The reactions of gallium metal with (p-MeOC$_6$H$_4$)$_3$AsI$_2$ and Et$_3$AsI$_2$; isolation of a novel gallium(II) arsine complex with a gallium–gallium bond and the X-ray crystal structures of GaI$_3$[(p-MeOC$_6$H$_4$)$_3$As] and Ga$_2$I$_4$(AsEt$_3$)$_2$

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The reactions of (p-MeOC$_6$H$_4$)$_3$AsI$_2$ and Et$_3$AsI$_2$ with gallium metal powder produce the metal complexes GaI$_3$[(p-MeOC$_6$H$_4$)$_3$As] and Ga$_2$I$_4$(AsEt$_3$)$_2$, respectively; the latter represents a unique example of a gallium–tertiary arsine complex containing a gallium–gallium bond, and both structures illustrate the subtle effect of the organic substituent on the arsenic atoms.

In contrast to the transition metals,[1] the chemistry of the main group metals containing tertiary phosphine and arsine donor ligands has received little attention; and there is little data concerning the structural nature of gallium complexes containing tertiary phosphine and arsine donor ligands. This has been illustrated in a recent review of this area by Norman,[2] who points out that workers have investigated a small number of triorganogallium phosphine complexes, R$_3$Ga(PR$_3$), *e.g.* GaMe$_3$(PMe),[3] Ga(CH$_2$Bu^t)$_3$(PHPh$_2$)[4] and GaPh$_3$[P(SiMe$_3$)$_3$].[5] In all cases, these complexes have distorted tetrahedral or trigonal-based pyramidal geometry for the gallium centre, dependent on the steric bulk of the ligands concerned. The diphosphine complex GaMe$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$) has also been structurally characterised,[6] showing the gallium centre in tetrahedral geometry. Only one gallium trihalide complex containing a tertiary phosphine bond has been structurally characterised, GaCl$_3$(PMe$_3$),[7] which again contains the gallium in tetrahedral geometry. No gallium halide complexes containing a tertiary arsine donor ligand were known until very recently: GaI$_3$(AsPh$_3$)[8] has been synthesised from the reaction of GaI$_3$·OEt$_3$ with AsPh$_3$; this molecular tetrahedral complex was found to be in equilibrium with the ionic complex [Ph$_3$AsI][GaI$_4$], and the latter represents the first arsenic(V) iodo complex to be crystallographically characterised.

There has also been great interest recently in certain gallium complexes for potential applications as MOCVD precursors *e.g.* [Bu^{t}GaS]$_4$,[9,10] [(Et$_2$MeC)GaS]$_4$ and [Bu^{t}GaSe]$_4$;[11] clearly, although a largely unexplored field, it may be expected that interest will grow rapidly.

We are engaged in a study of the oxidising power of a variety of R$_3$EX$_2$ compounds (E = P, As, Sb; X$_2$ = Br$_2$, I$_2$, IBr) with unactivated metal powders in diethyl ether solution.[12–17]

We have now turned our attention to the reaction of these new oxidising agents with gallium metal powder, principally for two reasons: first, very little is known concerning the coordination chemistry of gallium(III) halides with tertiary arsine donor ligands, and, secondly, such complexes may have applications in the microelectronics industry as precursors for MOCVD. (p-MeOC$_6$H$_4$)$_3$AsI$_2$ reacts with gallium metal powder according to eqn. (1).

$$3(p\text{-MeOC}_6\text{H}_4)_3\text{AsI}_2 + 2\text{Ga} \xrightarrow[\text{Et}_2\text{O}]{ca.\ 1\text{d, Ar}} 2\text{GaI}_3[(p\text{-MeOC}_6\text{H}_4)_3\text{As}] \quad (1)$$

Recrystallisation of the white powder from diethyl ether solution produced a large quantity of colourless crystals,† from which one was selected for analysis by single-crystal X-ray diffraction. The structure‡ of the gallium complex was revealed to be GaI$_3$[(p-MeOC$_6$H$_4$)$_3$As], Fig. 1. The gallium atom is in the expected tetrahedral environment; however, this stoichiometry has only one precedent, GaI$_3$(AsPh$_3$), synthesised by Baker *et al.* from the direct reaction of gallium triiodide and a triphenylarsine.[8] The synthesis of GaI$_3$[(p-MeOC$_6$H$_4$)$_3$As] described here indicates that gallium(III) tertiary arsine complexes are also available from our new synthetic route, *viz.* the direct reaction of gallium metal with R$_3$AsI$_2$ species. In contrast to the findings of Baker *et al.*,[8] no equilibrium with the arsenic(V) complex [(p-MeOC$_6$H$_4$)$_3$AsI][GaI$_4$] was observed. This may be due to the greater basicity of (p-MeOC$_6$H$_4$)$_3$As compared to Ph$_3$As, thus rendering the gallium–arsenic bond stronger in the complex described here and therefore less susceptible to cleavage by diiodine.

