Cyclic and Polycyclic Gallium-Antimony Compounds: Synthesis and Crystal Structures of $[GaCl(PnPr_2Ph)(SbSi\textit{i}Pr_3)]_2$ and $[(GaCl)_4(SbSi\textit{i}Pr_3)_4(PnPr_2Ph)_2]$

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The reaction of $[(DME)LiE(SiMe_3)_2]$ (E = As, Sb) with iPr_3SiCl in DME yields the mixed silylated compounds $iPr_3SiE(SiMe_3)_2$ (**1**: E = As, **2**: E = Sb). Compounds **1** and **2** were characterised by multinuclear NMR spectroscopy and mass spectrometry. The antimony compound **2** reacts with $[GaCl_3PnPr_2Ph]$ to give the cyclic compound $[GaCl(PnPr_2Ph)(SbSi\textit{i}Pr_3)]_2$ (**3**). The polycyclic Ga-Sb compound $[(GaCl)_4(SbSi\textit{i}Pr_3)_4(PnPr_2Ph)_2]$ (**4**) can be obtained from a solution of **3** in benzene. The central structural motif of **3** is a folded Ga_2Sb_2 four-membered ring. Compound **4** consists of a ladder-like Ga_4Sb_4 unit and is the first polycyclic Ga-Sb compound described. Compounds **3** and **4** were characterised by single crystal X-ray diffraction. The thermal decomposition of both compounds results in the formation of the binary phase GaSb.

Introduction

In the last few years different groups have reported the synthesis of four- and six-membered Ga-Sb ring compounds of the general formula $[R_2GaSbR'_2]_n$ (R = alkyl, chloride; R′ = alkyl, silyl; n = 2, 3).[1] In these compounds the Ga and Sb atoms have the coordination number four. Cyclic compounds with lower coordinated Ga and/or Sb atoms or polycyclic molecules are unknown so far. In contrast, several cyclic or polycyclic gallium phosphorus or gallium arsenic compounds with low-coordinate Ga and P/As atoms have been described.[2,3] We obtained the cyclic and polycyclic Ga-Sb compounds $[GaCl(PnPr_2Ph)(SbSi\textit{i}Pr_3)]_2$ (**3**) and $[(GaCl)_4(SbSi\textit{i}Pr_3)_4(PnPr_2Ph)_2]$ (**4**) from the reaction of the mixed silylated antimony compound $iPr_3SiSb(SiMe_3)_2$ (**2**) with the gallium chloride phosphane complex $[GaCl_3PnPr_2Ph]$. The structure of compounds **3** and **4** was determined by X-ray crystal structure analysis.[4]

Results and Discussion

The reaction of $[(DME)LiE(SiMe_3)_2]_2$ (E = As, Sb) with iPr_3SiCl in DME at 0 °C yields the mixed silylated compounds $iPr_3SiE(SiMe_3)_2$ (**1**: E = As, **2**: E = Sb). These compounds are highly viscous liquids which solidify to a glass-like solid when cooled to −78 °C. Both compounds were characterised by multinuclear NMR spectroscopy and mass spectrometry. Whereas the arsenic compound **1** shows no reaction towards gallium chloride phosphane complexes the antimony compound **2** reacts with the phosphane complex $[GaCl_3PnPr_2Ph]$ in diisopropyl ether to give the cyclic compound **3** as illustrated in Equation (1). Compound **3** can be obtained in crystalline form by cooling the reaction mixture to 6 °C.

$$2\,[GaCl_3{\cdot}PnPr_2Ph] + 2\,iPr_3SiSb(SiMe_3)_2 \rightarrow [GaCl(PnPr_2Ph)(SbSi\textit{i}Pr_3)]_2\,(\mathbf{3}) + 4\,Me_3SiCl \qquad (1)$$

