Synthesis and Characterization of the Monomeric Phosphinogallanes Bu^t₂GaPR'R" (R', R" = bulky aryl or silyl groups) and Related Compounds[†]

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The use of bulky substituent groups has allowed the isolation and spectroscopic and structural characterization of several monomeric phosphinogallanes wherein gallium and phosphorus are three-co-ordinate. These new compounds have the formula Bu^{*}₂GaP(R)(SiPh₃) (R = C₆H₂Bu^{*}₃-2,4,6 1, C₆H₂Pr^{*}₃-2,4,6 2, C₆H₂Me₃-2,4,6 3 or SiMe₃ 4). Variable-temperature ¹H NMR studies indicate that there is a rotational barrier of *ca*. 12.7 kcal mol⁻¹ around the Ga–P bond in 1 which has been attributed to weak Ga–P π bonding. The synthesis and structures of the related aluminium-phosphorus species Bu^{*}₂Al(Et₂O)-P(C₆H₂Pr^{*}₃-2,4,6)(SiPh₃) 5 and the gallium-arsenic species Bu^{*}₂GaAs[CH(SiMe₃)₂](SiPh₃) 6 are also reported. In addition, variable-temperature ¹H NMR studies of the precursor asymmetric phosphines (Ph₃Si)P(R)H (R = C₆H₂Bu^{*}₃-2,4,6 7, C₆H₂Pr^{*}₃-2,4,6 8 or C₆H₂Me₃-2,4,6 9) as well as the X-ray structures of (Ph₃Si)P(C₆H₂Bu^{*}₃-2,4,6)H 7 and (Ph₃Si)P(SiMe₃)₂ 10 are discussed. Crystal data with Mo-Ka radiation ($\lambda = 0.710$ 69 Å) at 130 K: 2, monoclinic, space group *P*2₁/*c*, *a* = 18.499(5), *b* = 10.028(4), *c* = 20.746(6) Å, $\beta = 90.45(1)^\circ$, *Z* = 4, *R* = 0.043; 5, triclinic, space group *P*1, *a* = 9.488(3), *b* = 11.416(5), *c* = 20.383(6) Å, $\alpha = 92.07(3)$, $\beta = 96.80(2)$, $\gamma = 103.17(3)^\circ$, *Z* = 2, *R* = 0.079; 6, triclinic, space group *P*1, *a* = 12.219(3), *b* = 14.174(3), *c* = 21.831(5) Å, $\alpha = 92.95(2)$, $\beta = 99.73(2)$, $\gamma = 99.47(2)^\circ$, *Z* = 4, *R* = 0.053; 7, monoclinic, space group *P*2₁/*c*, *a* = 17.710(6), *b* = 16.635(5), *c* = 10.838(4) Å, $\beta = 97.43(3)^\circ$, *Z* = 4, *R* = 0.050.

There has been widespread interest in multiple bonding between the Main Group 13 and 15 elements for many years. Much of this work has been concerned with boron-nitrogen compounds and it is only very recently that π bonding between boron and the heavier Group 15 elements phosphorus and arsenic has become well established.¹⁻⁴ Likewise, information regarding π bonding in compounds where both of the Main Group 13 and 15 atoms are heavier members of their respective groups has been very sparse. Nonetheless, the recently reported structures of the Zintl anions $[M_2E_4]^{6-}$ (M = Al or Ga, E = P or As), which have planar M_2E_2 cores and short M-E bond lengths, support the presence of considerable M-E multiple interaction.⁵ In addition, the synthesis and structural characterization of gallium-phosphorus species which are analogues of ethylene, $Bu_{2}^{i}GaP(C_{6}H_{2}Bu_{3}^{i}-2,4,6)(SiPh_{3})$ or the allyl cation, $(C_{6}H_{2}Me_{3}-2,4,6)P[Ga(C_{6}H_{2}Pr_{3}^{i}-2,4,6)_{2}]_{2}$ were very recently communicated from this laboratory.^{6,7} Their structures consist of almost planar C2GaP(C)Si and CP(GaC2)2 cores and relatively short Ga-P distances, 2.295(5) and 2.257(3) Å, respectively. Variable-temperature ¹H NMR studies of these gallium-phosphorus species indicated barriers to rotation around the Ga-P bonds of 12.7 and 10.6 kcal mol⁻¹, respectively. These barriers were attributed to weak Ga-P π interactions. It appears that one of the major factors in determining the extent of multiple bonding in these species and compounds of the general formulae $R_2ME(R')R''$ (where M = Ga or Al and E = P or As) is the inversion barrier at the phosphorus or arsenic centre. This normally ranges from ca. 0 to 36 kcal mol⁻¹ for phosphanes and can be as high as 45 kcal mol⁻¹ for arsanes.⁸ It has been shown that, in certain boronphosphorus and -arsenic compounds, large and electropositive substituents at phosphorus or arsenic lower the inversion barrier and induce stronger multiple bonding.^{4,9} This paper reports similar investigations of Ga–P and Ga–As species. Several examples of new gallium-phosphorus compounds of the formulae $Bu_2^GaP(R)(SiPh_3)$ (R = bulky aryl or silyl group) and related aluminium-phosphorus and galliumarsenic species are reported here. In addition, variabletemperature ¹H NMR studies of the asymmetric phosphine precursors (Ph₃Si)P(R)H are also presented.

Experimental

All experiments were performed either by using modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 dry box under nitrogen. Solvents were freshly distilled from a sodium-potassium alloy and degassed twice prior to use. Phosphorus-31 and ¹H NMR spectra were recorded in C_6D_6 or C_7D_8 solutions using a General Electric QE-300 spectrometer. The compounds GaBu¹₂Cl,¹⁰ AlBu¹₂Cl,¹¹ PH₂(C₆H₂Bu¹₃-2,4,6),¹² PH₂(C₆H₂Prⁱ₃-2,4,6),¹³ PH₂(C₆H₂Me₃-2,4,6),¹⁴ (Me₃Si)₂PLi-2thf¹⁵ (thf = tetrahydrofuran) and (Me₃Si)₂-CHAsH₂¹⁶ were synthesized according to literature methods. Chlorotriphenylsilane was purchased commercially and used as received.

Preparations.—Bu¹₂GaP(R)(SiPh₃) (R = C₆H₂Bu¹₃-2,4,6 1, C₆H₂Prⁱ₃-2,4,6 2 or C₆H₂Me₃-2,4,6 3). The compounds 1–3 were prepared in an identical manner. The synthesis of 1 is described here. An Et₂O (20 cm³) solution of (Ph₃Si)P(C₆H₂-Bu¹₃-2,4,6)H (2.15 g, 4 mmol) 7 (synthesis described below) was treated dropwise with LiBuⁿ (2.5 cm³ of a 1.6 mol dm⁻³ hexane solution, 4 mmol). After stirring for 3 h at room temperature GaBu¹₂Cl (0.86, 4 mmol) in Et₂O (15 cm³) was added dropwise and the solution was stirred for a further 4 h. The volatile materials were removed under reduced pressure and the residue was taken up in pentane (30 cm³). Filtration and concentration

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1993, Issue 1, pp. xxiii–xxviii. Non-SI unit employed: cal \approx 4.184 J.

Table 1	Microanalytical data for compou	inds 2–11 *	
Compou	ind	С	н
2 Bu ¹ ₂ C	$GaP(C_6H_2Pr^{i_3}-2,4,6)(SiPh_3)$	72.90 (72.65)	8.40 (8.35)
3 Bu'2C	$GaP(C_6H_2Me_3-2,4,6)(SiPh_3)$	71.00 (70.80)	7.50 (7.45)
4 Bu ¹ ₂ C	GaP(SiMe ₃)(SiPh ₃)	62.70 (62.50)	9.45 (9.40)
5 Bu' ₂	$Al(Et_2O)P(C_6H_2Pr^i_3-2,4,6)(SiPh_3)$	76.10 (76.20)	9.40 (9.40)
6 Bu ¹ ₂ C	$GaAs[CH(SiMe_3)_2](SiPh_3)$	58.45 (58.50)	7.80 (7.75)
7 (Ph ₃ S	$Si)P(C_6H_2Bu_3^t-2,4,6)H$	79.10 (78.95)	8.35 (8.30)
8 (Ph ₃ S	$Si)P(C_6H_2Pr^i_3-2,4,6)H$	80.60 (80.10)	8.00 (7.95)
9 (Ph ₃ S	$Si)P(C_6H_2Me_3-2,4,6)H$	80.40 (79.00)	6.95 (6.65)
10 $(Ph_3Si)P(SiMe_3)_2$		66.35 (66.00)	7.65 (7.60)
11 (SiMe	e ₃)(SiPh ₃)PLi•dme	65.85 (65.20)	7.80 (7.45)

