From Gallium Hydride Halides to Molecular Gallium Sulfides

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Received June 2nd, 2004.

Dedicated to Professor Martin Jansen on the Occasion of his 60th Birthday

Abstract. Complexes of the type (L)$GaHCl_2$, with L =tertiary phosphines or pyridines, have been prepared from $(HGaCl_2)_2$ and the ligands in diethyl ether. The products are stable crystalline solids soluble in common organic solvents. The presence of the Ga-H function has been confirmed by IR and NMR spectroscopy and by single crystal X-ray diffraction, carried out for the 1:1 adducts with L = PCy_3 and PPh_3 (two polymorphs) and for the 2:1 adduct with L = $(CH_2PPh_2)_2$ (dppe, two different solvates). The reaction of PVi_3 with $(HGaCl_2)_2$ gives an insoluble polymer owing to the hydrogallation of vinyl groups by the gallium hydride units (no Ga-H functions are left in the product).Treatment of the complexes $(R_3P)GaHCl_2$ with H_2S, metal sulfides or $(Me_3Si)_2S$ gave only insoluble, ill-defined products. − The 1:1 adduct $(L')GaHCl_2$, with L′ = 4-dimethylamino-pyridine, reacts with $(Me_3Si)_2S$ in acetonitrile at ambient temperature to give an only partially sulfur-substituted product of the net formula $(L')GaSH_{0.66}Cl_{0.34}$. With excess ligand L′, under reflux conditions and after longer reaction times, a pyridine complex of the tetranuclear, molecular gallium sulfide Ga_4S_6 is obtained in low yield. The core of the compound with the composition $(L')_4Ga_4S_6$ has an adamantane structure resembling a cluster unit of the binary gallium sulfide polymorphs Ga_2S_3. The edge-sharing Ga_3S_3 six-membered rings are all in a chair conformation as found previously for the pyridine complexes of the ternary compounds $[(L)GaEX]_3$(with E = S, Se and X = Cl, Br) and for the bicyclic dication $[(L)_6Ga_4S_5]^{2+}$. Thermolysis and degradation under mass spectrometry conditions lead to sublimation of L′ and leave amorphous Ga_2S_3. The reaction of $(L')GaCl_3$ with $(Me_3Si)_2S$ did not afford any molecular gallium sulfide complex. A comparison of the structural data for $(L')GaCl_3$ and $(L')_4Ga_4S_6$ suggests a much poorer acceptor character of the gallium sulfide cluster.

Keywords: Gallium; Gallium hydride halides; Gallium sulfides

Von Galliumhydridhalogeniden zu molekularen Galliumsulfiden

Inhaltsübersicht. Komplexe des Typs (L)$GaHCl_2$, mit L = tertiäre Phosphine oder Pyridine, wurden aus $(HGaCl_2)_2$ und den Liganden in Diethylether dargestellt. Als Produkte wurden kristalline, stabile und in den üblichen organischen Lösungsmitteln lösliche Feststoffe erhalten. Die Anwesenheit der Ga-H-Funktion wurde durch IR- und NMR-Spektroskopie, sowie durch Einkristallröntgenstrukturanalysen der Addukte mit L = PCy_3 und PPh_3 (zwei polymorphe Formen) und des 2:1-Addukts mit L = $(CH_2PPh_2)_2$ (dppe, zwei verschiedene Solvate), bestätigt. Die Reaktion von PVi_3 mit $(HGaCl_2)_2$ führte aufgrund der Hydrogallierung der Vinylgruppen zu einem polymeren Produkt (im Produkt sind keine Ga-H-Funktionen mehr enthalten). Die Behandlung der Komplexe $(R_3P)GaHCl_2$ mit H_2S, Metallsulfiden oder $(Me_3Si)_2S$ ergab lediglich schwerlösliche, undefinierte Produkte. − Das 1:1-Addukt $(L')GaHCl_2$, mit L′ = 4-Dimethylaminopyridin, reagiert bei Raumtemperatur in Acetonitril mit $(Me_3Si)_2S$ zu einem teilweise Schwefel-substituierten Produkt der Nettozusammensetzung $(L')GaSH_{0.66}Cl_{0.34}$. Die längere Behandlung dieses Produkts mit überschüssigem Liganden L′ unter Rückfluß liefert in niedrigen Ausbeuten den Pyridinkomplex des vierkernigen molekularen Galliumsulfids Ga_4S_6. Das Grundgerüst der Verbindung $(L')_4Ga_4S_6$ mit adamantanartiger Struktur ähnelt einem Ausschnitt aus dem Gitter des binären Galliumsulfids Ga_2S_3. Die kondensierten Ga_3S_3-Sechsringe liegen in der Sesselkonformation vor, wie sie früher bereits bei den Pyridinkomplexen $[(L)GaEX]_3$ der ternären Verbindungen (mit E = S, Se und X = Cl, Br) und im bicyclischen Dikation $[(L)_6Ga_4S_5]^{2+}$ gefunden wurden. Thermolyse und Zersetzung unter massenspektroskopischen Bedingungen führen zur Sublimation von L′ unter Bildung von amorphem Ga_2S_3. Die Reaktion von $(L')GaCl_3$ mit $(Me_3Si)_2S$ ergab keine molekularen Galliumsulfid-Komplexe. Ein Vergleich der Strukturparameter von $(L')GaCl_3$ und $(L')_4Ga_4S_6$ weist auf ein deutlich vermindertes Akzeptorvermögen des Galliumsulfid-Clusters hin.