Et$_3$AsI$_2$ reacts with gallium metal powder according to eqn. (2).

$$2\text{Et}_3\text{AsI}_2 + 2\text{Ga} \longrightarrow [\text{GaI}_2(\text{AsEt}_3)_2]_2 \quad (2)$$

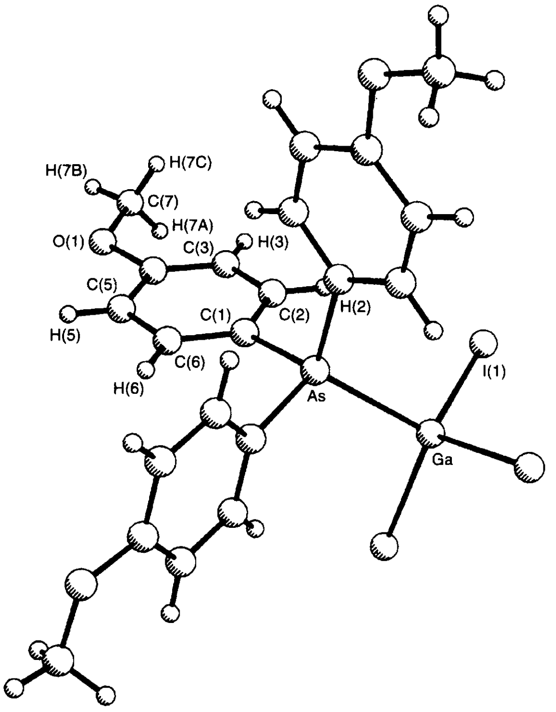

Fig. 1 Perspective view of the molecular structure of GaI$_3$[(p-MeOC$_6$H$_4$)$_3$As]. Selected bond lengths (Å) and angles (°): Ga–I(1) 2.505(1), Ga–As 2.509(3), Ga–As–C(1) 114.0(3), I(1)–Ga–I(1) 111.62(5), I(1)–Ga–As 107.23(5).

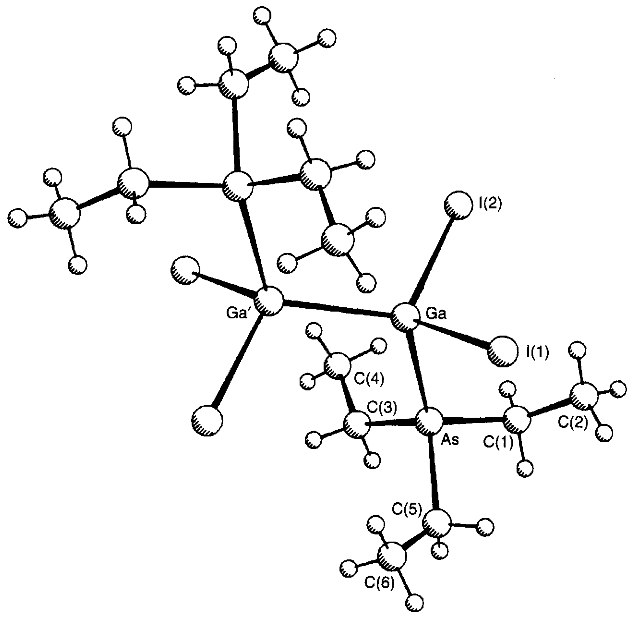

Fig. 2 Perspective view of the molecular structure of $[GaI_2(AsEt_3)]_2$. Selected bond lengths (Å) and angles (°): Ga–Ga 2.428(7), Ga–I(1) 2.564(4), Ga–I(2) 2.568(4), Ga–As 2.484(5); I(1)–Ga–I(2) 109.0(1), I(1)–Ga–As 101.8(2), I(1)–Ga–Ga' 115.7(2), I(2)–Ga–As 101.6(2), I(2)–Ga–Ga' 113.0(2), As–Ga–Ga' 114.4(2).