* Required values are given in parentheses.

to *ca*. 10 cm³ and cooling to -78 °C gave a white solid which may be recrystallized from a minimum volume of hexane or Et₂O in a freezer at -20 °C. Bu¹₂GaP(C₆H₂Bu¹₃-2,4,6)(SiPh₃) 1: yield 2.07 g, 72%; m.p. 154–158 °C. NMR: ¹H (C₇D₈, 25 °C), δ 1.12 (s, 18 H, GaBu¹₂), 1.58 (s, 18 H, *o*-Bu¹), 1.3 (s, 9 H, *p*-Bu¹), 7.05 (m, 8 H, *m*-H of C₆H₂Bu¹₃-2,4,6 and SiPh₃) and 7.65 (mm, 9 H, *o*- and *p*-H of SiPh₃); ³¹P (C₆D₆), δ – 119. Bu¹₂GaP(C₆H₂-Pr¹₃-2,4,6)(SiPh₃) **2**: yield 68%; m.p. 138–143 °C. NMR: ¹H (C₇D₈), δ 1.02 [d, 12 H, *o*-CH(CH₃)₂], 1.03 (s, 18 H, GaBu¹₂), 1.19 [d, 6 H, *p*-CH(CH₃)₂], 2.77 [spt, 1 H, *p*-CH(CH₃)₂], 4.39 [spt, 2 H, *o*-CH(CH₃)₂], 7.12 (m, 8 H, *m*-H of C₆H₂Pr¹₃-2,4,6 and SiPh₃) and 7.65 (mm, 9 H, *o*- and *p*-H of SiPh₃); ³¹P (C₆D₆), δ – 146. Bu¹₂GaP(C₆H₂Me₃-2,4,6)(SiPh₃) **3**: yield 52%; m.p. 74–79 °C. NMR (C₇D₈): ¹H, δ 1.03 (s, 18 H, GaBu¹₂), 2.04 (s, 3 H, *p*-Me), 2.37 (s, 3 H, *o*-Me), 7.12 (m, 8 H, *m*-H of C₆H₂Me₃-2,4,6 and SiPh₃) and 7.70 (m, 9 H, *o*- and *p*-H of SiPh₃); ³¹P, δ – 141.

Bu¹₂GaP(SiMe₃)(SiPh₃) 4. A dimethoxyethane (dme) solution (20 cm³) of (Ph₃Si)P(SiMe₃)₂ 10 (1.62 g, 3.7 mmol) at -10 °C was treated dropwise with a 1.5 mol dm⁻³ Et₂O solution of LiMe (2.47 cm³, 3.7 mmol). After stirring for 3 h at -10 °C the solution was allowed to warm and stirred for another 12 h. The volatile materials were removed under reduced pressure and the residue was dissolved in Et₂O (20 cm³). The Et₂O solution of 11 was added *via* cannula to GaBu¹₂Cl (0.81 g, 3.7 mmol) in Et₂O (20 cm³) at 0 °C. After warming to room temperature and stirring for 5 h, the Et₂O was removed and replaced with pentane (50 cm³, the product decomposes if heated). Filtration, and concentration to *ca*. 15 cm³ then cooling to -20 °C for 2 d gave 4 as colourless prisms. Yield: 1.42 g, 70%; m.p. 111–118 °C (decomp. to yellow oil). NMR: ¹H (C₇D₈), δ 0.194 (d, 9 H, SiMe₃, ³J_{P-H} 5.7 Hz), 1.10 (s, 18 H, GaBu¹₂), 7.14 (m, 6 H, *m*-H of SiPh₃) and 7.80 (m, 9 H, *o* and *p*-H of SiPh₃); ³¹P (C₆D₆), δ -267. Bu¹₂Al(Et₂O)P(C₆H₂Pr¹₃-2,4,6)(SiPh₃) **5**. To a solution of **8**

Bu²₂Al(Et₂O)P(C₆H₂Pr³₃-2,4,6)(SlPh₃) **5**. To a solution of **8** (1.48 g, 3 mmol) in pentane (30 cm³), was rapidly added LiBuⁿ (1.88 cm³, 1.6 mol dm⁻³ in hexanes). No reaction was observed until ≈ 5 cm³ of Et₂O was added to the solution. After stirring for 3 h, all volatiles were removed and the solid rinsed twice with two portions of pentane (30 cm³). A pentane solution (20 cm³) of AlBu¹₂Cl (0.53 g, 3 mmol) was added to a pentane (30 cm³) slurry of the resulting solid and the solution was stirred for a further 3 h. Filtration and concentration to *ca*. 3 cm³ and cooling in a freezer at -20 °C afforded a crystalline product; yield 0.91 g, 43%; m.p. 109-112 °C. NMR: ¹H (C₇D₈), δ 0.781 (m, 6 H, Et₂O), 1.06 (s, 18 H, AlBu¹₂), 1.10 [d, 12 H, *o*-CH(CH₃)₂], 3.63 (m, 4 H, Et₂O), 4.78 [spt, 2 H, *o*-CH(CH₃)₂], 7.08 (m, 8 H, *m*-H of C₆H₂Pr¹₃-2,4,6 and SiPh₃) and 7.62 (m, 9 H, *o*- and *p*-H of SiPh₃); ³¹P(C₆D₆), δ -199.

 $Bu_2^tGaAs[CH(SiMe_3)_2](SiPh_3)$ 6. In a typical preparation of the asymmetric arsine the primary arsine (Me_3Si)_2CHAsH_2 (2.36 g, 10 mmol) was slowly treated dropwise with LiBuⁿ (6.25 cm³ of 1.6 mol dm⁻³ solution in hexanes, 10 mmol) in Et₂O (40

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cm³) at -78 °C. After warming to room temperature and stirring for 30 min an Et₂O (20 cm³) solution of Ph₃SiCl (2.95 g, 10 mmol) was added dropwise at 0 °C. After stirring for ≈ 12 h all volatile materials were removed and the residue extracted with pentane (40 cm³) and filtered over Celite. Colourless crystals of the product separated from solution after cooling to -20 °C in an almost quantitative yield. The species 6 was prepared from the secondary arsine Ph₃SiAs[CH(SiMe₃)₂]H in an identical manner to 1–3 in $\approx 55\%$ yield, m.p. > 115 °C (decomp. to yellow oil). ¹H NMR (C₆D₆), δ 0.07 [s, 18 H, CH(SiMe₃)₂], 1.07 (s, 18 H, GaBu'₂), 1.85 [s, 1 H, CH(SiMe₃)₂], 7.08 (m, 6 H, *m*-H of SiPh₃) and 7.85 (9 H, *o*- and *p*-H of SiPh₃).

