

Dichlorogallane (HGaCl₂)₂: Its Molecular Structure and Synthetic Potential

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Dichlorogallane (HGaCl₂)₂ is readily prepared from gallium trichloride and triethylsilane in quantitative yield. Its crystal structure has been determined by single crystal X-ray diffraction. In the chlorine-bridged dimers of crystallographically imposed C_{2h} symmetry, the terminal hydrogen atoms are in trans positions. In the reaction with 2 equiv of triethylphosphine, the mononuclear complex (Et₃P)GaHCl₂ is formed. Thermal decomposition of (HGaCl₂)₂ affords hydrogen gas and quantitative yields of “GaCl₂” as mixed-valent Ga[GaCl₄]. Treatment of this product with triethylphosphine gives the symmetrical, Ga–Ga-bonded gallium(II) complex [GaCl₂(PEt₃)₂] with an ethane-type structure and with the phosphine ligands in a single-trans conformation. The corresponding [GaBr₂(PEt₃)₂] complex is prepared from Ga[GaBr₄] and has an analogous structure. (Et₃P)GaCl₃ has been synthesized and structurally characterized as a reference compound.

Introduction

Simple binary and ternary gallium hydrides were elusive compounds for several decades until important prototypes could be isolated and characterized by advanced preparative, spectroscopic, and structural techniques.^{1–4} One of these approaches used the reaction of anhydrous gallium chloride (GaCl₃)₂ with trimethylsilane, Me₃SiH, which was first found to give the monosubstitution product (HGaCl₂)₂ in 1965.² Under modified reaction conditions this method could be extended to the synthesis of chlorogallane (H₂GaCl)₂ and finally gallane (GaH₃)₂ in 1988 and 1989, respectively.^{3,4} While the structures of the di- and trihydride could since be determined by electron diffraction methods,^{3,4} the original proposal of the structure of the monohydride (a chlorine-bridged dimer with trans-terminal hydrogen atoms)^{2,5} has not

yet been confirmed. In the present study this structure has been verified in a low-temperature single-crystal study.

Because HGaCl₂ was found to be a useful starting material for a number of conversions, including some hydrogallation reactions,⁶ the preparative procedure used for its synthesis has recently been optimized for the more convenient liquid triethylsilane instead of gaseous trimethylsilane.⁷ In the course of this work it was observed that the thermolabile (HGaCl₂)₂ is an excellent source for pure “GaCl₂”. This is demonstrated here by a convenient high-yield synthesis of the triethylphosphine complex [GaCl₂(PEt₃)₂] via this route. The corresponding bromine compound has also been isolated and structurally characterized. Finally, the complexes (Et₃P)-GaHCl₂ and (Et₃P)GaCl₃ were synthesized as reference compounds, and the structure of the latter was determined.

Results

Dichlorogallane and Its Triethylphosphine Complex. Treatment of anhydrous GaCl₃ with equimolar quantities of triethylsilane in the absence of a solvent at –20 °C and

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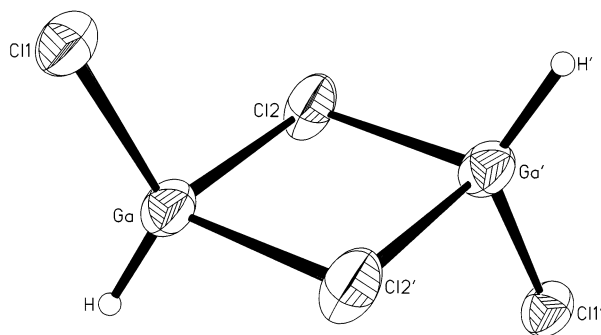


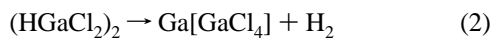
Figure 1. ORTEP drawing for $(\text{HGaCl}_2)_2$ showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Bond lengths (in angstroms) and angles (in degrees) are as follows: Ga–Cl1, 2.1538(5); Ga–Cl2, 2.3165(5); Ga–Cl2', 2.3383(5); Ga–H, 1.39(2); Cl1–Ga–Cl2, 104.77; Cl1–Ga–Cl2', 101.98(2); Cl2–Ga–Cl2', 89.47(2); Ga–Cl2–Ga', 90.53(2); Cl1–Ga–H, 127(1); Cl2–Ga–H, 112(1); Cl2'–Ga–H, 114(1).

subsequent warming to 5 °C affords virtually quantitative yields of $(\text{HGaCl}_2)_2$ (eq 1). Cooling of the clear and colorless liquid reaction mixture to –30 °C overnight gives large single crystals of the product in a mother liquor of chlorotriethylsilane.