Compound **3** crystallises with an orthorhombic unit cell containing four molecules in the space group $Pna2_1$, and has been refined as an inversion twin (Figure 1). The central structural motif is a folded Ga_2Sb_2 four-membered ring in which the Sb atoms are trigonal pyramidally coordinated by two Ga atoms and one $Si\textit{i}Pr_3$ group. The gallium centres have a distorted tetrahedral geometry consisting of a chloride atom, a $PnPr_2Ph$ ligand and the two Sb atoms. Due to the mutual repulsion of the sterically demanding $PnPr_2Ph$ and $Si\textit{i}Pr_3$ groups they are orientated on different sides of the ring. The shape of **3** is therefore similar to the recently described gallium phosphorus and gallium arsenic compounds $[GaCl(PtBu_2Me)(ESiMe_3)]_2$ (E = P, As).[2b] The clear folding of the ring — the Sb−Ga−Sb planes have an angle of 139.0° to each other — is caused by the lower coordination number at the Sb atoms and by the *cis* orientation of the sterically demanding $Si\textit{i}Pr_3$ and $PnPr_2Ph$ groups. The Ga−Sb bonds in **3** are 264.1 pm on average and therefore shorter than in the Ga−Sb ring compounds with coordination number four at the gallium and the antimony atoms (267−277 pm) mentioned above. This shortening can be explained by the lower coordination number of the Sb atoms and the purely covalent character of the Ga−Sb bonds in **3**. A Ga−Sb bond length of 264.8(1) pm, however, can be observed in the acyclic compound $[LGaEt_2{-}Sb(SiMe_3)_2]$ [L = 4-(dimethylamino)pyridine], also featuring coordination number three at the anti-

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mony and four at the gallium atom.[5] The endocyclic angles in **3** are 98.7° at the gallium and 75.2° at the antimony atoms. The Ga−Cl bonds are, on average, 225.2 pm long, and the exocyclic dative P−Ga bond is 244.2 pm long. Compound **3** is stable in the mother liquor but decomposes over a period of two weeks time with release of the phosphane ligands and the formation of a brown residue when isolated.

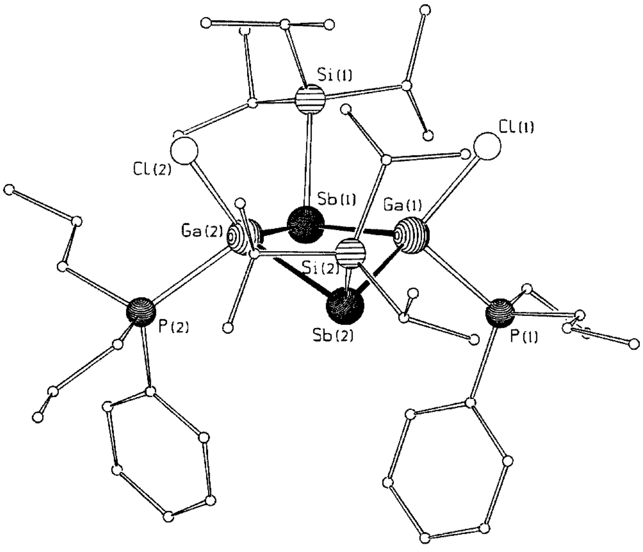

Figure 1. Molecular structure of **3**; selected bond lengths (pm) and bond angles (°): Ga(1)−Sb(1) 264.1(1), Ga(1)−Sb(2) 265.1 (1), Ga(2)−Sb(1) 263.5 (1), Ga(2)−Sb(2) 263.6(1), Ga(1)−Cl(1) 224.8(2), Ga(1)−P(1) 244.8(2), Ga(2)−Cl(2) 225.6(2), Ga(2)−P(2) 243.6(2), Sb(1)−Si(1) 258.1(2), Sb(2)−Si(2) 258.2(2); Ga(1)−Sb(1)−Ga(2) 75.3(1), Ga(1)−Sb(2)−Ga(2) 75.1(1), Sb(1)−Ga(1)−Sb(2) 98.4(1), Sb(1)−Ga(2)−Sb(2) 99.0(1), Cl(1)−Ga(1)−P(1) 93.7(1), Cl(2)−Ga(2)−P(2) 92.3(1), Si(1)−Sb(1)−Ga(1) 107.5(1), Si(1)−Sb(1)−Ga(2) 116.0(1), Si(2)−Sb(2)−Ga(1) 117.1(1), Si(2)−Sb(2)−Ga(2) 105.9(1)

Red crystals with the composition $[(GaCl)_4(SbSi\text{-}iPr_3)_4(PnPr_2Ph)_2]$ (**4**) · 2 C_6H_6 were obtained from a solution of **3** in benzene over a period of three days. Obviously compound **3** undergoes a condensation reaction to give **4** and two free phosphane molecules [Equation (2)].