 $(Ph_3Si)P(R)H (R = C_6H_2Bu_3^{i}-2,4,6,7, C_6H_2Pr_3^{i}-2,4,6,8 \text{ or})$ $C_6H_2Me_3-2,4,6$ 9). The asymmetrically substituted phosphines were prepared in an analogous manner. The synthesis of 7 is described here. To an Et_2O (50 cm³) solution of LiPH(C₆H₂- $Bu_{3}^{t}-2,4,6$ (10 mmol) prepared in situ from $PH_{2}(C_{6}H_{2}Bu_{3}^{t}-2,4,6)$ 2,4,6) (2.78 g, 10 mmol) and LiBuⁿ (6.25 cm³, 10 mmol) was added Ph₃SiCl (2.95 g, 10 mmol) in Et₂O (30 cm³) dropwise. The cloudy solution was allowed to stir for 12 h. All volatile materials were removed under reduced pressure and the residue was taken up in pentane (40 cm³). After filtration the solution was pumped down to incipient crystallization. Slow cooling in a freezer at -20 °C overnight afforded the product in $\approx 90\%$ yield. (Ph₃Si)P(C₆H₂Bu^t₃-2,4,6)H 7: m.p. 153-156 °C. NMR (C₆D₆): ¹H, δ 1.36 (s, 9 H, p-Buⁱ), 1.43 (d, 18 H, o-Buⁱ), 5.19 (d, 1 H, P–H), 7.09 (m, 8 H, *m*-H of $C_6H_2Bu_3^{t}$ -2,4,6 and SiPh₃), 7.44 (m, 9 H, *o*- and *p*-H of SiPh₃); ³¹P, δ –132 (J_{P-H} 220 Hz). $(Ph_3Si)P(C_6H_2Pr_3^i-2,4,6)H$ 8: m.p. 120–127 °C. NMR (C_6D_6) : ¹H, δ 0.98 [d, 6 H, o- or p-CH(CH₃)₂], 1.09 [d, 6 H, o- or p-CH(CH₃)₂], 1.29 [d, 6 H, o- or p-CH(CH₃)₂], 2.83 [spt, 1 H, p-CH(CH₃)₂], 3.52 [spt, 2 H, o-CH(CH₃)₂], 4.44 (d, 1 H, P-H), 7.18 (m, 8 H, *m*-H of $C_6H_2Pr_{3}^i$ -2,4,6 and SiPh₃) and 7.60 (m, 9 H, *o*- and *p*-H of SiPh₃); ³¹P, δ -169 (J_{P-H} 211 Hz). (Ph₃Si)P($C_6H_2Me_3$ -2,4,6)H **9**: m.p. 92–96 °C. NMR (C_6D_6): ¹H, δ 2.1 (s, 6 H, o-Me), 2.14 (s, 3 H, p-CH₃), 4.21 (d, 1 H, P-H), 7.2 (m, 8 H, m-H of C₆H₂Me₃-2,4,6 and SiPh₃), 7.61 (9 H, o- and p-H of SiPh₃); ³¹P, $\delta - 162$, $(J_{P-H} 210 \text{ Hz})$.

(Ph₃Si)P(SiMe₃)₂ 10. An Et₂O (20 cm³) solution of Ph₃SiCl (2.65 g, 9 mmol) was added dropwise at 0 °C to $(Me_3Si)_2$ -PLi-2thf (2.96 g, 9 mmol) in Et₂O (30 cm³). The solution was allowed to stir for 12 h. After removing all volatile materials, the residue was extracted with warm hexane (40 cm³) and filtered through Celite. Colourless crystals of the product separated from solution after cooling to -20 °C. Yield: 3.38 g, 86%; m.p. 97–99 °C. NMR (C₆D₆): ¹H, δ 0.254 (d, 18 H, SiMe₃, ³J_{P-H} 3.9 Hz), 7.10 (m, 6 H, Ph) and 7.88 (m, 9 H, Ph); ³¹P, δ - 254.

(Me₃Si)(Ph₃Si)PLi-dme 11. The detailed *in situ* preparation of 11 has been described earlier as part of the synthesis of 4. Recrystallization of the dme solvated 11 is possible from Et₂Ohexane (2:1) in $\approx 80\%$ yield. NMR (C₇D₈): ¹H, δ 0.274 (d, 9 H, SiMe₃), 2.97 (s, 6 H, OMe), 3.04 (s, 4 H, OCH₂), 7.21 (m, 6 H, Ph) and 7.98 (m, 9 H, Ph); ³¹P, δ -315.

Analytical data for the new complexes are given in Table 1.

X-Ray Data Collection and the Solution and Refinement of the Structures.—Crystallographic data for compounds 2, 5–7 and 10 are given in Table 2. Crystals of 2, 5–7 and 10 were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fibre by silicon grease and immediately placed in the low-temperature N_2 stream.¹⁷ X-ray data were collected with Siemens R3 m/V and Syntex P2₁ diffractometers equipped with a graphite monochromator and a locally modified Enraf-Nonius low-temperature apparatus. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program system.¹⁸ Neutral atom scattering factors and the correction for anomalous dispersion were from ref. 19. The structures of all molecules were solved by direct methods. Atomic coordinates

Compound	2	5	6	7	10
Formula	C41H36GaPSi	C45H66AlOPSi	C11Hc1AsGaSi1	C36H45PSi	C24H33PSi3
М.	677.6	709	677.7	547.5	436.7
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P_1/c	РĪ	РĪ	$P2_1/c$	Pbca
a/Å	18,499(5)	9.488(3)	12.219(3)	17.710(6)	16.092(5)
b/Å	10.028(4)	11.416(5)	14.174(3)	16.635(5)	16.841(5)
c/Å	20.746(6)	20.383(6)	21.831(5)	10.838(4)	18.778(5)
$\alpha/^{o}$	90	92.07(3)	92.95(2)	90	90
β/°	90.45(2)	96.80(2)	99.73(2)	97.43(3)	90
$\gamma/^{\circ}$	90	103.17(3)	99.47(2)	90	90
\ddot{U}/\dot{A}	3848(2)	2127.2(16)	3663.7(15)	3166(2)	5089(3)
Z	4	2	4	4	8
$D_c/\mathrm{g}\mathrm{cm}^{-3}$	1.170	1.107	1.229	1.126	1.140
μ/mm^{-1}	0.813	0.145	1.765	0.147	0.257
20 range/°	0-55	0-50	0-55	055	0-55
Number of observed reflections	$5307 [I > 3\sigma(I)]$	$3921 [I > 2\sigma(I)]$	$11957[I > 2\sigma(I)]$	$5745 [I > 2\sigma(I)]$	$2843 [I > 2\sigma(I)]$
Number of variables	398	442	614	347	253
R, R'	0.043, 0.045	0.079, 0.086	0.053, 0.104	0.044, 0.043	0.050, 0.052

* All data were collected at 130 K with Mo-Ka radiation ($\lambda = 0.710$ 69 Å).



Fig. 1 Computer-generated thermal ellipsoid (30%) plot of compound 1. Hydrogen atoms are omitted for clarity

for 2, 5–7 and 10 are given in Table 3. An X-ray data set was also collected for 4, however, severe disorder problems were encountered. Nonetheless, the data could be refined sufficiently to show that the Ga–P distance was 2.358(4) Å, and $\Sigma^{\circ}P$ was *ca.* 326°. Furthermore, a value of *ca.* 76.5° was calculated for the angle between the perpendiculars to the GaC₂ and PSi₂ planes.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results

Structural Descriptions.—The structure of compound 1, shown in Fig. 1, was previously reported in a preliminary communication.⁶ The structural descriptions of 7 and 10 are considered together here owing to the similarity of their formulae whereas 2 is considered separately. The structures of 5



Fig. 2 Computer-generated thermal ellipsoid (30%) plot of compound 2. Hydrogen atoms are omitted for clarity

and 6 are also described. Selected structural parameters for 1, 2 and Bu_{2}^{t} GaP(Ph)B(C₆H₂Me₃-2,4,6) 12²⁰ are summarized in Table 4. Important structural parameters for 5–7 and 10 are represented in Table 5.

Bu¹₂GaP(C₆H₄Prⁱ₃-2,4,6)(SiPh₃) **2**. The structure of **2**, which is illustrated in Fig. 2, consists of well separated monomers. The co-ordination at the phosphorus centre is pyramidal and the sum of the interligand angles (Σ° P) at phosphorus is 340.5°. The angle between the bisectors of the C₂Ga and CSiP planes is 1.9°. The Ga–P bond length is 2.296(1) Å and the P–Si and Ga–C distances are 2.249(2) and 2.012 Å (av.). The co-ordination geometry at gallium is trigonal planar.

Bu¹₂Al(Et₂O)P(C₆H₂Pr¹₃-2,4,6)(SiPh₃) **5**. The molecular structure of **5**, which is represented in Fig. 3, contains phosphorus and aluminium centres with co-ordination numbers of three and four, respectively. The aluminium has distorted tetrahedral geometry with ligands that include $P(C_6H_2Pr^{1}_{3}-2,4,6)(SiPh_3)$, two *tert*-butyl groups and an Et₂O solvent molecule. The interligand angles at aluminium span the range 101.0(2) to 116.3(3)°, however, the sum of the angles between the two *tert*-butyl and phosphido groups is 341.7°. The sum of the angles at phosphorus ($\Sigma^{\circ}P = 351.6^{\circ}$) indicate a very flattened co-ordination. The Al-P bond length is 2.416(3) Å. The Al-O and Al-C distances are 1.950(6) and 2.021 Å (av.), respectively and the P-C(1) and P-Si bond lengths are 1.856(6) and 2.223(3) Å.

