Electrochemical Studies of Group 3 Alkyl Derivatives. Part 1. Synthesis of Trimethylgallium Adducts

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Electrolysis of dimethylmagnesium in tetrahydrofuran (thf) with a gallium anode yields the adduct $GaMe_3 \cdot thf$ directly; the trialkylamine and trialkylphosphine adducts $GaMe_3 \cdot L$ (L = NEt_3, PMe_3, or PEt_3) are obtained by direct addition of an excess of L to $GaMe_3 \cdot thf$. Free $GaMe_3$ is obtained by reaction of MeI with a Mg–Ga alloy in an ether solvent.

For the vapour phase epitaxial production of semiconductors such as GaAs, both Group 3 alkyl derivatives MR_3 (M = Ga or In) and their adducts with Group 5 Lewis bases (*e.g.* PR_3, AsR_3, or NR_3) have obvious potential as volatile sources either of the metals or of the semiconductors. Thus InP and related substances have been grown by pyrolysis of $InMe_3 \cdot L$ (L = PEt_3 or NEt_3) in the presence of a Group 5 hydride;[1] smooth layers of InP are formed by the pyrolysis of $InMe_3 \cdot PMe_3$ in the presence of PCl_3,[2] and epitaxial GaAs has been grown by pyrolysis of $GaEt_2Cl \cdot AsEt_3$.[3]

The requirement for very pure alkyl derivatives or their adducts has led us to a study of methods for their preparation. Conventional methods involve reaction of either the metal or its trihalide with another alkylmetal (*e.g.* of Li, Al, Zn, or Hg)[4] or with the Grignard reagent in ether;[5] many of these methods are either inconvenient for larger scale use or result in an impure product. However the synthesis of pure $GaMe_3$ by reaction of mixtures or alloys of Ga and Mg with methyl iodide in appropriate solvents has been reported,[6] and we have investigated this method further. The electrolysis of organomagnesium compounds with sacrificial metal anodes has provided a simple route to a number of organometallic compounds.[7] More specifically, electrochemical methods of preparation have been used for the production of $InRX_2$ and InR_2X (X = halogen) compounds using an indium anode[8] or cathode,[9] and Group 3 alkyl derivatives have been produced by electrolysis of $NaF \cdot AlR_3$[10] (or mixtures of alkyl-zinc and -aluminium derivatives containing alkali-metal halides[11]) using an appropriate anode. The successful production of alkyl-lead compounds by electrochemical means[12] encouraged us to study the application of similar methods to Group 3 alkyls, and we now report the direct one-step synthesis of a $GaMe_3$ ether adduct from gallium metal, and the formation of adducts $GaMe_3 \cdot QR_3$ (Q = N or P) from this by simple ligand exchange. A synthesis of ligand-free $GaMe_3$ from an alloy, Mg_5Ga_2, is also described.

Results and Discussion

Electrochemical Synthesis.—Electrolysis of $MgMe_2$ in tetrahydrofuran (thf) with a platinum cathode and a gallium pool anode in the presence of NEt_4ClO_4 as supporting electrolyte causes deposition of magnesium at the cathode and the production of a colourless solution from which a colourless air-sensitive liquid can be distilled after removal of thf *in vacuo*. Infrared, ^1H n.m.r., and mass spectral studies of this liquid strongly suggest that it has the limiting composition $GaMe_3 \cdot thf$, but the difficulty of removing the last traces of unbound thf from the product, as well as its air-sensitivity, preclude reproducible elemental analysis. This compound (and the others reported later) all show two or three characteristic i.r. peaks between 500 and 580 cm^{-1}, attributable[13] to stretching modes of the GaC_3 skeleton. Table 1 shows the ^1H n.m.r. spectral data, confirming the presence of $GaMe_3$ and co-ordinated thf. The mass spectral data are collected in Table 2; although a molecular ion is not observed, fragments corresponding to $[GaMe_2 \cdot thf]^+$, $[Ga \cdot thf]^+$, $[GaMe_3]^+$, $[GaMe_2]^+$, $[GaMe]^+$, $[Ga]^+$, and $[thf]^+$ support the proposed formulation. Final confirmation that the product is $GaMe_3 \cdot$