Crystals of $(\text{HGaCl}_2)_2$ are monoclinic, space group $C2/c$, with $Z = 4$ molecules in the unit cell. The asymmetric unit contains a HGaCl_2 monomer from which the dimer can be generated through the symmetry operations of point group C_{2h} , which places the two hydrogen atoms in trans positions (Figure 1). Dimerization thus occurs via chlorine bridges as proposed on the basis of early spectroscopic data.^{2,5} The four-membered ring is almost an ideal square, with the Ga–Cl–Ga' and Cl–Ga–Cl' angles at 90.53(2)° and 89.47(2)° and Ga–Cl2 and Ga–Cl2' distances of 2.3165(5) and 2.3383(5) Å, respectively. As expected, these bridge distances are longer than the terminal distances Ga–Cl1/Ga–Cl1' of 2.1538(5) Å. The data are generally in good agreement with reference values^{3,8} of $(\text{H}_2\text{GaCl}_2)_2$ and $(\text{GaCl}_3)_2$. The two hydrogen atoms have been located at a Ga–H distance of 1.39(2) Å with an exocyclic angle H–Ga–Cl1 of 127(1)°. Figure 2 shows the shortest contacts between molecules in the crystal. All intermolecular Ga–Cl distances are close to the standard van der Waals distances.

Removal of all volatiles from the reaction mixture obtained from gallium trichloride and triethylsilane (eq 1) leaves crude $(\text{HGaCl}_2)_2$ in quantitative yield. Heating of this residue to 150 °C for 1 h induces strong effervescence and complete dehydrogenation to give colorless crystalline “ GaCl_2 ”. The residual mass corresponds to quantitative conversion.



For purification the product can be crystallized from benzene or other aromatic hydrocarbons (where the compound dissolves as a thermolabile arene adduct),⁹ but owing to the high solubility of the compound, this process leads to

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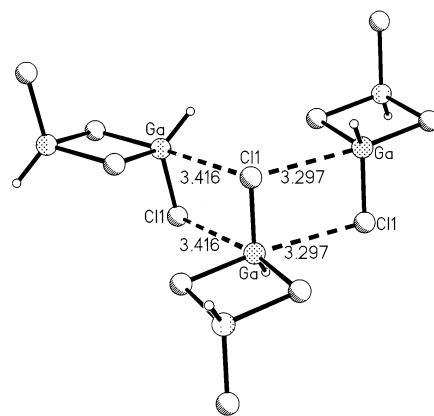
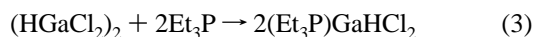


Figure 2. Shortest intermolecular Ga–Cl distances in the lattice of $(\text{HGaCl}_2)_2$.

a serious lowering of the yield. For conversion of “ GaCl_2 ”, which is known to exist as mixed-valent $\text{Ga}[\text{GaCl}_4]$ both in the solid¹⁰ and in hydrocarbon solution,⁹ into its complexes or derivatives, purification through crystallization is generally not necessary.



For the preparation of the 1:1 complex of HGaCl_2 and PEt_3 , 2 equiv of triethylphosphine are added slowly to a solution of $(\text{HGaCl}_2)_2$ in diethyl ether at –20 °C (eq 3). Cooling of the reaction mixture to –78 °C gives a colorless precipitate, which can be isolated (92% yield) by filtration, washing with cold pentane, and drying in a vacuum (mp 4–7 °C). The composition has been confirmed by elemental analysis. The IR spectrum has a strong Ga–H stretching vibration band at 1930 cm^{-1} . Solutions in benzene- d_6 give a broad ^1H NMR signal at 5.3 ppm for Ga–H, together with the expected dt and dq multiplets for the methyl and methylene hydrogen atoms, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows two doublet signals for methyl and methylene carbon atoms, and the $^{31}\text{P}\{^1\text{H}\}$ spectrum has only a broad singlet signal at –9.1 ppm, probably owing to quadrupole broadening induced by the neighboring gallium nuclei. Attempts to prepare the corresponding dibromogallane $(\text{HGaBr}_2)_2$ by the analogous procedure were not successful. The reactions of trimethyl- or triethylsilane with GaBr_3 gave only unstable gallium bromide hydrides of ill-defined stoichiometry.