Introduction

There is currently an increasing interest in the construction of well-defined metal sulfides in the form of clusters, nanoparticles and larger frameworks [1]. While for several main group and transition metal sulfides great progress has been made in providing suitable starting materials and methodologies [2], this it not true for group XIII sulfides in general (B, Al, Ga, In, Tl), and for gallium sulfides in particular. Binary gallium sulfides are known to have complicated structures („defect structures“) with poor ordering in many of its polymorphs [3], and it was only recently that a few examples of smaller clusters have been introduced which represent building blocks of larger structures [4].

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DOI: 10.1002/zaac.200400203

In previous studies we have investigated the preparation, structure and derivatization of molecular, trinuclear units of the stoichiometry $[GaSX(L)]_3$. These complexes feature six-membered rings $(GaS)_3$ in chair or boat conformations with halogen substituents X and pyridine ligands L in axial and equatorial positions at each metal center in various isomeric patterns [5, 6]. The six-membered rings can be viewed as structural units of the gallium sulfide polymorphs with functional groups that can be used for the design and construction of larger arrays.

In the present account we show that these structural elements can be further extended to cage-type units including a molecular gallium sulfide Ga_4S_6 protected by *pyridine* ligands. It turned out that the pyridine ligands are essential for the formation and stability of the adducts. All complementary experiments, e.g. with tertiary *phosphines* as ligands L, were not successful. A series of complexes of gallium chlorides and hydride chlorides with tertiary phosphines were isolated and structurally characterized, as described below, but could not be converted into the corresponding gallium sulfide complexes.

Preparative Results

Recent investigations have shown that dichlorogallane $[HGaCl_2]_2$ − owing to its mixed functionality − is a particularly useful starting material for the preparation of mixed gallium chalcogenide halides (GaEX) and their complexes $[GaEX(L)]_n$ with E = S, Se and X = Cl, Br. With ligands L = *pyridines*, a large family of complexes has been obtained [5, 6]. Continuing this study, a series of analogous complexes with other ligands was now prepared.

$[HGaCl_2]_2$ is readily available from the reaction of anhydrous $[GaCl_3]_2$ with Et_3SiH without any solvent. Quantitative yields of a colorless crystalline, low-melting solid are obtained after removal of the volatile Et_3SiCl by-product [7, 8]. This dimeric product can be reacted with *tertiary phosphines* in the molar ratio 1:2 in diethyl ether to give high yields of the mononuclear complexes $[HGaCl_2(L)]$ (Equation (1)). With $[CH_2PPh_2]_2$ (dppe) the 1:2 complex is formed, which was crystallized as a 1:1 benzene and as a 2:1 diethyl ether solvate. Of $(Ph_3P)GaHCl_2$, solvent-free crystals of a triclinic and a monoclinic polymorph were obtained.

$$(HGaCl_2)_2 + 2\ PR_3 \rightarrow 2\ (R_3P)GaHCl_2 \qquad \begin{array}{l} PR_3 = PCy_3,\ PEt_3 \\ \qquad\quad PPh_3,\ 1/2\ \text{dppe} \end{array} \tag{1}$$