Table 1. ^1H N.m.r. data for $GaMe_3 \cdot L$ compounds

L	δ */p.p.m.
thf	−0.3 [s, 9 H, $Ga(CH_3)_3$], 1.6 (m, 4 H, $CH_2C\mathit{H}_2C\mathit{H}_2CH_2O$), 3.6 (t, 4 H, $C\mathit{H}_2CH_2CH_2C\mathit{H}_2O$)
PMe_3	0.0 [s, 9 H, $Ga(CH_3)_3$], 0.6 [d, 9 H, $P(CH_3)_3$]
PEt_3	0.0 [s, 9 H, $Ga(CH_3)_3$], 0.7, 1.1 [m, 15 H, $P(C\mathit{H}_2C\mathit{H}_3)_3$]
NEt_3	−0.2 [s, 9 H, $Ga(CH_3)_3$], 0.9 [t, 9 H, $N(CH_2C\mathit{H}_3)_3$], 2.4 [q, 6 H, $N(C\mathit{H}_2CH_3)_3$]
$NBu^n{}_3$	0.0 [s, 9 H, $Ga(CH_3)_3$], 1.0 [t, 9 H, $N(CH_2CH_2CH_2C\mathit{H}_3)_3$], 1.4 [m, 12 H, $N(CH_2C\mathit{H}_2C\mathit{H}_2CH_3)_3$], 2.6 [t, 6 H, $N(C\mathit{H}_2CH_2CH_2CH_3)_3$]

* In benzene; reference benzene protons at δ 7.3 relative to $SiMe_4$.

Table 2. Mass spectral data for $GaMe_3 \cdot L$ compounds [a]

L	*m/z*
thf [b]	69/71, $[Ga]^+$; 71, $[C_4H_7O]^+$; 72, $[C_4H_8O]^+$; 84/86, $[GaMe]^+$; 99/101, $[GaMe_2]^+$; 114/116, $[GaMe^+{}_3]$; 141/143, $[Ga \cdot thf]^+$; 171/173, $[GaMe_2 \cdot thf]^+$ (*s* = 125 °C, *I* = 13 eV)
PMe_3 [b]	61, $[C_2H_6P]^+$; 69/71, $[Ga]^+$; 76, $[C_3H_9P]^+$; 84/86, $[GaMe]^+$; 99/101, $[GaMe_2]^+$; 114/116, $[GaMe_3]^+$; 175/177, $[GaMe_2 \cdot PMe_3]^+$ (*s* = 125 °C, *I* = 15 eV)
PEt_3 [c]	61, $[C_2H_6P]^+$; 62, $[C_2H_7P]^+$; 69/71, $[Ga]^+$; 75, $[C_3H_8P]^+$; 84/86, $[GaMe]^+$; 90, $[C_4H_{11}P]^+$; 99/101, $[GaMe_2]^+$; 103, $[C_5H_{12}P]^+$; 118, $[C_6H_{15}P]^+$ (*s* = 200 °C, *I* = 70 eV)
NEt_3 [b]	69/71, $[Ga]^+$; 84/86, $[GaMe]^+$; 86, $[C_5H_{12}N]^+$; 99/101, $[GaMe_2]^+$; 101, $[C_6H_{15}N]^+$; 114/116, $[GaMe_3]^+$ (*s* = 150 °C, *I* = 15 eV)
$NBu^n{}_3$ [c]	69/71, $[Ga]^+$; 84/86, $[GaMe]^+$; 86, $[C_5H_{12}N]^+$; 99/101, $[GaMe_2]^+$; 100, $[C_6H_{14}N]^+$; 114/116, $[GaMe_3]^+$; 142, $[C_9H_{20}N]^+$; 185, $[C_{12}H_{27}N]^+$ (*s* = 90 °C, *I* = 30 eV)

[a] Abbreviations: *s* = source temp.; *I* = ionisation energy. 1 eV ≈ 1.60×10^{-19} J. [b] Batch inlet. [c] Solid probe.

thf was obtained by independent synthesis of stoicheiometric $GaMe_3$·thf, by reaction of equimolar amounts of thf and $GaMe_3$, prepared as described later; the product has spectral properties identical with those of the substance prepared electrochemically.