$$2\,[GaCl(PnPr_2Ph)(SbSiiPr_3)]_2 \rightarrow [(GaCl)_4(SbSiiPr_3)_4(PnPr_2Ph)_2]\,(\mathbf{4}) + 2\,PnPr_2Ph \qquad (2)$$

The molecular structure of **4** (Figure 2), which contains an inversion centre, consists of a central planar Ga_2Sb_2 four-membered ring in which the silyl groups and the Cl atoms are *trans* orientated. Two slightly folded Ga_2Sb_2 rings with an all *cis* orientation of the silyl groups and the Cl atoms are connected to the central ring on opposite sides. These three Ga_2Sb_2 rings are not coplanar, instead the three moieties form a chair-like structure. A similar structure has been observed for the aluminium-phosphorus compound $[(AlCl)_4(PR)_4(OEt_2)_2]$ (R = $SiiPr_3$, $SiiPr_2Me$) which was recently obtained by reaction of $AlCl_3$ with Li_2PR in diethyl ether.[6]

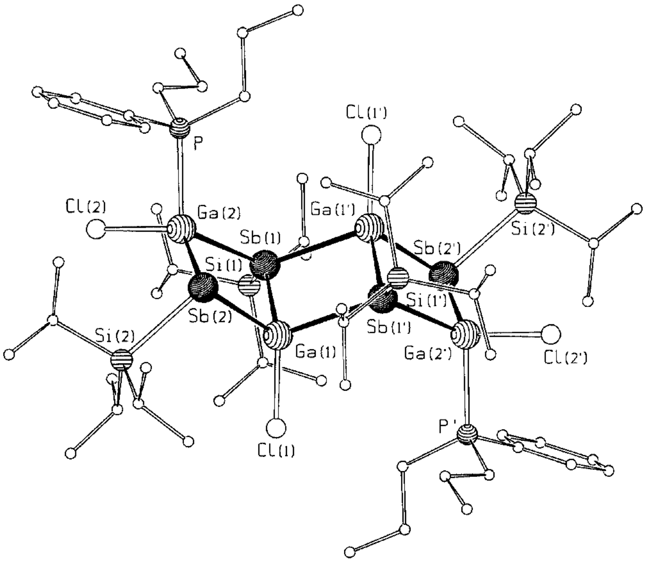

Figure 2. Molecular structure of **4**; selected bond lengths (pm) and bond angles (°): Ga(1)−Sb(1) 271.7(1), Ga(1)−Sb(1′) 269.1(1), Ga(1)−Sb(2) 264.4(1), Ga(2)−Sb(1) 266.2(1) Ga(2)−Sb(2) 261.8(1), Ga(1)−Cl(1) 222.5(2), Ga(2)−Cl(2) 222.9(2), Ga(2)−P: 242.9(2), Sb(1)−Si(1) 258.9(2), Sb(2)−Si(2) 259.1(2); Ga(1)−Sb(1)−Ga(2) 80.4(1), Ga(1)−Sb(1)−Ga(1′) 86.3(1), Ga(1′)−Sb(1)−Ga(2) 117.7(1), Ga(1)−Sb(2)−Ga(2) 82.6(1), Sb(1)−Ga(1)−Sb(2) 97. 0(1), Sb(1)−Ga(1)−Sb(1′) 93.7(1), Sb(1′)−Ga(1)−Sb(2) 110.9(1), Sb(1)−Ga(2)−Sb(2) 99.0(1), Cl(2)−Ga(2)−P 93.3(1)

The coordination sphere of the outer Ga atoms [Ga(2) and Ga(2′)] in **4** is completed by the phosphane ligands, so that all Ga atoms have coordination number four. The Sb atoms in **4** have two different coordination numbers: the Sb atoms of the central ring [Sb(1) and Sb(1′)] have a coordination number of four, whereas the outer Sb atoms are trigonal pyramidal coordinated. The Ga−Sb bond lengths in **4** vary greatly. In the central ring they are 269.1(1) to 271.7(1) pm long, whereas the Ga(1)−Sb(2) and the Ga(2)−Sb(1) bond lengths are 264.4(1) and 266.2(1) pm, respectively. The shortest Ga−Sb bond known so far can be observed between Ga(2) and Sb(2) [261.8(1) pm].

The UV/Vis spectrum of the yellow compound **3** shows a first absorption maxima at 425 nm. The red compound **4** reveals the first absorption maxima at 450 nm. In the IR spectra of both compounds the typical peaks of the $PnPr_2Ph$ ligands and the $SiiPr_3$ groups are observed.