The adducts are colorless air-sensitive liquids ($L = Et_3P$) [8] or solids ($L = Cy_3P$ [9], Ph_3P, dppe) which are soluble in common inert organic solvents. The compounds have been identified by microanalytical and spectral data. The conservation of the Ga-H function in all products − except $(Vi_3P)GaHCl_2$ − is readily demonstrated by a strong IR absorption in the range 1920 − 1950 cm^{-1} and a broad proton resonance near 5.6 ppm. The complex with trivinylphosphine [10] is also unusual in that it is insoluble even in polar organic solvents and shows decomposition only on heating to elevated temperatures (Equation (2)). These observations indicate that the product is a polymer generated in the *hydrogallation* of vinyl substituents by the Ga-H functions.

$$n\ (HGaCl_2)_2 + 2n\ PVi_3 \rightarrow [Vi_2P(C_2H_4)GaCl_2]_{2n} \tag{2}$$

Upon complexation with $HGaCl_2$, the ^{31}P resonances of most phosphine ligands are shifted *upfield* relative to the free ligands, which at first sight may be unexpected, but for this phenomenon there are parallels in the literature [9, 11]. It appears that metal(III) halides MX_3 with larger halogen atoms X quite generally induce drastic *shielding* of the attached phosphorus nuclei, while with most other acceptors the usual *deshielding* is observed. All other NMR data show no anomalies.

Treatment of the complexes $[(R_3P)GaHCl_2]$ with sulfides [H_2S, SH^-, $(Me_3Si)_2S$ etc.] did not yield the expected gallium hydride sulfides. Insoluble products were formed the elemental analysis of which showed no clear stoichiometry. This route therefore was abandoned and efforts again turned to the *pyridine* complexes.

(*p*-Dimethylamino-pyridine)dichlorogallane [12] was chosen as the substrate, because its particularly powerful pyridine donor ligand (L′) suggested higher stablity of more delicate products [6]. This compound was treated with equimolar quantities of bis(trimethylsilyl)sulfide in acetonitrile in the temperature range from −25 to 25 °C. After 36 h a colorless precipitate had formed in almost 80 % yield which was shown to be a mixed sulfide/hydride/chloride of the net formula $[(L')GaSH_{0.64}Cl_{0.36}]$, indicating incomplete conversion (Equation (3)). It should be noted that the singular (non-pyridine) hydrogen contained in this product is attached to the gallium and not to the sulfur atom as easily demonstrated by IR spectroscopy. The compound therefore should be classified as a gallium(III) sulfide hydride chloride and not a gallium(I) (hydrogensulfide) chloride.

$$n\ (L')GaHCl_2 \xrightarrow[-Me_3SiCl,\ Me_3SiH]{(Me_3Si)_2S} [(L')GaSH_{0.064}Cl_{0.36}]_n \tag{3}$$

When this product was subsequently reacted with excess L′ for another 8 h in boiling acetonitrile, a soluble compound could be extracted from the residue of the reaction mixture (after removal of the acetonitrile solvent) with dichloromethane. This product was finally isolated in the form of colorless single crystals (from CH_2Cl_2 at −30 °C) in 21 % yield. Another, less pure crop was recovered from the mother liquor (Equation (4)). The compound was identified as a tetranuclear complex of the formula $[(L')_4Ga_4S_6]$ by microanalysis and FAB mass spectrometry. The parent peak at m/e 959.9 for M^+ is followed by fragments with the number of ligands L′ gradually reduced. The solutions in dichloromethane show one set of proton resonances for the ligand L′ suggesting that all four ligands are equivalent. Thermal decomposition of the solid affords a sublimate of the ligand and leaves amorphous gallium sulfide Ga_2S_3.

$$6\,[(L')GaSH_{0.64}Cl_{0.36}]_n \xrightarrow[-2n\,''(L')GaH_{1.92}Cl_{1.08}'']{L'} n\,[(L')_4Ga_4S_6] \qquad (4)$$

With the existence of $(L')_4Ga_4S_6$ confirmed, alternative and potentially improved synthetic pathways were tested. However, the most obvious precursor molecule, $(L')GaCl_3$, did not afford any soluble, molecular gallium sulfide complex upon treatment with $(Me_3Si)_2S$ in boiling acetonitrile or dichloromethane. Only insoluble products were obtained which were not characterized any further.