Bu¹₂GaAs[CH(SiMe₃)₂](SiPh₃) 6. There are two structurally similar monomeric gallium–arsenic molecules per asymmetric

z

2 515(2) 2 154(2) 2 798(2) 3 071(2) - 130(2) - 676(2)

-676(2) -1288(2) -1365(2) -829(2) -220(2) 1218(2)1881(2)

1 881(2) 2 257(2) 1 989(2) 1 340(2) 957(2) 608(2)

290(2) 176(2) 376(2) 704(2)

812(2)

2 781(3) 2 317(3) 2 396(3) 2 952(4) 3 431(4) 3 353(3) 3 389(3) 3 883(3) 4 380(4) 4 380(4) 4 411(4) 3 927(4) 3 436(3) 4 247(3) 4 063(3) 4 527(3) 4 813(3) 3 691(3) 4 223(3) 3 967(3) 3 089(3) 3 428(5) 3 374(5) 2 386(3) 1 875(3)

4 991(2)

4 921

4 465

4 078

4 1 4 7

4 603

6 193

6 291

5 918

5 722(2)

Compound 2						
Ga	8 211(1)	9 883(1)	1 930(1)	C(20)	7 745(2)	8 546(3)
Р	7 660(1)	10 408(1)	967(1)	C(21)	7 165(2)	7 756(4)
Si	6 484(1)	10 270(1)	693(1)	C(22)	8 298(2)	7 543(4)
C(1)	7 915(2)	12 142(3)	774(2)	C(23)	7 405(2)	9 326(4)
C(2)	8 285(2)	12 372(3)	190(2)	C(24)	6 435(2)	11 061(3)
C(3)	8 526(2)	13 660(3)	51(2)	C(25)	6 276(2)	10 299(4)
C(4)	8 403(2)	14 734(3)	459(2)	C(26)	6 231(2)	10 864(4)
C(5)	8 011(2)	14 491(3)	1 013(2)	C(27)	6 351(2)	12 225(4)
C(6)	7 759(2)	13 233(3)	1 178(2)	C(28)	6 511(2)	13 004(4)
C(7)	8 432(2)	11 253(3)	- 292(2)	C(29)	6 551(2)	12 435(3)
C(8)	9 130(2)	10 525(4)	- 129(2)	C(30)	5 787(2)	11 092(3)
C(9)	8 447(2)	11 723(4)	-991(2)	C(31)	5 739(2)	10 819(4)
C(10)	8 681(2)	16 132(4)	329(2)	C(32)	5 212(2)	11 399(5)
C(11)	8 684(3)	16 502(4)	- 384(2)	C(33)	4 726(2)	12 303(4)
C(12)	9 421(2)	16 312(5)	638(2)	C(34)	4 758(2)	12 577(4)
C(13)	7 317(2)	13 116(3)	1 798(2)	C(35)	5 276(2)	11 982(3)
C(14)	6 664(2)	14 044(3)	1 788(2)	C(36)	6 265(2)	8 450(3)
C(15)	7 788(2)	13 389(5)	2 395(2)	C(37)	6 738(2)	7 591(3)
C(16)	9 245(2)	10 473(4)	2 053(2)	C(38)	6 561(2)	6 268(3)
J(17)	9 695(2)	9 277(4)	1 830(2)	C(39)	5 902(2)	5 777(3)
J(18)	9 410(2)	10 719(4)	2 769(2)	C(40)	5 430(2)	6 593(3)
J(19)	9 471(2)	11 702(4)	1 676(2)	C(41)	5 607(2)	7 917(3)
Compound 5						
Р	2 087(2)	8 050(2)	2 584(1)	C(22)	4 370(6)	11 039(6)
Si	2 453(2)	10 046(2)	2 674(1)	C(23)	4 855(7)	11 857(6)
AI	2 351(2)	6 739(2)	3 471(1)	C(24)	6 276(7)	12 571(7)
)	2 936(5)	5 436(4)	3 011(2)	C(25)	7 226(7)	12 504(7)
(1)	2 622(6)	7 694(6)	1 767(3)	C(26)	6 762(7)	11 747(7)
C(2)	1 517(6)	7 172(6)	1 236(3)	C(27)	5 370(6)	11 012(6)
C(3)	1 857(6)	7 030(6)	610(3)	C(28)	1 512(6)	10 381(6)
2(4)	3 283(6)	7 369(6)	457(3)	C(29)	2 112(7)	11 319(7)
2(5)	4 383(6)	7 821(6)	984(3)	C(30)	1 346(9)	11 588(9)
(6)	4 083(6)	7 980(6)	1 622(3)	C(31)	- 76(9)	10 935(9)
<i>(</i> /)	-112(6)	6 772(6)	1 337(3)	C(32)	- 694(8)	9 988(8)
2(8)	776(7)	5 462(7)	1 079(4)	C(33)	77(7)	9 735(7)
2(9)	- 995(7)	7 594(7)	1 002(4)	C(34)	3 878(6)	7 430(6)
(10) (11)	3 621(7)	7 278(6)	-253(3)	C(35)	5 422(7)	/ 920(7)
J(11) Z(12)	4 600(9)	6 424(9)	- 545(4)	C(36)	3 396(7)	8 523(7)
J(12) J(12)	4 283(8)	8 501(7)	-484(3)	C(3/)	4 022(8)	0 393(7) 5 032(6)
J(15) T(14)	5 588(6)	8 4 <i>55</i> (6)	2 10/(3)	C(38)	340(7) 122(8)	5 952(b) 6 672(8)
2(14) 2(15)	0 U0U(7)	7.580(7)	2 577(5)	C(39)	- 132(8)	(8) (7) 0 0 (7)
2(12)	0 208(0)	9 440(6)	1 900(3)	C(40)	5U8(8)	4 07/(/)
-(10) -(17)	1 501(6)	10 349(0)	1 900(3)	C(41)	- 803(/)	5 /0/(/) 4 206(12)
-(1/) 	1 911(7)	10 391(0)	1 2/3(3)	C(42)	34/0(11)	4 370(13)
2(18) 2(10)	1 213(7)	10 803(/)	724(3)	C(43)	4 710(13)	4 040(12)
2(19) 2(20)	8/(8) 227(7)	11 53/(8)	/85(3) 1 208(4)	C(44)	2 002(8)	4 808(/)
C(20) C(21)	- 337(7) 367(6)	11 135(6)	1 955(3)	C(43)	2 910(8)	4 323(8)
Compound 6						
As(1)	2 018(1)	7 058(1)	1 302(1)	As (2)	8 370(1)	3 147(1)
Ga(1)	444(1)	7 796(1)	1 551(1)	Ga(2)	6 502(1)	2 724(1)
Si(1)	2 134(1)	7 583(1)	298(1)	Si(4)	7 949(1)	2 375(1)
Si(2)	4 742(1)	7 523(1)	1 824(1)	Si(5)	9 463(2)	3 098(1)
Si(3)	2 983(1)	7 247(1)	2 739(1)	Si(6)	10 775(1)	2 382(1)
C(4)	4 559	5 913	-616	C(35)	5 624(3)	2 494(2)
C(5)	4 670	6 906	-635	C(36)	4716	2 884
C(6)	3 957	7 403	- 361	C(37)	4910	3 718
2(1)	3 133	6 907	- 69	C(38)	6012	4 162
C(8)	3 048(3)	9 587(2)	657(1)	C(39)	6 920	3 773
C(9)	3 372	10 538	532	C(34)	6 726	2 939
C(10)	3 193	10 796	-81	C(41)	6 773(3)	600(2)

- 568 - 443

170

-733

-816

- 571

-242

-159

-404(2)

C(42)

C(43)

C(44)

C(45)

C(40)

C(40) C(47) C(48) C(49)

C(50)

6 392

6715

7 4 2 0

7 802

7 479

10 535

11 095

10710

9 590(3)

- 390

-955

-532

1 024

2 288

3 2 3 8

3 928

458

2 028(2)

10 103

9 1 5 2

8 894

5 955

6 6 2 6

7 574

7 852

7 182

6 234(2)

Table 3 Atomic coordinates ($\times 10^4$) for compounds 2, 5–7 and 10

y

x

z

Atom

x

y

Atom

C(11)

C(12)

C(7)

C(14)

C(15)

C(16)

C(17)

C(18)

C(13)

2 690

2 367

2 546

-850

- 89

630

- 1 569

-1188

250(2)

Table 3 (continued)

