)	520		
Crystal dimensions (mm^3)	0.4 × 0.25 × 0.10	0.4 × 0.3 × 0.15	0.3 × 0.3 × 0.25
Temperature (°C)	25	25	25
Radiation	Mo Kα (0.71073 Å, graphite monochromator)		
μ (cm^{-1})	1.98	17.7	2.63
2θ limit (°)	50	50	50
No. of collected reflections	1495	1183	2179
No. of observed reflections [$I > 2.5\sigma(I)$]	1105	531	856
R	0.069	0.073	0.064
R_w	0.077	0.087	0.075
s	1.25	3.01	1.60

tri-t-butylphosphine adduct of trimethylaluminum, and has been explained by a more open R–P–R angle on complexation [28]; (iv) ^{27}Al NMR chemical shift for compound **1**, 121.8 ppm, compares with those of four coordinate mono-tertiary amine adducts of alane [22]. The ^{27}Al NMR chemical shifts for **6** and **7** [22] are significantly less, 100.5 and 105.3 ppm, respectively, reflecting greater solvation at the metal centre, and are similar to those for bis-tertiary amine adducts [3].

Two methods of synthesis were used, *viz*. elimination of LiCl and ligand displacement, as established by Greenwood *et al.* [15]. No reaction was evident between $LiMH_4$, M = Al and Ga, and the phosphines in diethyl ether, even though for $LiGaH_4$ in the presence of PCy_3 and $(Me_2PCH_2)_2$ [14] there is elimination of LiH and formation of adducts. However, in the presence of diethyl ether solutions of HCl, which presumably generate MH_3 *in situ*, the target adducts **1–4** are readily accessible; this method has recently been used to prepare some related alane/phosphine adducts, including compound **6** [4]. The ligand displacement method involving H_3GaNMe_3 was applicable for the synthesis of **2** and **3** [14], but not **4**, or gallane adducts of $(Ph_2PCH_2CH_2)_2PPh$, which relates to the weaker base strength of the diaryl phosphine centres. A similar approach for alane results in the formation of five coordinate species, **5**, of a type noted previously in the formation of compound **7** [22], or no reaction for $(Ph_2PCH_2)_2$, $(Ph_2P)_2CH_2$ and $(Ph_2PCH_2CH_2)_2PPh$ [4], again in agreement with the weaker base strength of the phosphines. Indeed, to form aryl phosphine adducts of alane and gallane, the LiCl elimination method is required, but the resulting adducts are intrinsically unstable. The alane adducts of $(Ph_2PCH_2)_2$ and $(Ph_2PCH_2CH_2)_2PPh$ rapidly decompose to polymeric alane at room temperature, whereas the gallane adducts decompose at room temperature with the formation of gallium metal, although the adduct of $(Ph_2PCH_2)_2$ (**4**) can be successfully isolated and characterized. Nevertheless, it slowly decomposes at room temperature. The triphenyl phosphine adduct of gallane is even less stable, decomposing in etheral solutions below room temperature [15].



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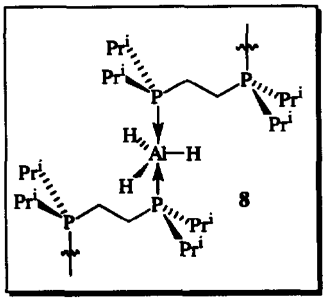

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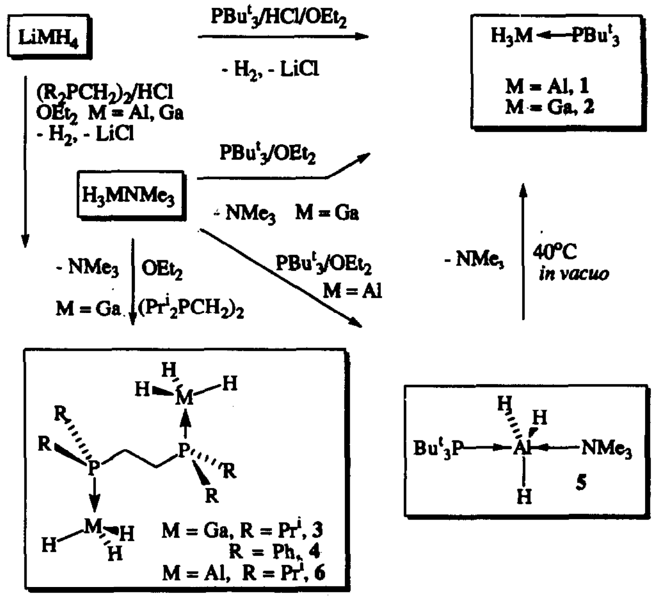
While the 1 : 1 adduct of $(^iPr_2PCH_2)_2$ and alane is accessible, **8**, [4] attempts to prepare the corresponding

