Mono- and Di-nuclear Phosphido and Arsenido Complexes of Gallium; $Ga(EBu^t_2)_3$, $Ga[PH(2,4,6\text{-}Bu^t_3C_6H_2)]_3$ and $[Ga(\mu\text{-}EBu^t_2)R_2]_2$, (E = P, As; R = Me, Bu^n)†

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The reaction of $GaCl_3$ with three equivalents of Bu^t_2PLi, Bu^t_2AsLi, or ArP(H)Li (Ar = 2,4,6-$Bu^t_3C_6H_2$) affords $Ga(PBu^t_2)_3$, $Ga(AsBu^t_2)_3$, and $Ga[P(H)Ar]_3$, respectively, whilst the reaction of $GaCl_3$ with one equivalent of Bu^t_2ELi and two equivalents of RLi results in dimeric phosphido- or arsenido-bridged compounds of the type $[Ga(\mu\text{-}EBu^t_2)R_2]_2$ (E = P, As; R = Me, Bu^n).

Despite their potential importance as precursors to semiconductors such as gallium arsenide and indium phosphide, relatively little is known about compounds featuring bonding between the heavier group 13 and 15 (Ölander numbering) elements.[1] Pioneering work by Coates *et al.* revealed that secondary phosphines and arsines undergo thermal reactions with Me_3Ga or Me_3In to afford materials of composition $(Me_2MER_2)_n$, (M = Ga, In; E = P, As).[2,3] However, no structural information is available for these compounds. More recently, Wells *et al.* have reported a novel gallium–arsenic cluster.[4] We report here (i) synthesis of the first per-(dialkylphosphido) and -(dialkylarsenido) compounds of gallium, (ii) synthesis of the first primary phosphido compound of gallium, and (iii) the first structural information on dialkylphosphido- and dialkylarsenido-bridged gallium dimers.

The use of bulky Bu^t substituents permits the isolation of monomeric perphosphido and perarsenido gallium compounds. Thus, treatment of $GaCl_3$ with 3 equivalents of Bu^t_2ELi (E = P, As) in toluene or tetrahydrofuran (THF) at −78 °C results in high yields of $Ga(PBu^t_2)_3$, (**1a**), and $Ga(AsBu^t_2)_3$, (**1b**), as red, air-sensitive, crystalline solids, equation (1). So far, we have not obtained crystals suitable for *X*-ray diffraction studies. Accordingly, the identification of (**1a**) and (**1b**) is based on spectroscopic and analytical data.‡ Thus, the 70 eV electron impact mass spectrum (e.i.m.s.) of (**1a**) exhibits apparent peak at *m/z* 504 and a fragmentation indicative of the sequential loss of Bu^t and PBu^t_2 moieties. The e.i.m.s. of (**1b**) is very similar to that of (**1a**); however, in this case, the highest *m/z* peak (579) corresponds to $M^+ - Bu^t$.

The primary phosphido compound, $Ga[P(H)Ar]_3$, (**2**) (Ar = 2,4,6-$Bu^t_3C_6H_2$) can be prepared in a similar fashion to (**1a, b**) using ArP(H)Li in place of Bu^t_2PLi, equation (2). The

† Since the submission of this work $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$ has been reported: C. G. Pitt, A. P. Purdy, K. T. Higa, and R. L. Wells, *Organometallics*, 1986, **5**, 1266.