Bis(triethylphosphine)digallium Tetrachloride and Tetra-bromide. The $\text{Ga}[\text{GaCl}_4]$ samples prepared by the above thermal dehydrogenation of $(\text{HGaCl}_2)_2$ are readily dissolved in toluene to give arene complexes.⁹ Addition of stoichiometric quantities of triethylphosphine (molar ratio 1:2) at –78 °C results in a red solution that becomes colorless upon

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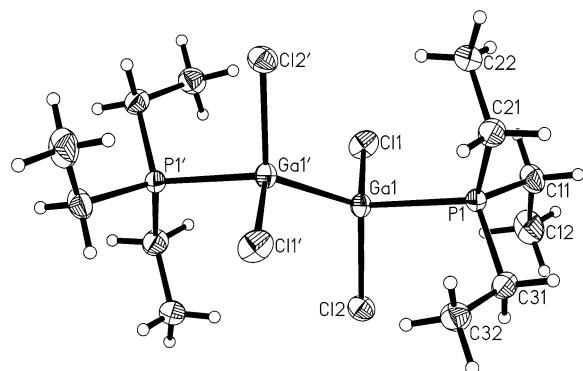
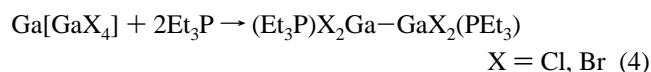


Figure 3. ORTEP drawing for $[\text{GaCl}_2(\text{PEt}_3)_2]$ showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (in angstroms) and angles (in degrees) are as follows: Ga–Ga', 2.4269(5); Ga–Cl1, 2.2248(6); Ga–Cl2, 2.2333(6); Ga–P, 2.4269(5); Cl1–Ga–Ga', 113.51(2); Cl2–Ga–Ga', 115.70(2); P–Ga–Ga', 117.65(2); Cl1–Ga–Cl2, 105.46(3); Cl1–Ga–P, 103.77(2); Cl2–Ga–P, 98.88(2).

warming to room temperature. Cooling to $-78\text{ }^\circ\text{C}$ affords colorless crystals of the product ($X = \text{Cl}$, mp $115\text{--}122\text{ }^\circ\text{C}$, 92% yield):



The corresponding bromide complex was obtained from PEt_3 and $\text{Ga}[\text{GaBr}_4]$ prepared via established synthetic methods¹¹ ($X = \text{Br}$, mp $132\text{--}137\text{ }^\circ\text{C}$, 94% yield).

The composition of both complexes was confirmed by elemental analyses. The $^{31}\text{P}\{^1\text{H}\}$ spectra of the two compounds (in C_6D_6 at $20\text{ }^\circ\text{C}$) show broad singlet resonances at -6.1 and -9.8 ppm for the chlorine and bromine compound, respectively, indicating equivalent phosphine ligands in both complexes. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra of $(\text{Et}_3\text{P})\text{Cl}_2\text{Ga} - \text{GaCl}_2(\text{PEt}_3)$ give only two broad resonances with unresolved coupling, probably owing to rapid ligand exchange in solution. By contrast, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra of $(\text{Et}_3\text{P})\text{Br}_2\text{Ga} - \text{GaBr}_2(\text{PEt}_3)$ show resonances of higher complexity. The multiplicity pattern is not in agreement with an $\text{A}_3\text{B}_2\text{X}$ spin system expected for a simple PEt_3 unit. This complexity originates from $^3J(^{31}\text{P} - ^{31}\text{P})$ coupling across the Ga–Ga bond, which leads to an $\text{A}_2\text{XX}'\text{A}'_2$ spin system for the methylene ^1H resonances and to an AXX' spin system for the methylene ^{13}C resonance. [Note that no such complexity is observed for $(\text{Et}_3\text{P})\text{GaHCl}_2$ with its single PEt_3 ligand.]

Crystals of $(\text{Et}_3\text{P})\text{Cl}_2\text{Ga} - \text{GaCl}_2(\text{PEt}_3)$ (from toluene/pentane) are orthorhombic, space group $Pbca$, with $Z = 4$ formula units in the unit cell. In each of the dinuclear molecules, the two halves are symmetry-related by centers of inversion midway between the two gallium atoms (Figure 3). The Ga–Ga' distance is $2.4269(5)\text{ \AA}$, in good agreement with reference compounds featuring a discrete Ga–Ga single bond.¹² The Ga–P distance is $2.3943(6)\text{ \AA}$, and the Ga–Cl distances are $2.2248(6)$ and $2.2333(6)\text{ \AA}$. The overall conformation can be described as ethane-like staggered and single-trans. The PEt_3 ligands show no structural anomalies.