Atom	x	У	z	Atom	x	У	Ζ
C(19)	3 321(3)	7 694(3)	1 972(2)	C(51)	9 765	3 668	5 447
C(20)	5 255(4)	8 394(4)	1 278(3)	C(46)	9 205	2 718	5 349
C(21)	4 725(4)	6 276(4)	1481(2)	C(52)	9 356(4)	2 476(3)	3 324(2)
C(22)	5 853(5)	7 784(5)	2 552(3)	C(53)	8 090(7)	3 446(5)	2 234(3)
C(23)	3 320(5)	6 012(4)	2821(3)	C(54)	10 533(7)	4 215(5)	2 713(4)
C(24)	3 757(5)	8 104(4)	3421(3)	C(55)	9 792(7)	2 247(5)	1 974(3)
C(25)	1 446(4)	7 134(4)	2774(2)	C(56)	11 745(5)	2 038(6)	3 304(3)
C(25)	550(5)	9 200(3)	1 810(2)	C(57)	11 443(6)	3 557(6)	4 261(4)
C(27)	260(5)	9 670(4)	1 198(3)	C(58)	10 664(6)	1 406(6)	4 348(3)
C(27)	200(5)	9070(4) 0245(4)	1 1 20(3)	C(50)	5 508(5)	3 791(4)	3 054(3)
C(20)	-342(0) 1 724(5)	9 5 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3 - 3 -	2 222(3) 2 151(3)	C(60)	5570(3)	4 184(5)	2 409(3)
C(29)	1 724(3)	6 972(2)	1 421(3)	C(60)	4 402(5)	$\frac{10}{3}$	2 409(3)
C(30)	-1030(4)	5 005(A)	1 + 31(2) 1 122(2)	C(01)	6 107(6)	4 600(5)	3561(4)
C(31)	-911(3)	3 903(4) 7 200(4)	1152(3)	C(02)	5 967(6)	1 420(4)	3501(+)
C(32)	-192/(4)	7 290(4)	990(3)	C(03)	5 112(7)	1 420(4)	2 000(3)
C(33)	-1 440(5)	0 / 30(4)	2 052(5)	C(04)	5112(7)	1 320(3)	2032(3)
				C(65)	0 / 39(0)	803(4) 947(4)	2 313(3)
				C(66)	5 110(0)	84/(4)	3 0 /8(3)
Compound	d 7						
D	1.050(1)	120(1)	112(1)	C(18)	2 106(1)	1 850(1)	-1.176(2)
r S:	1 9 50(1)	150(1)	-113(1)	C(10)	2 190(1)	-1839(1)	-1170(2)
51	5 251(1)	1/4(1)	-9(1)	C(19)	3010(1)	-479(1)	-1210(2)
C(1)	1 597(1)	03(1) 790(1)	-1803(2)	C(20)	3330(1)	-369(1)	-2407(2)
C(2)	1 441(1)	/89(1)	- 2 498(2)	C(21)	3 333(1)	-932(1)	-3339(2)
C(3)	1 429(1)	/52(1)	- 3 /80(2)	C(22)	4 031(1)	-15/3(1)	-2982(2)
C(4)	1 491(1)	42(1)	-4 438(2)	C(23)	4 313(1)	-1 002(1)	-1/36(2)
C(5)	1 496(1)	-662(1)	-3759(2)	C(24)	4 101(1)	-1125(1)	-86/(2)
C(6)	1 534(1)	-682(1)	-2460(2)	C(25)	3 595(1)	1 235(1)	- 125(2)
C (7)	1 197(1)	1 595(1)	-1945(2)	C(26)	3 992(1)	1 484(1)	-1.088(2)
C(8)	1 843(1)	2 045(1)	-1165(2)	C(27)	4 183(1)	2 291(2)	-1216(2)
C(9)	544(1)	1 430(1)	-1156(2)	C(28)	3 977(1)	2 858(1)	- 394(2)
C(10)	861(1)	2 180(1)	-2 967(2)	C(29)	3 601(1)	2 623(1)	584(2)
C(11)	1 497(1)	65(1)	- 5 853(2)	C(30)	3 419(1)	1 821(1)	723(2)
C(12)	2 207(1)	527(1)	-6 142(2)	C(31)	3 628(1)	-244(1)	1 563(2)
C(13)	1 518(1)	- 776(1)	-6 414(2)	C(32)	4 289(1)	81(1)	2 225(2)
C(14)	778(1)	488(1)	-6 482(2)	C(33)	4 639(1)	-275(1)	3 308(2)
C(15)	1 445(1)	-1 520(1)	-1 852(2)	C(34)	4 334(1)	960(1)	3 760(2)
C(16)	1 161(1)	-2153(1)	-2 843(2)	C(35)	3 675(1)	-1 285(1)	3 143(2)
C(17)	825(1)	-1 484(1)	-978(2)	C(36)	3 330(1)	-930(1)	2 056(2)
C	110						
Compound	a IV 7 (81/1)	1 010/11	2 420(1)	0(11)	7 (00/2)	1 656(0)	6 602(2)
P	/ 681(1)	2 819(1)	3 4 3 9 (1)	C(11)	/ 609(3)	4 555(2)	5 503(2)
Si(1)	8 860(1)	3 144(1)	4 006(1)	C(12)	7770(2)	4 034(2)	4 946(2)
S1(2)	8 009(1)	2 446(1)	2 317(1)	C(13)	9 468(2)	2 294(2)	4 406(2)
Si(3)	7 181(1)	1 733(1)	3 995(1)	C(14)	9 535(2)	2 207(2)	5 136(3)
C(1)	9 510(2)	3 724(2)	3 352(2)	C(15)	9 961(3)	1 582(2)	5 453(3)
C(2)	10 282(2)	3 474(2)	3 094(2)	C(16)	10 351(2)	1 022(2)	5 027(3)
C(3)	10 708(2)	3 894(2)	2 582(3)	C(17)	10 296(2)	1 094(2)	4 297(3)
C(4)	10 381(3)	4 593(2)	2 315(2)	C(18)	9 863(2)	1 719(2)	3 991(2)
C(5)	9 632(3)	4 865(2)	2 573(2)	C(19)	8 1 1 0 (3)	3 378(3)	1 786(2)
C(6)	9 203(2)	4 432(2)	3 081(2)	C(20)	7 112(2)	1 854(3)	1 973(2)
C(7)	8 581(2)	3 839(2)	4 749(2)	C(21)	8 966(2)	1 846(2)	2 185(2)
C(8)	9 225(2)	4 202(2)	5 135(2)	C(22)	7 800(3)	813(2)	3 827(3)
C(9)	9 067(3)	4 717(2)	5 697(2)	C(23)	6 097(2)	1 586(2)	3 679(3)
C(10)	8 255(3)	4 889(2)	5 876(2)	C(24)	7 130(3)	1 957(3)	4 962(2)

unit, one of which is shown in Fig. 4. The co-ordination at the arsenic centres is quite pyramidal [$\Sigma^{\circ}As = 316^{\circ}$ (av.)] with average interligand angles of 113.4, 102.7 and 99.8°. The widest angles involve the very bulky SiPh₃ and CH(SiMe₃)₂ groups. There is also a large angle 70.6° (av.) between the bisectors of the C-As-Si and C-Ga-C planes. The co-ordination at gallium is distorted trigonal planar with angles that span the range 113.8(2)-124.8(2)°. The Ga-As and Ga-C bonds are 2.459 (av.) and 2.019 Å (av.) in length. The As-C and As-Si distances are 2.025 (av.) and 2.366 Å (av.), respectively.

 $(Ph_3Si)P(R)R'(R, R' = C_6H_2Bu'_3-2,4,6, H 7; SiMe_3, SiMe_3$ 10). The molecular structures of the asymmetrically substituted phosphine, 7, and trisilylphosphine, 10 are illustrated in Figs. 5 and 6. In both molecules the co-ordination at the phosphorus centres is strongly pyramidal. The sum of angles, $\Sigma^{\circ}P$, at phosphorus are 303.9° (7) and 321.3° (10). The P-Si bond lengths are P-Si 2.293(1) Å (7) and P-Si(1) 2.243(2) Å, P-Si(2) 2.261(2) Å and P-Si(3), 2.254(2) Å (10). In addition, the P-C and P-H distances for 7 are 1.863(2) and 1.199(22) Å, respectively.