‡ Satisfactory chemical analyses were obtained for all new compounds. Compound (**1a**) ^1H n.m.r. (C_6D_6, 360 MHz, ambient temperature) δ 1.55 (d, $^3J_{PH}$ 12 Hz); $^{31}P\{^1H\}$ n.m.r. (C_6D_6, 32.2 MHz, ambient temperature) δ 54.8 (s). Compound (**1b**) ^1H n.m.r. (C_6D_6, 90 MHz, ambient temperature) δ 1.15 (s). Compound (**2**) ^1H n.m.r. (C_6D_6, 90 MHz, ambient temperature) δ 1.38 (9H, s, *para* Bu^t), 1.58 (18H, s, *ortho* Bu^t), 4.05 (1H, d, $^1J_{PH}$ 216 Hz, PH), 7.48 (2H, s, CH); ^{31}P n.m.r. (C_6D_6, 32.2 MHz, ambient temperature), δ −91.6 (d, $^1J_{PH}$ 215.6 Hz). Compound (**3a**) ^1H n.m.r. (C_6D_6, 90 MHz, ambient temperature) δ 0.28 (12H, t, $^3J_{PH}$ 3 Hz, GaMe), 1.29 (36H, t, $^3J_{PH}$ 6 Hz, Bu^t_2P); $^{31}P\{^1H\}$ n.m.r. (C_6D_6, 32.2 MHz, ambient temperature) δ 28.4 (s). Compound (**3b**) ^1H n.m.r. (C_6D_6, 360 MHz, ambient temperature) δ 1.06 (20H, m), 1.60 (8H, m) 1.74 (8H, m) (all Bu^n), 1.40 (36H, t, $^3J_{PH}$ 6 Hz, Bu^t_2P); $^{31}P\{^1H\}$ n.m.r. (C_6D_6, 32.2 MHz, ambient temperature) δ 32.9 (s). Compound (**4a**) ^1H n.m.r. (C_6D_6, 90 MHz, ambient temperature) δ 0.30 (12H, s, GaMe), 1.40 (36H, s, Bu^t_2As). Compound (**4b**) ^1H n.m.r. (C_6D_6, ambient temperature) δ 1.04—1.06 (20H, m), 1.57 (8H, m), 1.71 (8H, m) (all Bu^n), 1.40 (36H, s, Bu^t_2As).

$$GaCl_3 + 3Bu^t_2ELi \xrightarrow[-78\ ^\circ C]{\text{Toluene or THF}} Ga(EBu^t_2)_3 + 3LiCl \quad (1)$$

(**1a**) E = P

(**1b**) E = As

$$GaCl_3 + 3ArP(H)Li \xrightarrow[-78\ ^\circ C]{\text{Toluene or THF}} Ga[P(H)Ar]_3 + 3LiCl \quad (2)$$

(**2**) Ar = 2,4,6-$Bu^t_3C_6H_2$

$$2GaCl_3 + 2Bu^t_2ELi + 4RLi \xrightarrow[-78\ ^\circ C]{\text{Toluene or THF}} R_2Ga(\mu\text{-}ER_2)_2GaR_2 + 4LiCl \quad (3)$$