Thermogravimetric analysis of compound **3** under vacuum shows a one-step decomposition in the temperature range of 110 to 160 °C. The on-line mass spectra of the cleavage products shows the phosphane ligands and the silyl groups. The overall mass loss is 70.0% (calculated for the formation of GaSb: 66.9%). Powder X-ray diffraction measurements of the grey residue obtained display only the reflections of cubic GaSb. From element analyses the carbon content of the residue was determined to be 1.5(5)%. Analogous thermogravimetric experiments on **4** show a two-step decomposition. In a first step, between 75 and 120 °C, the cleavage of the crystal solvent can be observed (mass loss: calcd. 7.5%, observed 7.1%). At 180 °C all volatile constituents have been eliminated and the formation of cubic GaSb occurs.

Experimental Section

All manipulations were performed with rigorous exclusion of oxygen and moisture using a Schlenk line and nitrogen atmosphere. Solvents were dried and freshly distilled before use. $[(DME)LiE(SiMe_3)_2]_2$ was prepared according to a literature procedure.[7] $GaCl_3$ (99.99%) and $i$$Pr_3SiCl$ (97%) were obtained from Aldrich and used as received.

$\boldsymbol{i}$Pr$_3$SiAs(SiMe$_3$)$_2$ (1): A mixture of $i$$Pr_3SiCl$ (12.1 g) in DME (20 mL) was added to a solution of $[(DME)LiAs(SiMe_3)_2]_2$ (20 g, 63 mmol) in DME (200 mL) over a period of two hours at 0 °C. Subsequently the reaction mixture was stirred for an additional 16 hours at room temperature and then filtered. All volatile components were then removed under vacuum and the resulting residue was fractionally distilled to give **1** as a highly viscous liquid at 90−100 °C and 10^{-3} mbar. Yield: 15.5 g (65%). ^1H NMR (C_6D_6): δ = 0.52 (s, 18 H, $SiMe_3$), 1.29 (m, 21 H, Si$i$$Pr_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 5.7 (s, $SiMe_3$), 15.8 [s, $CH(CH_3)_2$], 20.3 [s, $CH(CH_3)_2$] ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = 2.4 (s, $SiMe_3$), 25.0 (s, Si$i$$Pr_3$) ppm. MS (EI, 70 eV): m/z (%) = 378 (30) [M^+], 363 (0.5) [M^+ − Me], 335 (1) [M^+ − iPr], 293 (0.7) [M^+ − iPr, − CH_2CHCH_3], 251 (0.7) [M^+ − 2iPr − CH_2CHCH_3], 206 (22) [M^+ − Me − Si$i$$Pr_3$], 157 (18) [Si$i$$Pr_3$], 73 (100) [$SiMe_3$].

$\boldsymbol{i}$Pr$_3$SiSb(SiMe$_3$)$_2$ (2): A mixture of $i$$Pr_3SiCl$ (10.5 g) in DME (20 mL) was added to a solution of $[(DME)LiSb(SiMe_3)_2]_2$ (20 g, 55 mmol) in DME (200 mL) over a period of two hours at 0 °C. Subsequently the reaction mixture was stirred for an additional 16 hours at room temperature and then filtered. All volatile components were removed under vacuum and the resulting residue was fractionally distilled to give **2** as a highly viscous liquid at 110−120 °C and 10^{-3} mbar. Yield: 13.5 g (58%). ^1H NMR (C_6D_6): δ = 0.58 (s, 18 H, $SiMe_3$), 1.27 (m, 21 H, Si$i$$Pr_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 6.0 (s, $SiMe_3$), 15.4 [s, $CH(CH_3)_2$], 20.6 [s, $CH(CH_3)_2$] ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ = −10.2 (s, $SiMe_3$), 27.1 (s, Si$i$$Pr_3$) ppm. MS (EI, 70 eV): m/z (%) = 424 (4) [M^+], 409 (0.4) [M^+ − Me], 252 (5) [M^+ − Me − Si$i$$Pr_3$], 157 (30) [Si$i$$Pr_3$], 73 (100) [$SiMe_3$].