The nature of the supporting electrolyte seems to be crucial. When $NBu^n_4ClO_4$ is used the product obtained is $GaMe_3 \cdot NBu^n_3$, presumably formed by abstraction of NBu^n_3 from the quaternary ion. Such degradations have previously been noted [14] during electrochemical reactions in the presence of tetra-alkylammonium salts.

Preparation of Adducts $GaMe_3 \cdot QR_3$.—Addition of an excess of Lewis base (NEt_3, PMe_3, or PEt_3) to $GaMe_3$·thf (prepared as just described) gives, on removal of the excess of base and liberated thf by evaporation, volatile solids $GaMe_3 \cdot QR_3$ (Q = P or N); analytical as well as spectroscopic data (Tables 1 and 2) confirm the 1 : 1 stoicheiometry. A similar process for the preparation of these adducts from $GaMe_3 \cdot OEt_2$ has been reported.[15] For $GaMe_3 \cdot NEt_3$ and $GaMe_3 \cdot NBu^n_3$ consistently low analytical values for C and H are attributable to occurrence of the previously reported photochemical decomposition.[15] Indeed, even when kept under dry dinitrogen, $GaMe_3 \cdot NEt_3$ changes from a white crystalline solid to a pale brown oil.

Preparation of Ligand-free Trimethylgallium.—A detailed study of the previously reported [6] reaction of Mg–Ga alloys (or mixtures of the two metals) with methyl iodide in different solvents has shown that rather specific conditions are required for the preparation of $GaMe_3$ by this route. Thus we have not been able to substantiate the claims [6] that mixtures of gallium and magnesium with methyl iodide in di-isopentyl ether give $GaMe_3$; we obtained only metallic gallium and a colourless solution, presumably the Grignard reagent. In contrast, the intermetallic compound Mg_5Ga_2 (prepared by fusing the two metals in these proportions in a well stirred vitreous carbon reactor) and methyl iodide, in the same solvent, react to form initially a white suspension (probably magnesium iodide). On cooling, a colourless crystalline solid is obtained; this presumably contains the involatile trimethylgallium–ether adduct,[15] which is sufficiently stable at 100 °C to allow methyl iodide to be removed by distillation; on raising the temperature to about 190 °C the adduct dissociates and fractional distillation effects separation of pure $GaMe_3$ from the isopentyl ether. The low yield (*ca.* 30%) obtained by this method can probably be attributed to problems associated with breakdown of the adduct rather than to reaction conditions; but formation of the $GaMe_3$–di-isopentyl ether adduct offers a useful method of purifying the trialkyl compound. Attempts to carry out the reaction in other solvents (*e.g.* di-n-butyl ether) were unsuccessful, although formation of a white precipitate suggested that MgI_2 and $GaMe_3$ were being formed; failure to recover the latter is attributable to the greater stability of the adduct with the solvent, and the lower volatility of the solvent, so that the adduct does not dissociate below the boiling point of the solvent.

Experimental

All preparations and manipulations were carried out in an atmosphere of dry deoxygenated dinitrogen using standard Schlenk-tube/catheter techniques.

All chemicals and solvents were dried, purified, and deaerated by standard methods before use except for trimethylphosphine and triethylphosphine (Strem Chemical Co Ltd.) which were used without further purification.