TABLE 4. Optimized geometries for alane, gallane and phosphine and trimethylphosphine adducts of alane and gallane

Molecule (symmetry)	Basis set	M–P (Å)	M–H (Å)	P–H(CH$_3$) (°)	P–M–H	M–P–H(CH$_3$) (°)	Ref.
H_3Al (D_{3h})	MP4/DZP	–	1.591	–	–	–	4
	MP2/D95*		1.585	–	–	–	This work
	RHF/D95*		1.581	–	–	–	
H_3Ga (D_{3h})	RHF/3-21G(*)	–	1.592	–	–	–	31
	MP2/D95*		1.570	–	–	–	This work
	RHF/D95*		1.579	–	–	–	
H_3AlPH_3 (C_{3v})	MP4/DZP	2.605	1.600	1.424	96.84	119.2	4
	MP2/D95*	2.598	1.595	1.416	96.91	119.0	This work
	RHF/D95*	2.659	1.593	1.404	97.01	118.38	
H_3AlPMe_3 (C_{3v})	MP2/D95*	2.498	1.602	1.844	99.2	115.0	22
	RHF/D95*	2.540	1.602	1.848	99.65	114.47	This work
$H_3Al(PH_3)_2$ (D_{3h})	MP2/D95*	2.828	1.597	1.420	90.0	120.6	This work
	RHF/D95*	2.975	1.592	1.409	90.0	120.0	
$H_3Al(PMe_3)_2$ (D_{3h})	DRHF/D95*	2.786	1.606	1.852	90.0	115.99	This work
H_3GaPH_3 (C_{3v})	–MP2/DZP	2.576	1.561	1.398	96.71	118.88	14
	DRHF/DZP	2.731	1.587	1.406	96.18	118.91	
H_3GaPMe_3 (C_{3v})	RHF/DZP	2.550	1.597	1.845	99.53	114.67	This work

gallane species resulted in the formation of a mixture of **3** and free phosphine. This reflects the ability of alane and not gallane to readily form five coordinate species, and for multidentate ligands, polymeric structures dominate, as for **8** and adducts based on bidentate tertiary amines [3,29], rather than the formation of chelate rings. Seemingly there is an inherent stability of a planar alane species [3] with the two donor groups in apical positions of trigonal bipyramidal stereochemistry. Interestingly, for higher polyfunctional tertiary amines, ionic species predominate [17], 1,3,5-trimethylhexahydro-1,3,5-triazine excepted [3].



Scheme 1.