(**3a**) E = P, R = Me (**4a**) E = As, R = Me

(**3b**) E = P, R = Bu^n (**4b**) E = As, R = Bu^n

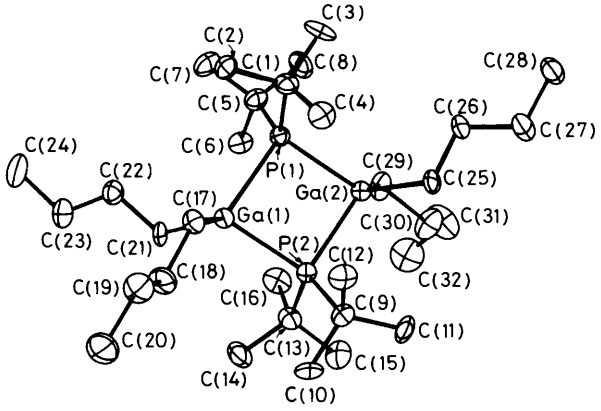

Figure 1. ORTEP view of (**3b**); key bond lengths (Å) and angles (°): Ga(1)–P(1) 2.477(5), Ga(1)–P(2) 2.476(4), Ga(2)–P(1) 2.468(4), Ga(2)–P(2) 2.483(5), Ga(1)–C(17) 2.018(15), Ga(1)–C(21) 2.030(15), P(1)–C(1) 1.92(2), P(1)–Ga(1)–P(2) 86.7(1), P(1)–Ga(2)–P(2) 86.7(2), Ga(1)–P(1)–Ga(2) 93.5(1), Ga(1)–P(2)–Ga(2) 93.1(2), P(1)–Ga(1)–C(17) 115.1(5), C(17)–Ga(1)–C(21) 107.0(6), C(1)–P(1)–C(5) 109.5(7). For (**4b**): As(1)–Ga(1) 2.552(3), As(1)–Ga(2) 2.548(3), As(2)–Ga(1) 2.551(2), As(2)–Ga(2) 2.557(3), Ga(1)–C(17) 2.02(2), As(1)–C(1) 2.06(2), Ga(1)–As(1)–Ga(2) 95.19(8), Ga(1)–As(2)–Ga(2) 94.96(8), As(1)–Ga(1)–As(2) 84.94(8), As(1)–Ga(2)–As(2) 84.91(8), As(1)–Ga(1)–C(17) 114.0(5), C(17)–Ga(1)–C(21) 110.9(7), C(1)–As(1)–C(5) 109.0(7).

e.i.m.s. of (**2**) revealed a parent peak at *m/z* 900 and peaks of significant intensity at *m/z* 623 and 346 corresponding to the loss of one and two ArPH groups respectively. The presence of ArPH groups was confirmed by n.m.r. spectroscopy.‡ *X*-Ray crystallographic studies of (**2**) have been hampered by poor crystal quality and ready solvent loss. Nevertheless, it was possible to discern the trigonal planar nature of the GaP_3

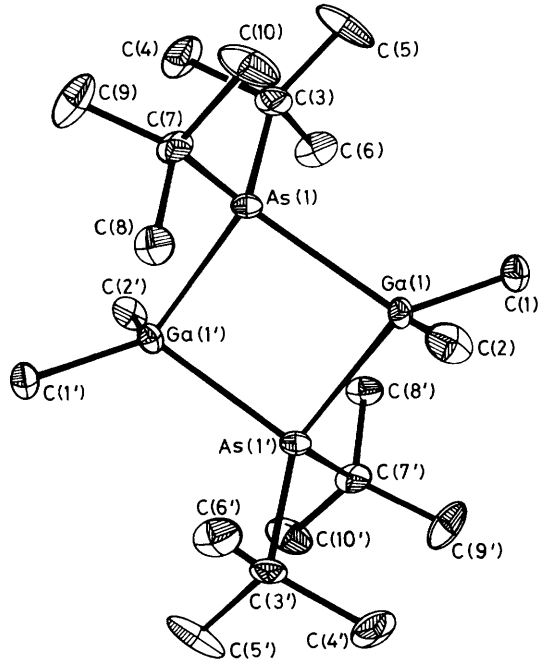

Figure 2. ORTEP view of (**4a**); key bond lengths (Å) and angles (°): As(1)–Ga(1) 2.541(1), As(1')–Ga(1) 2.558(1), Ga(1)–C(1) 2.016(5), Ga(1)–C(2) 2.028(5), As(1)–C(3), 2.046(5), Ga(1)–As(1)–Ga(1') 95.69(2), As(1)–Ga(1)–As(1') 84.31, As(1)–Ga(1)–C(1) 115.1(2), As(1)–Ga(1)–C(2) 116.2(2), C(1)–Ga(1)–C(2) 109.3(3), C(3)–As(1)–C(7) 110.3(2). For (**3a**): Ga(1)–P(1') 2.467 (5), Ga(1)–P(1) 2.481(3), Ga(1)–C(1) 2.024(10), Ga(1)–C(2) 2.016(11), P(1)–C(3) 1.910(9), Ga(1)–P(1)–Ga(1') 93.5(1), P(1)–Ga(1)–P(1') 86.5(1), P(1)–Ga(1)–C(1) 115.8(4), P(1)–Ga(1)–C(2) 116.8(4), C(1)–Ga(1)–C(2) 106.3(5), C(3)–P(1)–C(7) 111.1(5).

framework [av. Ga–P distance = 2.34(1) Å]. Similar skeletal geometries are proposed for (**1a**) and (**1b**).