The electrochemical cell was a three-necked flask fitted with a water condenser, platinum cathode (1 × 1 cm plate), and a gallium pool anode. The d.c. power supply used in the electrolyses was a Solartron Vari-Pack model SRS 153.

Dimethylmagnesium was prepared by the precipitation of the dioxan–magnesium iodide complex from an ethereal solution of methylmagnesium iodide.[16] The alloy samples used for the direct preparation of trimethylgallium from gallium–magnesium alloy were supplied by R.S.R.E. Malvern and B.D.H. Ltd.

Mass spectra were measured with a VG Micromass 13 spectrometer using a batch inlet or a solid probe. Proton n.m.r. spectra were recorded with a Perkin-Elmer R12B spectrometer at 60 MHz; i.r. spectra were recorded with a Perkin-Elmer 577 spectrometer using thin films or Nujol mulls between caesium iodide plates.

Microanalyses were performed by Elemental Micro-Analysis Ltd.; the gallium analyses by ashing.

Electrochemical Preparations: Trimethylgallium–Tetrahydrofuran Adduct.—A mixture of dimethylmagnesium (0.9 g, 17 mmol) and tetraethylammonium perchlorate (1.0 g, 4 mmol) in thf (100 cm^3) was electrolysed using a Pt cathode and gallium pool anode (40 g). The mixture was heated to 70 °C and was stirred continuously throughout the reaction. Initially a current of 40 mA was obtained at an applied voltage of 100 V. The reaction (which was not observed in the absence of current) was allowed to proceed for 56 h, during which time the mixture darkened and became nearly black. At the end of the reaction the current had fallen to 3 mA at 100 V. After cooling the mixture was allowed to settle and was then filtered. The thf was removed *in vacuo* to leave a colourless air-sensitive oil, from which the product was obtained by vacuum distillation (60 °C) into a *ca.* −196 °C cold trap (**CAUTION**: perchlorate); yield of $GaMe_3$·thf 40% (based on $MgMe_2$). Since a gallium pool anode was used it is difficult to determine the amount of gallium consumed and hence current efficiencies have not been calculated. The i.r. spectrum showed $\nu_{max.}$ (film) at 2 980m, 2 940s, 2 890m, 1 450w, 1 365vw, 1 340vw, 1 250vw br, 1 190m, 1 030s, 915w, 875m, 740s (sh), 720s, 670w, 645w (sh), 550vs, and 515vw cm^{-1}.

Trimethylgallium–Trimethylphosphine Adduct.—Trimethylphosphine (5 g, 66 mmol) was added to the liquid product just described. The mixture was stirred for 30 min at ambient temperature and the trimethylphosphine was then removed *in vacuo* to leave a colourless crystalline solid. The final product (m.p. 54 °C) was obtained by vacuum sublimation at ambient temperature into a −196 °C trap (Found: C, 37.8; H, 9.8; Ga, 34.2; P, 17.3. $C_6H_{18}GaP$ requires C, 37.8; H, 9.4; Ga, 36.5; P, 16.3%); $\nu_{max.}$ (Nujol) at 1 300m (sh), 1 285s, 1 180s, 950s (sh), 940vs, 840w, 740vs (sh), 720vs, 650w (sh), 535vs, and 505m cm^{-1}.