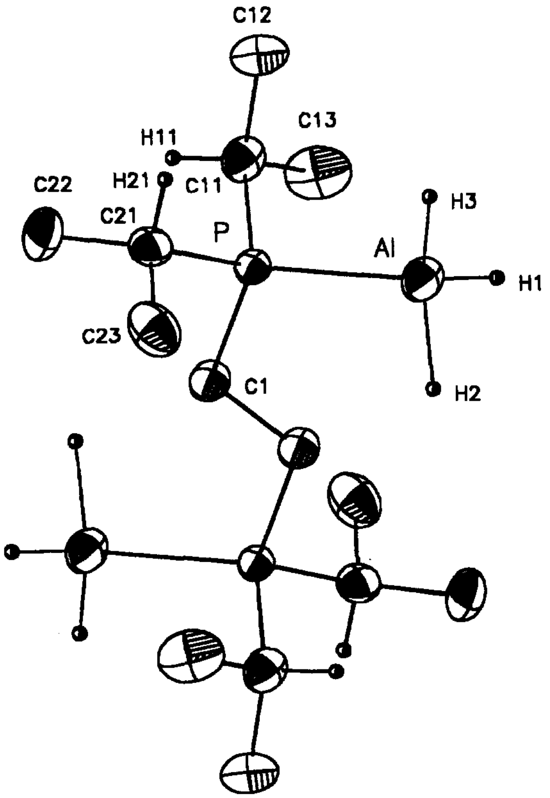


Fig. 2. Molecular projection of $[(H_3Al)_2\{(P^iPr_2CH_2)_2\}]$ (**6**) showing the labelling scheme; thermal ellipsoids are drawn at the 20% probability level and only selected hydrogens with arbitrary radii are shown for clarity. Selected bond distances (Å) and angles (°) are as follows: Al–P, 2.451(3); P–C1,11,21, 1.850(8), 1.83(1), 1.859(9); Al–H1,2,3, 1.5(1), 1.5(1), 1.6(1); P–Al–H1,2,3, 106(3), 107(3), 109(3); H1–Al–H2,3, 100(5), 119(5); H2–Al–H3, 115(6); Al–P–C1,11,21, 115.9(3), 113.0(3), 110.4(3); C1–P–C11,21, 105.8(5), 104.4(4); C11–P–C21, 106.5(5).

Compound **1** has remarkably high thermal stability, decomposing > 180°C yielding aluminium, similar to other adducts based on bulky phosphines [4], and comparable to tertiary amine adducts of alane [2,3]. For less hindered phosphine ligands decomposition prevails under even mild conditions, above *ca.* −20°C, giving polymeric alane rather than decomposing directly to metal [4,9,30]. The extra hindrance to stabilize alane adducts presumably precludes the formation of hydride bridges found in some tertiary amine adducts [2]. Theory predicts that while complexation of phosphines to alane is energetically favoured, association en route to dialane and free phosphine is more favoured [4]. Such association, at least *via* hydride bridges may be blocked by the steric hindrance of the phosphines in the present study. The mixed donor adduct, **5**, is unstable at *ca.* 40°C *in vacuo*, decomposing to **1** and trimethyl amine. This is surprising considering the donor strengths of the ligands towards alane, theoretical considerations [2–4], and the stability of the similar compound, **7**, which sublimes at *ca.* 50°C. The exceptional large steric hindrance of the phosphine coupled with the volatility of the amine most likely results in shift of equilibria to favour **1**.

$$PBu^t_3 + H_3AlNMe_3 \rightleftharpoons \underset{(5)}{{}^tBu_3PAl(H)_3NMe_3} \rightleftharpoons \underset{(1)}{H_3AlP^tBu_3} + NMe_3$$

Reasonable volatility of **5**, and also the related compound **7**, but low volatility of **1** and the gallane adducts **2** and **3** relates to the expected reduced dipole moment in the mixed donor species relative to four coordinate species. Even so, the gallane adducts **2** and **3** are thermally robust decomposing to gallium metal above *ca.* 114 and 130°C, respectively, similar to related compounds, e.g. H_3GaPCy_3, dec. > 130°C [14], and better than any tertiary amine gallane adducts [13]. Clearly incorporating aryl groups on the phosphine, compound **4**, diminishes the stability of the adduct. The new compounds only slowly decompose in air which is related to steric protection at the metal centers by the bulk ligands.

3.2. Structural studies

Compounds **1** and **2** crystallize with molecules lying on mirror planes, although the unique ^{t}Bu groups are disordered across the planes; compound **6** crystallizes with centrosymmetric molecules, such that the two alane units are remote, ruling out intramolecular hydride bridges of the type found in some mono-amine adducts of alane [2]. Indeed, consideration of internuclear distances for **6** and **1** also rule out such association as an intermolecular process, which would dictate Al $\cdots$ Al distances close to 2.9 Å [2]. Thus the metal centres in both structures are deemed four coordinate, at least in the absence of the location of the hydride atoms in **1**. Similarly the metal centre in **2** is four coordinate as is usual for Lewis base adducts of gallane.