Structural Results

The Gallium Sulfide Complex

Crystals of $[(L')_4Ga_4S_6]$ are monoclinic, space group *C2/c*, with Z = 4 formula units in the unit cell. The tetranuclear molecules have crystallographically imposed point group C_2 symmetry with the twofold axis passing through atoms S2 and S4 (Figure 1). The $N_4Ga_4S_6$ core has an *adamantane* structure with a quasi-tetrahedral arrangement of the sulfur and nitrogen atoms at each gallium atom and almost symmetrical Ga-S-Ga bridges. The average of the six independent Ga-S distances is 2.544 Å, that of the two Ga-N distances is 2.016 Å. Referring to data of other molecular gallium sulfide compounds, these distances and the Ga-S-Ga angles between 95.81(9) and 97.76(6)° show that the adamantane unit can be taken as a construction based on six-membered ring units $[Ga_3S_3]$ in their *chair* conformation. It is interesting to note that all S-Ga-S angles are much larger than the tetrahedral standard, while the N-Ga-S angles are correspondingly much smaller. The GaS_3 pyramids are thus rather flat suggesting that the apical donor-acceptor bonding of the pyridine ligand is not very strong, as also indicated by the mass spectra. The ligands L′ show no structural anomalies. The crystals contain several partially disordered molecules of dichloromethane. The plot of the arrangement of the molecules in the unit cell shows the channels in which the solvent is accommodated. There are no sub-van der Waals contacts between the molecules (Figure 2).

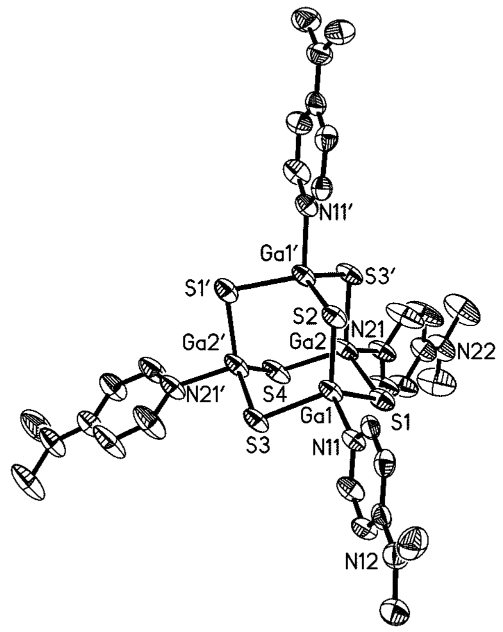

Figure 1. Molecular structure of $(4\text{-}Me_2N\text{-}C_5H_4N)_4Ga_4S_6$ with atomic numbering (ORTEP, 50 % probability ellipsoids, hydrogen atoms − except Ga-*H* − and disordered dichloromethane solvent molecules omitted). Selected bond lengths/Å and angles/°:

Ga1-N11 2.007(5), Ga2-N22 2.015(5), Ga1-S1 2.261(2), Ga1-S2 2.246(2), Ga1-S3 2.258(2); Ga2-S1 2.256(2), Ga2−S3 2.239(2), Ga2-S4 2.255(2); S1-Ga1-S2 115.09(5), S1-Ga1-S3 113.03(7), S2-Ga1-S3 116.39(6), S1-Ga2-S3′ 114.48(7), S1-Ga2-S4 116.00(5), S3′-Ga2-S4 114.56(6), Ga1-S1-Ga2 97.19(8), Ga1-S2-Ga1′ 96.27(9), Ga1-S3-Ga2′ 97.74(6), Ga2-S4-Ga2′ 95.81(9), N11-Ga1-S1 105.74(16), N11-Ga1-S2 104.14(15), N11-Ga1-S3 100.15(14), N21-Ga2-S1 105.65(18), N21-Ga2-S3′ 102.18(16), N21-Ga2-S4 101.46(17).