Phosphorus-31 and Variable-temperature ¹H NMR Studies.— Table 6 presents the ³¹P NMR chemical shifts for compounds 1–5, 7–11 and other related species. The temperature dependence of the ¹H NMR spectra of 2–4 and 6–8 in the range + 100 to -100 °C was investigated in C₇D₈ solution. A similar study of 1, as previously communicated,⁶ indicated a splitting of the GaBu¹₂ singlet at low temperatures (see Fig. 7). A barrier of 12.7 kcal mol⁻¹ was estimated for the dynamic process. Energy barriers (ΔG^{\ddagger}) for the observed dynamic processes were Table 4 Selected bond distances (Å) and angles (°) for compounds Bu'2GaPRR' 1, 2 and 12"

	1	2	12
Ga-P	2.295(3)	2.296(1)	2.319(1)
P-R "	2.259(4)	2.249(2)	1.838(3)
P-R'*	1.890(8)	1.847(3)	1.820(3)
Ga-C	2.014(11)	2.008(4)	2.012(3)
	2.015(11)	2.016(4)	2.005(3)
R-P-R'	108.6(3)	104.6(1)	116.0(1)
Ga-P-R	125.3(1)	128.9(1)	117.3(1)
Ga-P-R'	112.5(3)	107.0(1)	110.9(1)
C-Ga-C	119.1(4)	122.0(1)	126.7(1)
C–Ga–P	121.2(3)	119.3(1)	116.6(1)
	112.5(3)	117.2(1)	115.8(1)
Sum of angles at phosphorus ($\Sigma^{\circ}P$)	346.4	340.5	344.2
Twist angle ^b	3.9	1.9	56.4

^a R,R' = SiPh₃, C₆H₂Bu'₃-2,4,6 1; SiPh₃, C₆H₂Pr'₃-2,4,6 2; B(C₆H₂-Me₃-2,4,6)₂, Ph 12. ^b Defined as the angles between the perpendiculars to the R-P-R' and C-Ga-C planes when viewed along the Ga-P bonds.

Table 5 Selected bond distances (Å) and angles (°) for compounds 5-7 and 10

Compour	Ы	5
Compoun	u	

Compound 5			
P-Al	2.416(3)	Si-P-Al	126.9(1)
P-Si	2.223(3)	Si-P-C(1)	105.3(2)
Si-C(16)	1.887(6)	AI - P - C(1)	119.4(2)
Si - C(22)	1.894(6)	P-Al-O	101.0(2)
Si-C(28)	1.869(7)	P-AI-C(34)	116.4(2)
A1-0	1.950(6)	P = A1 = C(38)	109.0(2)
$A_{1-C(34)}$	2 017(6)	C(34) - A = C(38)	116 3(3)
$A_{1-C(38)}$	2.017(0)	$\Omega_{-A} = C(34)$	109 2(3)
/	2.025(0)	O = A I = C(38)	102.9(2)
		0 /11 0(50)	102.7(2)
Compound 6			
As(1)-Ga(1)	2.458(1)	Si(4)-C(46)	1.906(3)
As(1)-Si(1)	2.371(1)	Si(5)-C(52)	1.892(5)
As(1)-C(19)	2.022(4)	Si(6)-C(52)	1.906(5)
Ga(1)-C(26)	2.019(5)		
Ga(1)-C(30)	2.019(4)	Ga(1) - As(1) - Si(1)	100.9(1)
Si(1)-C(1)	1.920(4)	Ga(1) - As(1) - C(19)	102.7(1)
Si(1)-C(7)	1.891(3)	Si(1) - As(1) - C(19)	113.7(1)
Si(1)-C(13)	1 916(3)	$A_{s(1)}-G_{a(1)}-C_{a(2)}$	124.8(2)
Si(2) - C(19)	1.870(5)	$A_{s(1)}-G_{a(1)}-C_{a(1)}$	113 8(2)
Si(2) - C(19)	1.907(5)	C(26)-Ga(1)-C(30)	121.4(2)
$A_{s}(2) - G_{a}(2)$	2461(1)	$G_{2}(2) - A_{2}(2) - Si(4)$	98 8(1)
$A_{s(2)} = Si(4)$	2.362(2)	Ga(2) - As(2) - C(52)	102 7(1)
$A_{s}(2) - C(52)$	2.002(2)	$Si(4) - A_{S}(2) - C(52)$	113 2(1)
$G_{2}(2) - C(52)$	2.020(5)	$A_{s}(2) - G_{a}(2) - C(59)$	114 7(1)
$G_{2}(2) - C(63)$	2.012(0) 2.026(5)	$A_{s}(2) - G_{a}(2) - C(5)$	124 7(2)
Si(4) - C(34)	1.910(4)	C(59)-Ga(2)-C(63)	120.6(2)
Si(4) = C(34) Si(4) = C(40)	1.910(4)	C(3)) Gu(2) C(3)	120.0(2)
51(4)-C(40)	1.077(3)		
Compound 7			
PSi	2.293(1)	Si-P-C(1)	104.9(1)
\mathbf{P} - $\mathbf{C}(1)$	1.863(2)	Si-P-H	93(1)
P-H	1.199(22)	C(1)-P-H	106(1)
Si-C(19)	1.874(2)	P-Si-C(19)	112.1(1)
Si-C(25)	1.876(2)	P-Si-C(25)	111.10)
Si - C(31)	1.881(2)	P-Si-C(31)	105.6(1)
5. 0(51)			
Compound 10	i -		
P-Si(1)	2.243(2)	Si(1)-P-Si(2)	108.2(1)
PSi(2)	2.261(2)	Si(1)-P-Si(3)	106.3(1)
P-Si(3)	2.254(2)	Si(2)P-Si(3)	106.8(1)
Si(1)-C(1)	1.887(4)	P-Si(1)-C(1)	106.6(1)
Si(1)-C(7)	1.876(4)	P-Si(1)-C(7)	107.7(1)
Si(1)-C(13)	1.890(4)	P-Si(1)-C(13)	116.2(1)

calculated by using an approximate formula as previously described.²¹ For 2, overlap of the o-CH(CH₃)₂ and GaBu¹₂ resonances in the above temperature range prevented a useful



Fig. 3 Computer-generated thermal ellipsoid (30%) plot of compound 5. Hydrogen atoms are omitted for clarity



Fig. 4 Computer-generated thermal ellipsoid (30%) plot of compound 6. Hydrogen atoms are omitted for clarity

interpretation of the dynamic behaviour. For the species 3, 4 and 6 all signals were well separated and splitting of the GaBu¹₂ singlet was not observed at temperatures as low as -100 °C. In fact no dynamic behaviour involving the other resonances in the species 3, 4 and 6 was observed. In the case of 7, at 25 °C, broad and sharp o-Bu^t and p-Bu^t singlets, respectively, were observed. Cooling the sample resulted in splitting of the o-Bu^t peak into two signals. Taking a T_c of 15 °C and a maximum peak separation of 57 Hz at -80 °C gives a barrier of 14.1 kcal mol⁻¹ for this dynamic process. For the C₆H₂Prⁱ₃-2,4,6 analogue 8, two well resolved sets of doublets were observed for the o- $CH(CH_3)_2$ protons at 25 °C. Upon increasing the temperature, the doublets broadened and coalescence of both sets of peaks was observed at $T_c = 75$ °C (Fig. 8). This T_c , along with a maximum peak separation of 83.4 Hz at 25 °C, gives a barrier (ΔG^{\ddagger}) of ca. 16.9 kcal mol⁻¹ for the dynamic process. Decreasing the temperature resulted in broadening of both o- $CH(CH_3)_2$ and $o-CH(CH_3)_2$ resonances. The $o-CH(CH_3)_2$ doublets appear to merge into a broad singlet and below -70 °C resolve into two or more broad singlets. In the case of the o-CH(CH₃)₂ septet, splitting into two broad peaks at $T_c =$ -65 °C was observed becoming sharper as the temperature is decreased. Taking this T_c and a peak separation of 243 Hz at -90 °C gives a ΔG^{\ddagger} of 9.43 kcal mol⁻¹. Singlets were observed for the mesityl o- and p-Me and m-H hydrogens of $(Ph_3Si)P(C_6H_2Me_3-2,4,6)H9$ at ambient temperature. Cooling of 9 in $[{}^{2}H_{8}]$ toluene caused a splitting of both the o-Me and m-H resonances. The approximate coalescence temperatures and peak separations (at -98 °C) of -80 °C and 104 Hz (o-Me)

 Table 6
 Phosphorus-31 NMR chemical shift values for 1-5, 7-11 and other related compounds