The Al–P distances (2.471(3) and 2.451(3) Å) in **1** and **6**, respectively, are similar to those established for the related compounds H_3AlPCy_3 and $(H_3AlPCy_2CH_2)_2$ (2.467(1) and 2.460(2) Å) [4] which collectively are marginally longer than Ga–P distances in **2** (2.444(6) Å) and related compounds, *viz.* 2.460(2) Å in H_3GaPCy_3 [14] and 2.403(1) Å in $(H_3GaPMe_2CH_2)_2$ [14,16]. This is consistent with the weaker binding of phosphines to alane relative to gallane. The bis(phosphine) adduct of alane, **8**, in contrast has exceptionally long Al–P distances (2.755(3) and 2.708(3) Å) [4], and thus weak P $\cdots$ Al interactions, which is consistent with the tendency of unhindered phosphines to form unstable adducts relative to polymerization of alane (see above), and with theoretical predictions (see below). For the mixed donor species, **7**, the Al–P distance is marginally shorter (2.688(5) Å) [22], but is still exceptionally long given that the Al–N distance in the same compound (2.155(9) Å) is typical for five coordinate alane species with two N-centres in apical positions of trigonal bipyramidal metal centres [3]. Disorder of one of the alkyl groups in **1** and **2** probably accounts for problems in locating the hydride groups. In compound **6**, however, the hydrides are well resolved giving meaningful Al–H distances (average 1.5 Å) which agree with other structural studies on alanes [2,3].

The conformation of the isopropyl groups with respect to the P-centres in **6** is such that the methine H-atoms lie astride AlH_3 or CH_2 and $CHMe_2$. In the related centrosymmetric molecule $(H_3AlPCy_2CH_2)_2$, the methine H-atoms lie astride AlH_3 or $CHMe_2$ and CH_2 [4].

Ab initio calculations on relevant model systems, $H_3PGaPMe_3$ and $H_3Al(PR_3)_2$, R = H or Me, are summarized in Table 4, along with details of calculations on other relevant species. The geometries for the present calculated structures compare favourably with experimental results with the closest agreement corresponding to incorporating methyl groups on the P-centres. Thus for mono-phosphine alane at the MP2/D95* level, the Al–P distance shrinks by 0.107 Å, being only 0.03 or 0.05 Å larger than experimental distances for **1** and **6**, respectively. Similarly bis-trimethylphosphine alane gives shorter M–P distances (2.786 Å) which approach those established for compound **8** (2.755(3) and 2.708(3) Å) [4]. For a lower level of theory, for the trimethylphosphine gallane adduct there is only a marginal improvement of theory with experimental results.

Stabilization energies for various complexation reactions are as follows:

$GaH_3 + PH_3 \rightarrow H_3GaPH_3$	-8.06 kcal mol^{-1}
$GaH_3 + PMe_3 \rightarrow H_3GaPMe_3$	-16.01 kcal mol^{-1}
$AlH_3 + PH_3 \rightarrow H_3AlPH_3$	-10.65 kcal mol^{-1}
$H_3AlPH_3 + PH_3 \rightarrow H_3Al(PH_3)_2$	-1.82 kcal mol^{-1}
$AlH_3 + PMe_3 \rightarrow H_3AlPMe_3$	-21.54 kcal mol^{-1}
$H_3AlPMe_3 + PMe_3 \rightarrow H_3Al(PMe_3)_2$	-2.26 kcal mol^{-1}

Thus trimethylphosphine gives greater stabilization energies relative to phosphine, in accordance with donor strength considerations. Moreover, for aluminum the uptake of a second phosphine is favoured by only 1.82 or 2.26 kcal mol^{-1}, *cf.* 10.74 kcal mol^{-1} for the corresponding N-donor system, *viz.* $H_3AlNH_3 + NH_3$ [3]. Here there is *ca.* 0.15 Å increase in metal–donor distance in good agreement with experiments [1,3], whereas the corresponding complexation involving PH_3, and also complexation of PMe_3 with H_3AlPMe_3, gives an increase of *ca.* 0.3 Å, also in agreement with experiment. Minima for $H_3Al(PR_3)_2$, R = H or Me, correspond to trigonal bipyramidal structures with the hydrides in equatorial positions. This is also the preferred arrangement for $H_3Al(NH_3)_2$, which has been studied on a theoretical basis [3].

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