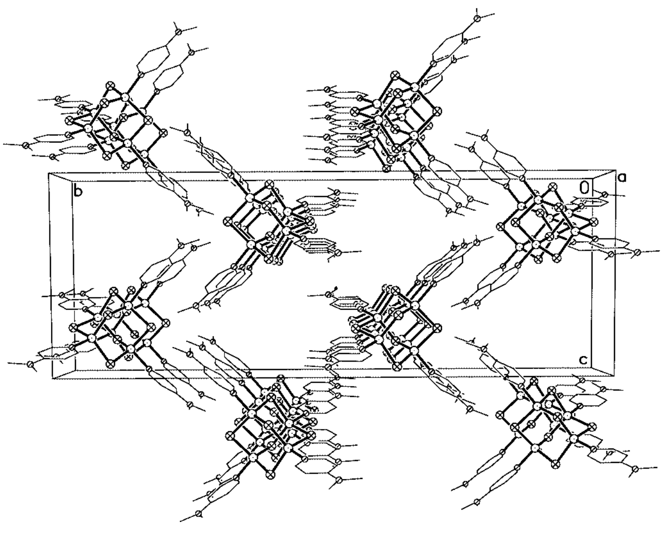

Figure 2 Packing of the molecules$(L')_4Ga_4S_6$ in the unit cell (L′ = *p*-dimethylamino-pyridine).

Crystals of $(L')GaCl_3$, obtained from acetonitrile at 0 °C, are orthorhombic, space group *Pnma*, with Z = 12 formula units in the unit cell. The asymmetric unit contains one complete molecule (I) with all atoms in general positions along with one half of another molecule (II), the second half of which is generated by a mirror plane (defined by atoms Cl5, Ga2 andN21, Figure 3). The structure of molecule I also approaches mirror symmetry (C_s) quite closely, the plane being defined by atoms Cl1, Ga1 and N11.

It should be noted that the Ga-N distances in the $GaCl_3$ adduct of L′ [1.948(2) and 1.946(3) Å for molecules I and II, respectively] are significantly shorter than those in the Ga_4S_6 adduct [2.011(5) and 2.022(5) Å] indicating much stronger donor-acceptor interactions in the former, i.e. weaker bonding of L′ at the gallium sulfide cluster. It has already been pointed out that the GaS_3 pyramid in the gallium sulfide complex is rather flat (with large S-Ga-S angles, average 114.9°), whereas in the gallium chloride complex

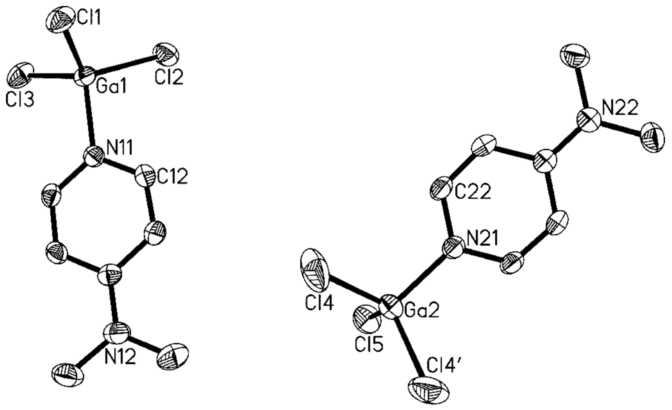

Figure 3 Molecular structure of (L′)$GaCl_3$ with atomic numbering. The atoms Cl5, Ga2, N21, C24 and N22 of Molecule II reside on a mirror plane. Molecule I also closely approaches mirror symmetry. (Hydrogen atoms are omitted). Selected bond lengths/Å and angles/°:

Ga1-N11 1.948(2), Ga1-Cl1 2.1609(7), Ga1-Cl2 2.1628(7), Ga1-Cl3 2.1614(7), Ga2-N21 1.946(3), Ga2-Cl4 2.1539(9), Ga2-Cl5 2.158(1); N11-Ga1-Cl1 109.86(6), N11-Ga1-Cl2 104.82(6), N11-Ga1-Cl3 106.56(6), Cl1-Ga1-Cl2 110.99(3), Cl1-Ga1-Cl3 111.91(3), Cl2-Ga1-Ga3 112.35(3); N21-Ga2-Cl4 106.85(5), N21-Ga2-Cl5 108.44(9), Cl4-Ga1-Cl5 110.41(3), Cl4-Ga2-Cl4′ 113.63(7).

the Cl-Ga-Cl angles are closer to the tetrahedral standard (average 111.7°).

The Dichlorogallane Complexes

The structure of the complex (Et_3P)$GaHCl_2$ [8] which is a liquid at room temperature has not been determined experimentally, but was calculated using standard quantum-chemical methods (Exp. Part). The result is shown in Figure 4. The molecule has a staggered, ethane-like conformation.