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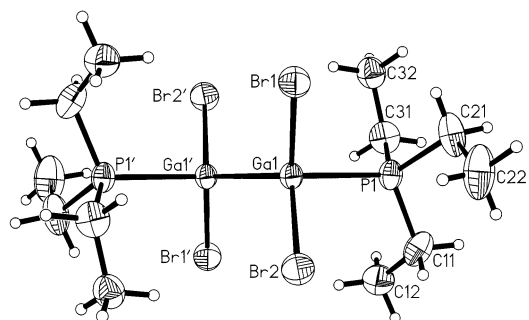
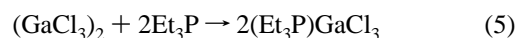


Figure 4. ORTEP drawing for $[\text{GaBr}_2(\text{PEt}_3)_2]$ showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (in angstroms) and angles (in degrees) are as follows: Ga–Ga', 2.427(1); Ga–Br1, 2.368(1); Ga–Br2, 2.377(1); Ga–P, 2.400(2); Br1–Ga–Ga', 113.11(5); Br2–Ga–Ga', 114.32(5); P–Ga–Ga', 117.60(6); Br1–Ga–Br2, 106.16(4); Br1–Ga–P, 102.38(6); Br2–Ga–P, 101.75(6).

Crystals of $(\text{Et}_3\text{P})\text{Br}_2\text{Ga} - \text{GaBr}_2(\text{PEt}_3)$ (from toluene) are monoclinic, space group $P2_1/c$, with $Z = 2$ formula units of the complex and some disordered toluene solvent in the unit cell. The substituents of the dinuclear molecule with its single-trans conformation are also related by a crystallographically imposed center of inversion (Figure 4). The Ga–Ga' distance of $2.427(1)\text{ \AA}$ is the same as in the chlorine analogue (above). The two gallium atoms are in a distorted tetrahedral environment with the Ga–P bond length at $2.400(2)$ and the Ga–Br bond lengths at $2.368(1)$ and $2.377(1)\text{ \AA}$.

(Triethylphosphine)trichlorogallium. $(\text{Et}_3\text{P})\text{GaCl}_3$ is readily obtained from equivalent quantities of gallium trichloride and triethylphosphine¹³ in diethyl ether. Solutions of the product in C_6D_6 ($20\text{ }^\circ\text{C}$) show the expected $\text{A}_3\text{B}_2\text{X}$ multiplicity for the proton resonances, two doublet ^{13}C resonances, and a quadrupole-broadened singlet as the ^{31}P resonance (at -4.6 ppm).



Crystals of $(\text{Et}_3\text{P})\text{GaCl}_3$ (from diethyl ether) are monoclinic, space group $P2_1/n$, with $Z = 4$ formula units in the unit cell. The molecule has no crystallographically imposed symmetry, but the deviations of the valence and torsional angles from an ethane-type configuration/conformation are small (Figure 5). The Ga–P distance [$2.3531(5)\text{ \AA}$] and the Ga–Cl distances [$2.1746(5)$, $2.1756(5)$, and $2.1836(5)\text{ \AA}$] in this gallium(III) complex are all shorter than those observed in the dinuclear gallium(II) compound (above), indicating the influence of the oxidation state of the metal atom.

Summary

A convenient high-yield synthesis of dichlorogallane dimer from $(\text{GaCl}_3)_2$ and triethylsilane is presented. The dinuclear,

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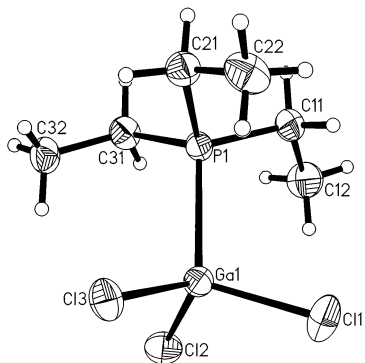