Compound	δ(³¹ P) ^{<i>a</i>}
$1 Bu'_{2}GaP(C_{6}H_{4}Bu'_{3}-2,4,6)(SiPh_{3})$	-119
2 $Bu_{2}^{1}GaP(C_{6}H_{2}Pr_{3}^{1}-2,4,6)(SiPh_{3})$	-146
$3 Bu'_{2}GaP(C_{6}H_{2}Me_{3}-2,4,6)(SiPh_{3})^{b}$	-141
4 Bu ¹ ₂ GaP(SiMe ₃)(SiPh ₃)	-267
5 $Bu_{3}^{i}Al(Et_{2}O)P(C_{6}H_{2}Pr_{3}^{i}-2,4,6)(SiPh_{3})$	- 199
7 (Ph ₃ Si)P($C_6H_2Bu_3^t$ -2,4,6)H	-132 (¹ J _{PH} 220 Hz)
8 (Ph ₃ Si)P(C ₆ H ₂ Pr ⁱ ₃ -2,4,6)H	—169 (¹ J _{PH} 211 Hz)
9 (Ph ₃ Si)P($C_6H_2Me_3-2,4,6$)H	$-162 (^{1}J_{PH} 210 \text{ Hz})$
10 $(Ph_3Si)P(SiMe_3)_2$	-254
11 (Me ₂ Si)(Ph ₂ Si)PLi·dme ^b	-315
$Bu^{t}Ga[PH(C_{\epsilon}H_{2}Bu^{t}_{3}-2.4.6)_{2}]$	$-113 (^{1}J_{PH} 203 \text{ Hz})^{22}$
$Ga[PH(C_6H_2Bu'_3-2,4,6)_2]_3$	$-91.6 ({}^{1}J_{PH} 216 \text{ Hz})^{22}$

^a Referenced externally to 85% H₃PO₄; in C₆D₆ unless otherwise stated. ^b In C₇D₈.



Fig. 5 Computer-generated thermal ellipsoid (30%) plot of compound 7. Hydrogen atoms except for the phosphorus hydrogen are omitted for clarity



Fig. 6 Computer-generated thermal ellipsoid (30%) plot of compound 10. Hydrogen atoms are omitted for clarity

and -90 °C and 47.1 Hz (*m*-H) afforded similar barriers of 9.05 and 8.85 kcal mol⁻¹, respectively.

Discussion

Syntheses.—The high yield syntheses of the bulky arylsilylphosphines 7–9 was accomplished in Et₂O solution by a saltelimination reaction between the primary phosphide LiPHR ($R = C_6H_2Bu_3^{-2}$ -2,4,6, $C_6H_2Pr_3^{i}$ -2,4,6 or $C_6H_2Me_3$ -2,4,6) and



Fig. 7 Variable-temperature ¹H NMR study (-50 to +25 °C) of Bu'₂GaP(C₆H₂Bu'₃-2,4,6)(SiPh₃) 1



Fig. 8 Variable-temperature ¹H NMR study (-90 to +90 °C) of $(Ph_3Si)P(C_6H_2Pri_3^{-2},4,6)H 8$

 $Ph_3SiCl.$ A similar method was used to synthesize the asymmetric arsine $(Ph_3Si)As[CH(SiMe_3)_2]H$ used in the preparation of the monomeric arsinogallane 6. The synthetic route to the disilylphosphide $(Me_3Si)(Ph_3Si)PLi$ -dme 11, was not as straightforward as illustrated by equations (1) and (2).

$$(Me_{3}Si)_{2}PLi \cdot 2thf + Ph_{3}SiCl \xrightarrow{Et_{2O, -LiCl}}_{0 \circ C}$$

$$(Ph_{3}Si)P(SiMe_{3})_{2} \quad (1)$$

$$(Ph_{3}Si)P(SiMe_{3})_{2} + LiMe \xrightarrow[-10^{\circ}C]{} (Me_{3}Si)(Ph_{3}Si)PLi \cdot dme \quad (2)$$

The first step involved treatment of $(Me_3Si)_2PLi$ 2thb with Ph_3SiCl to give $(Ph_3Si)P(SiMe_3)_2$ 10 [equation (1)] followed by the addition of methyllithium to 10 in dme to yield the asymmetric lithium salt of 10 [equation (2)]. The phosphino-gallanes 1–4, and arsenogallane 6, and the aluminium phosphide 5 were also prepared by salt-elimination reaction as shown in equation (3), where M = Ga or Al, E = P or As, R = bulky aryl, alkyl or silyl group. In the case of 5 (M = Al,

 $MBu_{2}^{t}Cl + Li(Ph_{3}Si)E(R) \xrightarrow{Et_{2}O, -LiCl}{0 \circ C}$

$$Bu_{2}^{t}ME(R)(SiPh_{3})$$
 (3)

E = P), the greater Lewis acidity of Al as compared to Ga results in a stable Et_2O adduct.

Structures.—The series of compounds 1–3 represent the first well characterized examples of unassociated monophosphinogallanes. In these compounds any possible π interaction between the gallium and phosphorus is confined to one bond. Thus these simple molecular Ga–P species allow the strength of the Ga–P π interaction to be more easily assessed. Structural and spectroscopic evidence for moderately strong π bonding in boron-nitrogen and -phosphorus R₂BE(R')R" (E = N and P) analogues of 1–3 has been previously observed.^{1,2,9} Manifestations of π bonding include B–E bond shortening and low angles between the lone pair on nitrogen or phosphorus and the empty 2p orbital on boron. In addition, barriers to rotation around the B–E bonds as high as 25 kcal mol⁻¹ have been reported.^{9,22}

Perhaps the most interesting aspect of the data in Table 4 is the correlation between Ga-P bond length and twist angle between the lone pair of phosphorus and the empty p orbital of gallium. For example, when the twist angles are less than 4°, as in 1 and 2, the Ga-P bonds are 2.295(1) and 2.296(1) Å. This trend also extends to the partially refined structure of 4 in which the Ga-P bond length is 2.358(4) Å and the twist angle is 76.5° It is also noteworthy that in spite of the large substituents in 1 and 2 the Ga-P distances are at the lower end of the currently known range for Ga-P single bonds.*.23 If the Ga-P bond were purely of a σ type, steric interactions could have been reduced by a rotation of the gallium and phosphorus ligand sets with respect to each other. It is therefore probable that there is a weak π interaction in the Ga-P bond. An analysis of various other structural details of 1, 2 and 4 supports this view. The change in the Ga-P distance between 1, 2 (both ca. 2.295 Å) and the partially refined 4 [2.358(4) Å] may be due either to the presence of a Ga–P π bond or a change in hybridization at phosphorus or both. Unfortunately, the relatively small (0.063 A) range of the Ga-P distances in 1, 2 and 4 makes the distinction between the effects of σ and π bonding difficult to assess. It is notable, however, that the difference between P-Si distances in 1 [2.259(4) Å] and that in its precursor 7 [2.293(1) Å] is 0.034 Å. The P-C distance in 1 [1.890(8) Å] is actually longer (presumably for steric reasons) than that observed in 7 [1.863(2) Å]. It appears, therefore, that as a result of σ -bonding changes a shortening of only 0.034 Å is expected in the Ga-P bond in this system. The actual difference observed between the Ga-P bonds in 1 and 4 is 0.063 Å. In addition, if it is borne in mind that the ligand set $(C_6H_2Bu_3^{\prime}-2,4,6 \text{ and } SiPh_3)$ on phosphorus in 1 is also more crowding than that (SiMe₃ and $SiPh_3$) in 4, it seems reasonable to conclude that the bond distances observed in 1 are indicative of weak π bonding. The weakness of this π interaction is apparent from a comparison with the structure $Bu_2^tGaP(Ph)B(C_6H_2Me_3-2,4,6)_2$ 12.²⁰ In this compound competition exists between the empty boron and gallium p orbitals for a share of the single phosphorus lone pair. In 12, the Ga-P distance is 2.319(1) Å and the angle between the planes at gallium and phosphorus is 56.4°. These values lie between those of 1, 2 and 4. In contrast, the B-P bond, 1.838(3) Å in 12 is relatively short and the angle between the boronphosphorus p orbitals is less than 10°. In other words, the π bonding in 12 is dominated by a B-P rather than a Ga-P interaction.