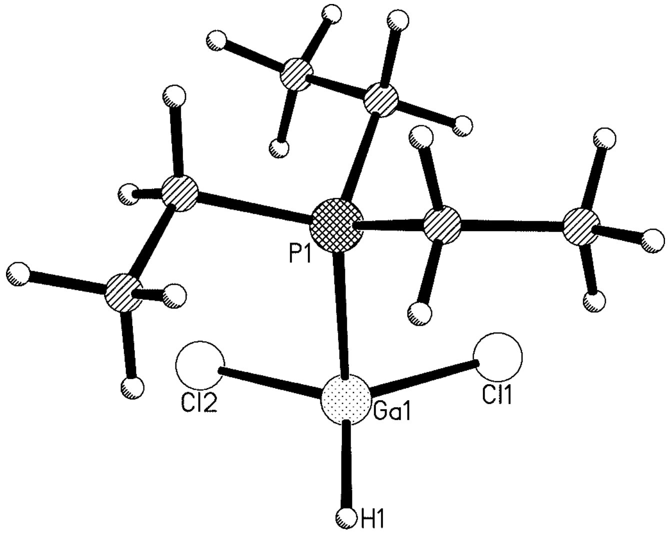

Figure 4 Calculated molecular structure of (Et_3P)$GaHCl_2$ with atomic numbering. Selected bond lengths/Å and angles/°:

Ga1-Cl1 2.1976, Ga1-Cl2 2.1978, Ga1-P1 2.4355, Ga1-H1 1.5570; Cl1-Ga1-Cl2 112.95, Cl1-Ga1-P1 98.16, Cl2-Ga1-P1 98.24, Cl1-Ga1-H1 116.42, Cl2-Ga1-H1 116.42, P1-Ga1-H1 110.94.

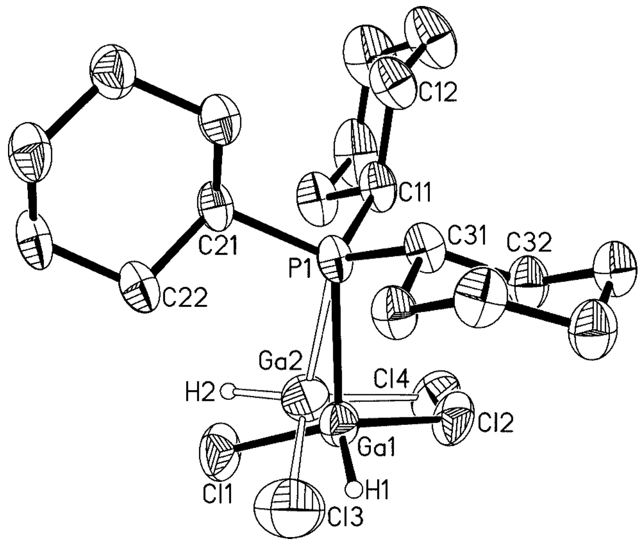

Figure 5 Molecular structure of (Cy_3P)$GaHCl_2$ with atomic numbering (hydrogen atoms − except Ga-*H* − omitted). Selected bond lengths/Å and angles/° for the major component of two disordered molecules:

Ga1-C1 2.182(2), Ga1-Cl2 2.200(2), Ga1-P1 2.432(1), Ga1-H1 1.46(5); Cl1-Ga1-Cl2 105.76(7), Cl1-Ga1-P1 110.92(6), Cl2-Ga1-P1 102.24(7), Cl1-Ga1-H1 115(2), Cl2-Ga1-H1 114(2), P1-Ga1-H1 107(2).

Crystals of (Cy_3P)$GaHCl_2$ (m.p. 174 °C with decomposition, solvent-free from diethyl ether) are monoclinic, space group *Cc*, with Z = 4 formula units in the unit cell. The molecules have the staggered conformation predicted by calculations, but the $GaHCl_2$ part is disordered over two sites (Figure 5). The Ga-*H* hydrogen atom of the major component was tentatively assigned to a residual electron density. The resulting refined geometry agrees reasonably well with those of other Ga-*H* compounds reported in the literature (Exp. Part). The hydrogen atom of the minor component was calculated with an idealized geometry using the Ga-*H* distance of the major component as a reference parameter.