Figure 5. ORTEP drawing for $(\text{Et}_3\text{P})\text{GaCl}_3$ showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (in angstroms) and angles (in degrees) are as follows: Ga–Cl1, 2.1746(5); Ga–Cl2, 2.1756(5); Ga–Cl3, 2.1836(5); Ga–P, 2.3531(5); Cl1–Ga–Cl2, 111.47(2); Cl1–Ga–Cl3, 108.60(2); Cl2–Ga–Cl3, 110.84(2); Cl1–Ga–P, 109.41(2); Cl2–Ga–P, 107.66(2); Cl3–Ga–P, 108.84(2).

chlorine-bridged trans-structure of $(\text{HGaCl}_2)_2$ has been confirmed by single-crystal low-temperature X-ray diffraction. The compound forms a mononuclear 1:1 complex with triethylphosphine $[(\text{Et}_3\text{P})\text{GaHCl}_2]$. Thermal decomposition of $(\text{HGaCl}_2)_2$ leads to quantitative conversion into mixed-valent $\text{Ga}[\text{GaCl}_4]$ with evolution of hydrogen gas. This procedure is presently the most economical preparative pathway for $\text{Ga}[\text{GaCl}_4]$ and its complexes.

Treatment of $\text{Ga}[\text{GaCl}_4]$ (in toluene) with triethylphosphine gives symmetrical, Ga–Ga-bonded $(\text{Et}_3\text{P})\text{Cl}_2\text{Ga}–\text{GaCl}_2(\text{PEt}_3)$. The corresponding bromine complex was obtained from $\text{Ga}[\text{GaBr}_4]$ and PEt_3 . The molecular structure of the two gallium(II) compounds have been determined. The molecules adopt ethane-like conformations (single-trans) with crystallographically imposed inversion symmetry. The Ga–Ga bond lengths [2.427(1) Å] represent standard metal–metal single bonds comparable to data available for a whole series of complexes of the general formula $\text{LX}_2\text{Ga}–\text{GaX}_2\text{L}$ with X = halogen and L = donor ligand.

The 1:1 complex $(\text{Et}_3\text{P})\text{GaCl}_3$ was prepared from its components in diethyl ether and its structure has been determined. A comparison with the above data shows the influence of the oxidation state of the metal atom on the bond lengths. Ga–P and Ga–Cl bonds are significantly shorter for gallium(III) than for gallium(II), while the general tetrahedral configuration of the gallium atoms is very similar.

Experimental Section

All experiments were carried out in an atmosphere of dry and pure nitrogen in Schlenk apparatus. Solvents were dried and saturated with nitrogen; glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. Gallium metal, gallium trichloride, triethylsilane, and triethylphosphine were commercially available. $\text{Ga}[\text{GaBr}_4]$ was prepared following a literature procedure.¹¹

Dichlorogallane(III) $(\text{HGaCl}_2)_2$ was synthesized with a slightly modified recent literature procedure⁷ by mixing anhydrous gallium trichloride (3.12 g, 8.86 mmol of dimer) and triethylsilane (2.27 g, 19.5 mmol, 1.63 mL) at -20°C . The reaction mixture was allowed to warm slowly to 5°C until a clear solution was formed. Cooling to -30°C overnight gave large single crystals. After filtration and

removal of all remaining volatiles in vacuo at 0°C pure $(\text{HGaCl}_2)_2$ was obtained; 2.38 g (95% yield).

(Triethylphosphine)dichlorogallane(III) $[(\text{Et}_3\text{P})\text{GaHCl}_2]$. Dichlorogallane(III) (2.01 g, 7.38 mmol of dimer) was dissolved in diethyl ether (20 mL) at -20°C , and triethylphosphine (1.76 g, 14.8 mmol) was added slowly with stirring. After 1 h the reaction mixture was cooled to -78°C to give a precipitate of the product, which was filtered, washed with cold pentane (2×20 mL, -15°C) and dried in a vacuum; mp $4–7^\circ\text{C}$, 3.53 g (92% yield). IR (film on KBr, cm^{-1}) 2977 s, 2931 s, 2901 m, 1930 s [$\nu(\text{Ga–H})$], 1455 s, 1411 s, 1388 m, 1261 w, 1046 s, 772 s, 740 m, 609 s, 672, s. ^1H NMR (C_6D_6 , 23°C) 0.67 (dt, $J = 7.7$ and 17.2 Hz, 9H, Me), 1.12 (dq, $J = 7.7$ and 12.5 Hz, 6H, CH_2), 5.3 (br s, 1H, GaH). $^{13}\text{C}\{^1\text{H}\}$ NMR 7.0 (s, Me); 12.3 (d, $J = 26.9$ Hz, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR -9.1 (br s). Anal. Calcd for $\text{C}_6\text{H}_{16}\text{Cl}_2\text{GaP}$: C, 27.74; H, 6.21; Cl, 27.29; P, 11.92. Found: C, 27.98; H, 6.19; Cl, 26.51; P, 11.54.