3: P$n$$Pr_2Ph$ (0.94 g, 4.88 mmol) was added to a solution of $GaCl_3$ (0.43 g, 2.44 mmol) in 30 mL of $i$$Pr_2O$. After stirring for one hour $i$$Pr_3SiSb(SiMe_3)_2$ (1.04 g, 2.44 mmol) was added. The reaction mixture was then stirred for an additional 24 hours. Subsequently the resulting red solution was filtered to remove small amounts of insoluble residues and the volume was reduced to 10 mL under vacuum. After addition of 5 mL heptane and cooling to 6 °C yellow crystals of **3** formed over a period of two days. Yield: 0.59 g (42%). $C_{42}H_{80}Cl_2Ga_2P_2Sb_2Si_2$ (1157.02): calcd. C 43.60, H 6.97; found C 43.16, H 6.98. $^{31}P\{^1H\}$ NMR (C_6D_6/P$n$$Pr_2Ph$): δ = −30.5 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3077(w), 3049(w), 2960(s), 2937(vs), 2860(vs), 1983(vw), 1959(vw), 1906(vw), 1806(vw), 1758(vw), 1484(m), 1463(vs), 1437(vs), 1407(m), 1380(m), 1364(w), 1358(w), 1226(m), 1105(w), 1068(s), 1027(m), 995(vs), 918(m), 882(s), 842(w), 828(m), 770(w), 746(vs), 693(s), 658(vs), 634(s), 557(vs), 503(m), 489(w), 459(s), 393(w) cm^{-1}. UV/Vis (suspension in mineral oil): λ_{max} = 425 nm (sh), 370 (sh), 260, 220.

4: Compound **3** (0.2 g) was dissolved in 2 mL benzene and stirred for two hours at room temperature. Subsequently the solution was cooled to 6 °C. After three days red crystals of **4** formed from this solution. Yield: 0.1 g (54%). $C_{60}H_{122}Cl_4Ga_4P_2Sb_4Si_4 \cdot 2\ C_6H_6$ (2081.77): calcd. C 41.54, H 6.49; found C 41.38, H 6.96. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −20.2 (s) ppm. IR (KBr): $\tilde{\nu}$ = 3087(vw), 3059(w), 3033(vw), 2960(s), 2939(vs), 2862(vs), 1959(vw), 1859(w), 1816(vw), 1459(vs), 1437(s), 1413(w), 1384(m), 1365(w), 1292(w), 1224(m), 1105(w), 1083(m), 1069(m), 1020(s), 993(s), 918(m), 878(vs), 846(w), 802(w), 740(m), 690(m), 693(s), 658(m), 639(s), 564(s), 520(w), 494(vs), 458(m) cm^{-1}. UV/Vis (suspension in mineral oil): λ_{max} = 450 nm, 380 (sh), 300.

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[4] STOE-IPDS2, graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å. **3**: a = 2070.9(4), b = 1201.7(2), c = 2125.6(4) pm, $\alpha = \beta = \gamma$ = 90°, V = 5290.0(2) × 10^6 pm^3; orthorhombic, $Pna2_1$, Flack parameter. 0.609, Z = 4, ρ_{ber} = 1.453 g/cm^3, μ(Mo-K_α) = 2.251 mm^{-1}, T = 200 K, 2Θ_{max} = 52°; 12172 reflections measured, 7798 independent reflections, (R_{int} = 0.0287), 7035 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2, 470 parameters (Ga, Sb, Si, P, Cl, C refined anisotropically, H atoms calculated at ideal positions), $R1$ = 0.0312, $wR2$ = 0.0856 (all data), residual electron density: 0.618 e/Å^3. **4**·2C_6H_6: a = 1386.4(3), b = 2006.5(4), c = 1679.2(3) pm, α = 90°, β = 97.12(3)°, γ = 90°, V = 4634.9(16) × 10^6 pm^3; monoclinic, $P2_1/n$, Z = 2, ρ_{ber} = 1.492 g/cm^3, μ(Mo-K_α) = 2.527 mm^{-1}, T = 200 K, 2Θ_{max} = 52°; 16486 reflections measured, 8252 independent reflections, (R_{int} = 0.0754), 5909 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2, 406 parameters

(Ga, Sb, Si, P, Cl, C refined anisotropically, H atoms calculated at ideal positions), $R1 = 0.0475$, $wR2 = 0.1126$ (all data), residual electron density: 1.365 e/Å^3. CCDC-187743 (**3**) and CCDC-187744 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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