Crystals of (Ph_3P)$GaHCl_2$were obtained from diethyl ether in two solvent-free polymorphic forms, one monoclinic (space group $P2_1/n$, Z = 4) and one triclinic (space group $P\bar{1}$, Z = 2). The latter was found to crystallize from diethyl ether, if excess PPh_3 was present in the solution. The molecular structures in both polymorphs are very similar (Figure 6) with differences arising only from variations in the conformative orientations as shown in the superposition presented in Figure 7. The Ga-*H* hydrogen atoms of both polymorphs were calculated in idealized positions accounting for a probable disorder of the $HGaCl_2$ unit similar to the one found in the structure of (Cy_3P)$GaHCl_2$ (Exp. Part).

Crystals of [(dppe)$(GaHCl_2)_2$](C_6H_6), (m.p. 203 °C, from benzene/pentane), are monoclinic, space group *C*2/*c*, with Z = 4 formula units in the unit cell. The two halves of the molecule are related by a center of inversion located midway between the C3-C3′ bond (Figure 8). As in some of the previous examples, the $HGaCl_2$ units are disordered over

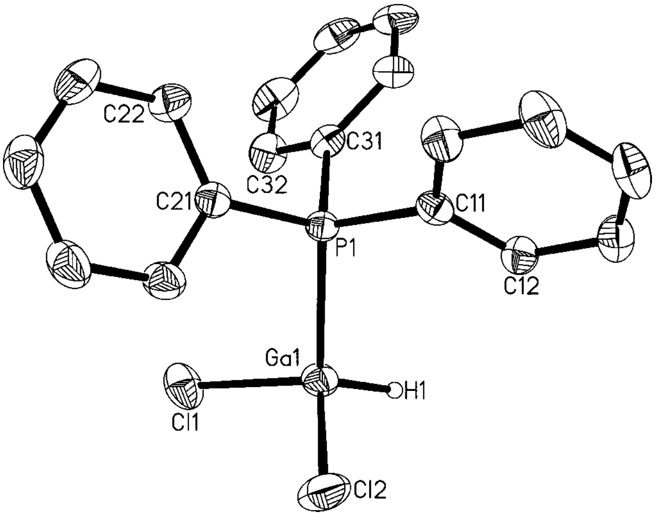

Figure 6 Molecular structure of $(Ph_3P)GaHCl_2$ in the monoclinic form with atomic numbering. (Hydrogen atoms − except Ga-*H* − omitted). Selected bond lengths/Å and angles/°:

Ga1-Cl1 2.1982(7), Ga1-Cl2 2.1913(7), Ga1-P1 2.4038(6), Ga1-H1 1.51 (fixed); Cl1-Ga1-Cl2 106.60(3), Cl1-Ga1-P1 103.92(3), Cl2-Ga1-P1 104.73(3), Cl1/Cl2/P1-Ga1-H1 113.6 (fixed).

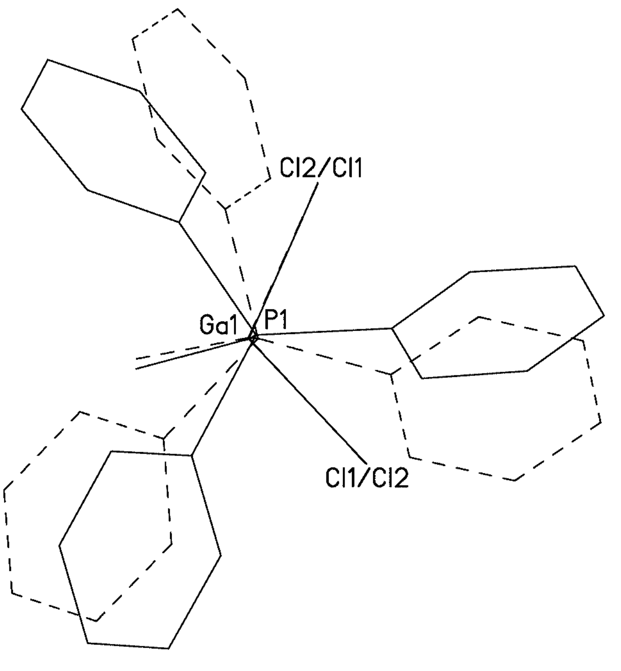

Figure 7 Superposition of the molecules $(Ph_3P)GaHCl_2$ in the triclinic and monoclinic polymorphs.

two orientations with a hydrogen and a chlorine atom changing positions. The members of the molecular chain are all in staggered all-*trans* conformations leading to an extended (stretched) structure. The Ga-*H* hydrogen atom of the major component was located and refined, that of the minor component was calculated with an idealized geometry using the Ga-*H* distance of the major component as a reference parameter (Exp. Part).