Bis(triethylphosphine)tetrachlorodigallane(II) $[\text{GaCl}_2(\text{PEt}_3)]_2$. Thermal decomposition of dichlorogallane(III) (835.62 mg, 2.95 mmol) by slowly heating the sample to 150°C (2 h) gave $\text{Ga}[\text{GaCl}_4]$ (830 mg, 2.95 mmol) and hydrogen gas. This product was dissolved in toluene (20 mL) at -78°C , and triethylphosphine (700 mg, 5.90 mmol) dissolved in toluene (20 mL) was added slowly and with stirring. The reaction mixture initially turned deep red but became colorless upon warming to room temperature. Cooling of the solution to -78°C overnight gave a precipitate of the product, which was filtered, washed with hexane (2×20 mL), and dried in a vacuum; mp $115–122^\circ\text{C}$, 1.40 g (92% yield). ^1H NMR (C_6D_6 , 23°C) 0.88 (br s, 9H, Me); 1.40 (br s, 6H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR 7.43 (br s, Me); 12.70 (s, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR -6.1 (br s). Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{Cl}_4\text{Ga}_2\text{P}_2$: C, 27.85; H, 5.84; Cl, 27.40; P, 10.53. Found: C, 27.39; H, 5.74; Cl, 27.07; P, 11.03.

Bis(triethylphosphine)tetrabromodigallane(II) $[\text{GaBr}_2(\text{PEt}_3)]_2$. To a vigorously stirred suspension of $\text{Ga}[\text{GaBr}_4]$ (955 mg, 2.08 mmol) in toluene (15 mL) was slowly added at -78°C a solution of triethylphosphine (500 mg, 4.19 mmol) in toluene (15 mL). The resulting deep red reaction mixture was allowed to warm to room temperature. After the color had disappeared completely, the clear solution was again cooled to -78°C overnight to give a precipitate, which was filtered, washed twice with hexane (2×15 mL), and dried in a vacuum; mp $132–137^\circ\text{C}$, 1.36 g (94% yield). ^1H NMR (C_6D_6 , 23°C) 0.90 (dt, $J = 7.7$ and 16.8 Hz, 9H, Me), 1.48 [$A_2XX'A_2$, $N = J(\text{AX}) - J(\text{AX}') = 7.2$ Hz, 6H, CH_2]. $^{13}\text{C}\{^1\text{H}\}$ NMR 7.51 (s, Me), 12.93 [AXX' , $N = J(\text{AX}) - J(\text{AX}') = 24.6$ Hz, CH_2]. $^{31}\text{P}\{^1\text{H}\}$ NMR -9.8 (br s). Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{Br}_4\text{Ga}_2\text{P}_2$: C, 20.73; H, 4.35; Br, 45.96; P, 8.90. Found: C, 20.50; H, 4.35; Br, 46.50; P, 8.33.

(Triethylphosphine)trichlorogallium(III) $(\text{Et}_3\text{P})\text{GaCl}_3$. Anhydrous gallium trichloride (1.03 g, 2.94 mmol of dimer) was dissolved in diethyl ether at -78°C , and triethylphosphine (0.70 g, 5.87 mmol) was slowly added with stirring. A colorless precipitate formed, which was filtered after warming to room temperature, washed with hexane (2×15 mL), and dried in a vacuum. Some more crystalline product can be obtained by slowly evaporating the diethyl ether from the mother liquor in a steady stream of dry nitrogen, mp $105–108^\circ\text{C}$, 1.68 g (97% yield). ^1H NMR (C_6D_6 , 23°C) 0.73 (dt, $J = 7.7$ and 18.1 Hz, 9H, Me), 1.20 (dq, $J = 7.7$ and 2.7 Hz, 6H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR 6.93 (d, $J = 3.6$ Hz, Me), 12.0 (d, $J = 29.1$ Hz, CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR -4.6 (br s). Anal. Calcd for $\text{C}_6\text{H}_{15}\text{Cl}_3\text{GaP}$: C, 24.29; H, 5.14; Cl, 36.15; P, 10.53. Found: C, 23.94; H, 4.97; Cl, 36.39; P, 9.85.