The structures of the bulky phosphines $(Ph_3Si)P(C_6H_2Bu'_3-2,4,6)H$ 7 and $(Ph_3Si)P(SiMe_3)_2$ 10 were determined to

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investigate bond lengths (i.e. P-Si and P-C) and geometry around the phosphorus centres in the absence of the GaBu¹₂ ligand. To our knowledge, 10 represents the first X-ray crystal structure of a trisilylphosphine. The sum of angles around the phosphorus atoms in both 7 and 10, 303.9 and 321.3°, indicate strongly pyramidal co-ordination at phosphorus. In the case of the trisilyl species 10, a more planar phosphorus co-ordination might have been expected since it is well known that silvl substituents reduce the inversion barrier at phosphorus by ca. 42, 37 and 25% for each successive substitution.⁸ The sum of angles at phosphorus for 7 lies below, and those of 10 between, those in the structures of PPh₃ ($\Sigma^{\circ}P = 310^{\circ}$)²⁴ and P(C₆H₂- $Me_3-2,4,6)_3$ ($\Sigma^{\circ}P = 329^{\circ}$).²⁵ A comparison of the structures of 4 and 10 supports the conclusions drawn from the discussion of the structures of 1 and 7 in the preceding paragraph. In the case of 4 and 10, the pyramidicities at the phosphorus atoms differ only slightly (326.2 vs. 321.3°) and only small differences (0.02 Å) are observed in the P-Si distances. Presumably, the similar size of the SiMe₃ and GaBut₂ ligands along with the absence of a Ga-P π interaction in 4 account for the structural similarity.

The compound $Bu_{2}^{i}Al(Et_{2}O)P(C_{6}H_{2}Pr_{3}^{i}-2,4,6)(SiPh_{3})$ 5 was obtained during attempts to synthesize aluminiumphosphorus analogues of 1-4. These species, successfully prepared, would also have represented a new class of Al-P compounds. The structure of 5, in contrast to those of 1-4, contains an Et₂O molecule bound to the aluminium centre. This result is in harmony with the greater size and higher Lewis acidity of aluminium in comparison to gallium. The molecule of 5, however, has some interesting features. One is that the geometry at phosphorus is almost flat and approaches planarity $(\Sigma^{\circ}P = 351.6^{\circ})$. Presumably, this is a consequence of steric crowding and the electropositive nature of aluminium and the silyl substituents. Furthermore, the Al-P bond length, 2.416(3) Å, although ≈ 0.06 Å shorter than that seen in the dimeric species (Ph₂PAlBuⁱ₂)₂ [2.476(1) Å],²⁶ is comparable to Al-P in the cubane, $[Bu'Al(\mu_3-PSiPh_3)]_4$ [2.414 Å (av.)].²⁷ The Al–O bond [1.950(6) Å] in 5 is slightly longer than those of other ether adducts of aluminium, $(PhH_2C)_3Al \cdot OEt_2$ [1.901(4) Å]²⁸ and $(C_6H_4Me-o)_3Al \cdot OEt_2$ [1.928(3) Å].²⁹ Presumably, this lengthening is also a consequence of the greater crowding at aluminium in 5.

The structure of 6 was determined to allow direct structural comparisons between phosphorus and arsenic in compounds of similar formulae to 1-4. Attempts to make a phosphorus analogue of 6 have proved unsuccessful so far. Well characterized monomeric arsinogallanes in the species $Bu_2^tGaAsBu_2^t$ 13 [Ga-As 2.466(3) Å, $\Sigma^{\circ}As \approx 317^{\circ}$]³⁰ and (C₅Me₅)₂GaAs-(SiMe₃)₂ 14 [Ga-As 2.433(4) Å, $\Sigma^{\circ}As \approx 320^{\circ}$]³¹ have already appeared in the literature. Compound 6, however, is the first structurally characterized monomeric arsinogallane in which arsenic is asymmetrically substituted. This permits measurement of restricted rotation around the Ga-As bond by variabletemperature ¹H NMR methods (see below). The structure of 6, however, is similar to those previously reported. The Ga-As single bond distance of 2.459 Å (av.) is comparable with the sum of covalent radii of Ga and As.^{32,*} As for 13 and 14, the coordination at arsenic is strongly pyramidal [$\Sigma^{\circ}As = 316^{\circ} (av.)$] and the twist angle between the lone pair of arsenic and the empty p orbital of Ga is high, 70.6° (av.). These structural parameters suggest that the Ga-As bond is a simple σ bond with no π component.

NMR Studies.—A common feature of all Ga–P compounds listed in Table 6 is their upfield ³¹P chemical shift. This is in sharp contrast to their boron–phosphorus analogues which have positive δ values. The more negative δ values of the gallium derivatives may be attributed to higher electron density on the phosphorus centre owing to the presence of the electropositive silyl and gallyl substituents. The weakness of Ga–P π bonding suggests that the phosphorus lone pair electron density remains

^{*} For example Ga-P = 2.34(1) Å in Ga[PH(C₆H₂Bu'₃-2,4,6)]₃ and 2.32 Å in Bu'Ga[PH(C₆H₂Bu'₃-2,4,6)]₂.

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located on phosphorus. Presumably, this also contributes to the upfield chemical shift. The large negative δ values observed for 4, 10 and 11 are due to the increased number of electropositive ligands (i.e. SiR_3 , $GaBu_2^t$ or Li^+) at phosphorus. Two opposing factors account for the intermediate ³¹P shift of 5; removal of electron density at phosphorus by rehybridization of the lone pair orbital from s to p character and electron donation to phosphorus through the Al-P σ bond. As expected, species with more planar phosphorus co-ordination in the series 1-3 and corresponding ligands 7-9 have the most downfield ³¹P chemical shifts. The $J_{\rm PH}$ coupling constants of 7–9 also support this correlation. A larger $J_{\rm PH}$ (7) corresponds to greater s character in the phosphorus bonding orbital to hydrogen. The shifts and coupling constants of 2 and 3, and 8 and 9 suggest similar environments at the phosphorus centres.

A variable-temperature ¹H NMR study was undertaken to investigate the strength of possible Ga-P multiple bonding in 2-4. A similar study of 1 was reported in a preliminary communication.⁶ In this case a barrier of 12.7 kcal mol⁻¹ to rotation around the Ga-P bond was observed. The variabletemperature ¹H NMR study of 2 was inconclusive owing to peak overlap, and splitting of the GaBut₂ singlet for 3 and 4 was not observed at temperatures as low as -100 °C. Therefore, the upper limit on Ga-P π bonding in 3 and 4 (taking a T_c of -100 °C) is probably not greater than 8-9 kcal mol⁻¹. In the case of 4, this data is consistent with structural evidence which suggests insignificant Ga-P p-p π overlap. It is also compatible with the structural differences observed in 1 and the larger barrier (12.7 kcal mol⁻¹) to rotation around the Ga-P bond. The variable-temperature ¹H NMR studies of the precursor phosphines 7-9 were undertaken to assess barriers to inversion of these new and sterically bulky asymmetric phosphines. Typically, inversion barriers have been measured by observing the temperature dependence of magnetically inequivalent diastereotopic groups such as the methyls of a prochiral ligand [*i.e.* $R(R')PCHMe_2$].† These groups become enantiotopic when inversion is fast on the NMR time-scale and coalescence is usually observed. In the compounds 7-9 (Ph₃Si)P(C₆H₂R₃-2,4,6)H (R = Bu^t 7, Prⁱ 8 or Me 9) the o-R groups have in effect the same function as the diastereotopic groups described above and may exhibit magnetic inequivalence even in the presence of fast P-C(aryl) bond rotation. The ¹H NMR data for 8 indicate the presence of two temperature-dependent processes that have barriers of ca. 9.43 and 16.9 kcal mol⁻¹. These two processes may be assigned to either inversion barrier at phosphorus or to aromatic ring flip. The latter is also a possibility since variabletemperature ¹H NMR studies of arylboryloxides such as $B(OMe)(C_6H_2Me_3-2,4,6)_2$ have given barriers as high as 12 which were assigned to ring flip of the mesityl kcal mol⁻¹ groups.³⁵ We note, however, that inversion barriers for the monosilylphosphines PhP(SiMe₃)CHMe₂ and Ph(Me)P-(SiPhMe₂) are *ca.* 19 kcal mol^{-1.36} This value is more consistent with the larger barrier detected for 8. Moreover, the larger value observed for 7 (14.2 kcal mol^{-1}), is in harmony with this result because of the greater steric crowding in 7. The barrier observed in the case of 9 is very similar to that in 8.

Acknowledgements

We thank the National Science Foundation for financial support.

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Received 6th November 1992; Paper 2/05925H

^{*} The radius of gallium is difficult to estimate owing to the complicated structure of the element itself.33

[†] For theoretical discussions and/or inversion barrier determinations at Group 15 elements see ref. 34.