The adducts $GaMe_3 \cdot L$ (L = PEt_3 or NEt_3) were prepared similarly by addition of an excess of phosphine or amine to $GaMe_3$·thf. For L = PEt_3, the excess of the latter was removed at 100 °C *in vacuo* to leave the pure product. For L = NEt_3, vacuum sublimation at 60 °C into a −196 °C trap was used. $GaMe_3 \cdot PEt_3$ (Found: C, 46.4; H, 10.1; Ga, 29.9; P, 11.8. $C_9H_{24}GaP$ requires C, 46.4; H, 10.3; Ga, 30.0; P, 13.3%) showed $\nu_{max.}$ (film) at 1 460vs, 1 415s, 1 385s, 1 255m, 1 185vs, 1 045s, 1 010w, 985w, 925w, 900vw br, 865vw (sh), 840w, 770s (sh), 750vs (sh), 720vs br, 620w (sh), 570w, 535vs, 510s, and 310vw cm^{-1}. $GaMe_3 \cdot NEt_3$ (Found: C, 46.2; H, 10.5; Ga, 34.1; N, 6.5. $C_9H_{24}GaN$ requires C, 50.1; H, 11.1; Ga, 32.3; N, 6.5%) showed $\nu_{max.}$ (film) at 1 450vs, 1 390vs, 1 330m, 1 320m, 1 300s, 1 190vs, 1 170vs, 1 160vs, 1 100vs, 1 090vs, 1 050vs, 1 030m, 1 010s, 905m, 830w (sh), 810s, 790s, 725vs br, 655s, 600w, 560s, 535vs, 510vs, 495m, 485m, 470m, 425w, and 335vw br cm^{-1}.

Preparation of Trimethylgallium–Tri-n-butylamine Adduct.—A mixture of dimethylmagnesium (2.0 g, 40 mmol) and tetrabutylammonium perchlorate (2.0 g, 6 mmol) in thf (100 cm^3) was electrolysed as described above. Initially a current of 100 mA was obtained at an applied voltage of 60 V. The reaction was allowed to proceed for 56 h, after which the current had fallen to 35 mA at 100 V and the mixture was nearly black. The mixture was allowed to cool and settle and was then filtered. Removal of the thf *in vacuo* left a crystalline solid from which the product was obtained by vacuum sublimation at 80 °C into a -196 °C trap (**CAUTION**: perchlorate) (Found: C, 54.3; H, 11.2; Ga, 20.4; N, 4.4. $C_{15}H_{35}GaN$ requires C, 60.0; H, 12.0; Ga, 23.3; N, 4.7%); $\nu_{max.}$ (film) at 1 460vs, 1 380m, 1 340w, 1 310vw, 1 250w br, 1 190vs, 1 160m, 1 110w, 1 070m, 1 035vs, 920m, 900m, 880s, 840m, 730vs br, 650m (sh), 590m, 550vs, 535vs, 510m, and 485w cm^{-1}.

Preparation of Ligand-free Trimethylgallium from Gallium–Magnesium Alloy.—Methyl iodide (84 cm^3, 1.34 mol) was added slowly to a magnetically stirred suspension of gallium–magnesium alloy (44 g, 0.34 mol dm^{-3} in Ga) in di-isopentyl ether (150 cm^3). After initiation with iodine (*ca.* 2 mg) a vigorous reaction set in; after stirring for 18 h the initially dark mixture had lightened considerably. After boiling under reflux for 24 h the mixture had become white, and on cooling to ambient temperature colourless needle-shaped crystals formed *in situ*. Traces of unchanged methyl iodide (b.p. 40—43 °C) were removed by distillation at a bath temperature of 100 °C through a column packed with Fenske helices. Pure trimethylgallium (b.p. 56 °C) was then obtained by distillation at a bath temperature of 190 °C. The yield of $GaMe_3$ was typically 30—50%; *m/z* (source 60 °C, ionisation energy 30 eV) 69/71, $[Ga]^+$; 84/86, $[GaMe]^+$; 99/101, $[GaMe_2]^+$; 114/116, $[GaMe_3]^+$.

$GaMe_3 \cdot thf$ was prepared by the reaction of equimolar amounts of thf and $GaMe_3$ (prepared from Mg_5Ga_2 alloy) and was purified by vacuum distillation (60 °C) into a -196 °C trap.

$GaMe_3 \cdot NEt_3$ was subsequently prepared by addition of an excess of triethylamine to $GaMe_3 \cdot thf$. The product had spectral properties identical with those of $GaMe_3 \cdot NEt_3$ prepared from electrochemically derived $GaMe_3 \cdot thf$.

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