Crystal Structure Determination. Specimens of suitable quality and size of $(\text{HGaCl}_2)_2$, $[\text{GaCl}_2(\text{PEt}_3)]_2$, $[\text{GaBr}_2(\text{PEt}_3)]_2$, and $(\text{Et}_3\text{P})\text{GaCl}_3$ were mounted on the ends of quartz fibers in F06206R oil

Table 1. Crystal Data, Data Collection, and Structure Refinement of (HGaCl₂)₂, [GaCl₂(PEt₃)₂]₂, [GaBr₂(PEt₃)₂]₂, and (Et₃P)GaCl₃

	[HGaCl ₂] ₂	[GaCl ₂ (PEt ₃) ₂] ₂	[GaBr ₂ (PEt ₃) ₂] ₂	[GaCl ₃ (PEt ₃)]
empirical formula	H ₂ Cl ₄ Ga ₂	C ₁₂ H ₃₀ Cl ₄ Ga ₂ P ₂	C ₁₂ H ₃₀ Br ₄ Ga ₂ P ₂ ^a	C ₆ H ₁₅ Cl ₃ GaP
M	283.26	517.54	695.38 ^a	294.22
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	6.2022(2)	11.0151(1)	13.1721(5)	7.3043(2)
<i>b</i> /Å	11.9315(4)	14.1424(1)	8.1498(3)	12.8006(4)
<i>c</i> /Å	9.8978(3)	14.2508(2)	13.7591(6)	13.3458(4)
α /deg	90	90	90	90
β /deg	93.518(2)	90	92.023(1)	91.546(1)
γ /deg	90	90	90	90
<i>U</i> /Å ³	731.07(4)	2219.99(4)	1476.1(1)	1247.37(6)
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.574	1.548	1.565 ^a	1.567
<i>Z</i>	4	4	2	4
<i>T</i> /K	143	143	143	143
reflns measured	15 708	65 230	61 557	46 636
reflns unique	1241	2460	3206	2657
<i>R</i> _{int}	0.058	0.049	0.0594	0.0396
refined parameters/restraints	32/0	152/0	92/0	160/0
<i>R</i> 1 [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0250	0.0327	0.0588	0.0227
<i>wR</i> 2	0.0594	0.0846	0.1518	0.0531
weighting scheme	<i>a</i> = 0.0000, <i>b</i> = 0.2656	<i>a</i> = 0.0516, <i>b</i> = 1.4302	<i>a</i> = 0.1365, <i>b</i> = 36.0216	<i>a</i> = 0.0164, <i>b</i> = 0.3903
σ_{fin} (max/min)/e Å ⁻³	0.539/−0.458	0.637/−0.706	1.264/−0.759	0.303/−0.293

^a Without contributions of disordered solvent.

and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo K α radiation. All manipulations concerning (HGaCl₂)₂ were carried out under cooled nitrogen (ca. −20 °C). The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on *F*² (SHELXL-97).¹⁴ The thermal motion was treated anisotropically for all non-hydrogen atoms. Hydrogen atoms of [GaBr₂(PEt₃)₂]₂ were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions. In all other compounds, hydrogens were located and refined isotropically. The hydrogen atom of (HGaCl₂)₂ was attributed to the largest peak of residual electron density after the thermal motion of gallium and chlorine were refined anisotropically. The scattering contributions of a highly disordered toluene molecule, lying on a center of inversion, in [GaBr₂(PEt₃)₂]₂ were taken into account by using the SQUEEZE method (total potential solvent accessible volume is 341.3 Å³

containing 59 electrons/cell) followed by an absorption correction with DELABS. For (HGaCl₂)₂ and (Et₃P)GaCl₃ an absorption correction was carried out with DELABS. The procedures SQUEEZE and DELABS are both part of the PLATON suite of programs.¹⁵ Further information on crystal data, data collection, and structure refinement are summarized in Table 1.

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Supporting Information Available: Tables listing crystal data, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths and angles, hydrogen coordinates, and torsion angles for nog12, nog13, nog14, and nog16 (PDF format) and X-ray crystallographic files for (HGaCl₂)₂, [GaCl₂(PEt₃)₂]₂, [GaBr₂(PEt₃)₂]₂ and (Et₃P)GaCl₃ (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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