Recrystallisation of the white powder† from diethyl ether solution at 0 °C produced a large quantity of colourless crystals, from which one was selected for analysis by single-crystal X-ray diffraction, revealing the dinuclear gallium(II) complex $[GaI_2(AsEt_3)_2]_2$.‡ This is a very surprising result, since we had anticipated a monomeric tetrahedral gallium(III) complex analogous to the tertiary arsine complex described above, and in agreement with the findings of Baker *et al.*[8] The gallium atoms are in tetrahedral geometry linked by a Ga–Ga bond of 2.428(7) Å. The gallium–arsenic bond is 2.484(5) Å, similar to that found for $GaI_3(AsPh_3)$, 2.490(5) Å. Although no complexes are known of a gallium–gallium bonded species containing tertiary arsine donor ligands, there nevertheless exist some crystallographically characterised gallium(II) com- plexes containing a gallium–gallium bond. The complexes of general formula $Ga_2X_4L_2$ (X = Cl,[19], Br,[20] L = dioxane; X = Br, L = pyridine)[21] have been crystallographically characterised by Small and coworkers. The gallium–gallium bond lengths for these three complexes were found to be 2.406(1), 2.395(6) and 2.421(3) Å, respectively, similar to $Ga_2I_4(AsEt_3)_2$, 2.428(7) Å, described here. Additionally, the organometallic complex $[Li([12]crown\text{-}4)_2]^+[Ga_2(C_6H_3Pr^i_3\text{-}2,4,6)]$[22] has recently been synthesised and shown to have Ga–Ga multiple bonding character, this phenomenon being reflected in the shorter gallium–gallium bond distance, 2.343(2) Å. Finally the interesting cluster compound $[\{(Et_2O)_2ClGa\}Ga\{GaCl_2(Et_2O)\}_3]$[23] containing a tetrahedral Ga_5 unit is known, which exhibits gallium–gallium bonds ranging from 2.417(2) to 2.450(2) Å. Again, in contrast to the findings of Baker *et al.*[8] no evidence for the formation of an arsenic(V) species, $[R_3AsI][GaI_4]$, was noted even on standing for several weeks.

Footnotes

† $GaI_3[(p\text{-}MeOC_6H_4)_3As]$, colourless crystals, *ca.* 70% yield, mp 160–161 °C, correct elemental analysis (C, H, I). ^1H NMR spectrum: δ 3.7 (s), 6.9 (d), 7.3 (d); relative intensities (3:2:2). Low-frequency Raman spectrum (50–550 cm^{-1}): 74 (Ga–As), 143 cm^{-1} (Ga–I).

$[GaI_2(AsEt_3)_2]$, quantitative yield, colourless crystals, mp 134–135 °C, correct elemental analysis (C, H, I). ^1H NMR spectrum: δ 1.2 (s), 1.4 (m), 2.1 (m); relative intensities (3:2:2). Low-frequency Raman spectrum (50–550 cm^{-1}): 72 (Ga–As), 142 (Ga–I), 222 cm^{-1} (Ga–Ga).

‡ *Crystal data*: for $GaI_3[As(p\text{-}MeOC_6H_4)_3]$: trigonal, space group $P\bar{3}$ (no. 147), a = 13.130(5), c = 8.846(4) Å, U = 1321(2) Å^3, Z = 2, D_c = 2.129 g cm^{-3}, μ = 57.68 cm^{-1}, F(000) = 788. The structure analysis is based on 5224 reflections (Mo-Kα, θ_{max} = 50.10°), 967 observed [($I > 3.00\sigma(I)$], 88 parameters. Absorption correction (min., max. transmission 0.74, 1.15). The structure was solved by direct methods and refined by full-matrix least squares. Final residuals R = 0.049, R_w = 0.050. For $[GaI_2(AsEt_3)]_2$: monoclinic, space group, $P2_1/n$ (no. 14), a = 10.137(4), b = 12.225(5), c = 10.895(5) Å, β = 92.34(3)°, U = 1349(2) Å^3, Z = 2, D_c = 2.391 g cm^{-3}, μ = 89.48 cm^{-1}, F(000) = 884. The structure analysis is based on 2432 reflections (Mo-Kα, $2\theta_{max}$ = 50.1°), 539 observed [$I > 3.00\sigma(I)$], 92 parameters. Absorption correction (min., max. transmission 0.80, 1.07). The structure was solved by direct methods and refind by full-matrix least squares. Final residuals R = 0.040, R_w = 0.038. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/114.

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