The reaction of $GaCl_3$ with one equivalent of Bu^t_2ELi (E = P, As) and two equivalents of RLi(R = Me, Bu^n) in toluene or THF at −78 °C affords the dinuclear phosphido or arsenido bridged dimers [(**3**) and (**4**)] in good yields following evaporation to dryness and recrystallisation from hexane,‡ equation (3). Complexes (**3a**), (**3b**), (**4a**), and (**4b**) are colourless, crystalline materials which may be recrystallised from hexane. In the solid state they are stable in the air for long periods (24 h). Spectroscopic data‡ are in accord with the structures determined by single crystal *X*-ray diffraction studies.§

§ *Crystal data* for (**3a**): $C_{20}H_{48}Ga_2P_4$, M = 489.99, monoclinic, $C2/c$ (No. 15), a = 13.664(2), b = 12.828(2), c = 15.148(3) Å, β = 104.221(1)°, U = 2573.8(5) Å^3, D_c = 1.264 g cm^{-3}, Z = 4, μ = 22.11 cm^{-1}, number of reflections used = 1279 [$I > 3\sigma(I)$], (2259 unique measured), R = 0.0531, R_w = 0.0680. (**3b**): $C_{32}H_{72}Ga_2P_2$, M = 658.32, monoclinic, $P2_1/n$ (No. 1014), a = 8.888(4), b = 20.123(2), c = 21.693(4) Å, β = 95.555(3)°, U = 3861.4(5) Å^3, D_c = 1.132 g cm^{-3}, Z = 4, number of reflections used = 2018 [$I > 3\sigma(I)$], (5966 unique measured), R = 0.0595, R_w = 0.0688. (**4a**): $C_{20}H_{48}As_2Ga_2$, M = 577.89, monoclinic, $C2/c$ (No. 15), a = 13.856(2), b = 12.882(1), c = 15.356(3), β = 104.398(1)°, U = 2654.9(5) Å^3, D_c = 1.446 g cm^{-3}, Z = 4, μ = 44.95 cm^{-1}, number of reflections used = 1396 [$I > 3\sigma(I)$], (2081 unique measured), R = 0.0452, R_w = 0.0630. (**4b**): $C_{32}H_{72}As_2Ga_2$, M = 746.22, monoclinic, $P2_1/n$ (No. 1014), a = 8.978(2), b = 20.087(1), c = 22.004(1) Å, β = 96.023(3)°, U = 3946.4(5) Å^3, D_c = 1.256 g cm^{-1}, Z = 4, μ = 30.38 cm^{-1}, number of reflections used = 2248 [$I > 3\sigma(I)$], (5392 unique measured), R = 0.0530, R_w = 0.0580. Data for all structures were collected on an Enraf–Nonius CAD-4 diffractometer, at 23 ± 2 °C, λ(Mo-K_α) = 0.71073 Å (graphite monochromator). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

The methyl compounds (**3a**) and (**4a**) are isostructural, as are the n-butyl analogues (**3b**) and (**4b**). The molecular structures of (**3b**) and (**4a**) are shown in Figures 1 and 2 respectively. All four compounds are dimeric and feature two bridging Bu^t_2E entities and four terminal alkyl groups in each case. The central Ga_2E_2 core is essentially planar, unlike the puckered ring observed in the bulky thiolate complex, $(Pr^iSGaI_2)_2$, in which a fold angle of 43.3(2)° was observed on the Ga · · · Ga′ diagonal.[5] The co-ordination about each Ga atom is roughly tetrahedral. Compounds (**3a**) and (**4a**) have a crystallographically imposed centre of symmetry at the mid-point of the molecule. Initial studies show that the indium analogues of these compounds can be prepared by similar methods.

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