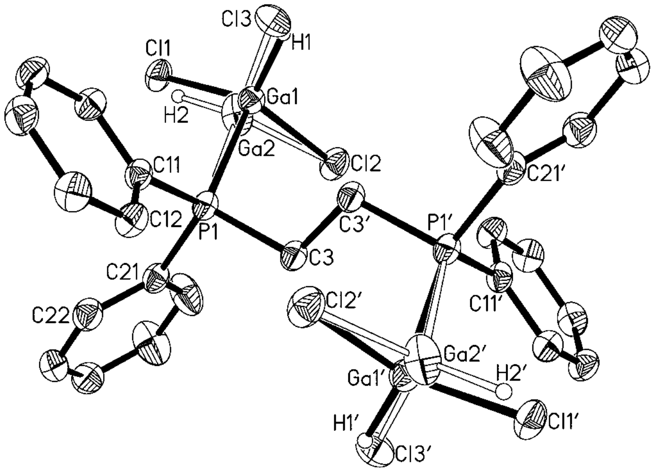

Figure 8 Molecular structure of $[(dppe)(GaHCl_2)_2]$ in the benzene solvate (1:1) with atomic numbering. There is a center of inversion midway between atoms C3 and C3′. Hydrogen atoms − except Ga-*H* − are omitted. Selected bond lengths/Å and angles/° for the major component of two disordered molecules:

Ga1-Cl12.1841(9), Ga1-Cl2 2.2056(8), Ga1-P1 2.426(1), Ga1-H1 1.48(3); Cl1-Ga1-Cl2 111.45(4), Cl1-Ga1-P1 104.22(3), Cl2-Ga1-P1 96.93(3), Cl1-Ga1-H1 91.15(1), Cl2-Ga1-H1 113(1), P1-Ga1-H1 112(1).

Crystals of $[(dppe)(GaHCl_2)_2](Et_2O)_2$ (from diethyl ether) are triclinic, space group $P\bar{1}$, with Z = 1 formula unit in the unit cell. The structure of the adduct (also point group C_i) is very similar to that described for the benzene solvate. The Ga-*H* hydrogen atom was calculated in an idealized position (Exp. Part).

Discussion

The present work has again demonstrated that pyridines appear to be the ideal ligands for molecular gallium(III) halides and chalcogenides. In particular pyridines with strong electron-donating substituents, such as 4-dimethylamino-pyridine L′, can be employed to stabilize even the binary gallium sulfide in a tetranuclear form Ga_4S_6 with an adamantane structure. This structure features exclusively the six-membered rings Ga_3S_3 in chair conformation which are also characteristic of the bulk gallium sulfide polymorphs Ga_2S_3.

The Ga-N bond lengths and the average Cl-Ga-Cl/S-Ga-S angles indicate that donor-acceptor bonding is weaker at Ga_4S_6 than at the strong acceptor $GaCl_3$. It is for this reason that the ligand L′ can be readily eliminated on heating, but concurrently the remaining Ga_4S_6 cages undergo polymerization.

The synthetic route involves reaction of $(L')GaHCl_2$ with $(Me_3Si)_2S$ which first affords a mixed gallium "hydride chloride sulfide" which finally can be converted into the product by reaction with excess ligand L′ in boiling acetonitrile. The simple metathesis reaction of $(L')GaCl_3$ with

$(Me_3Si)_2S$ does not afford any soluble gallium sulfide complexes.

Pyridines have previously been found to dissolve readily the ternary gallium chalcogenide halides GaEX to form trinuclear complexes with six-membered ring structures (E = S, Se; X = Cl, Br) [5, 6]. With *tertiary phosphines*, these ternary compounds show no reaction. Similarly, treatment of the $(L)GaHCl_2$ complexes with sulfides gave only ill-defined, insoluble substitution products, probably because not only the halogen atoms but also some of the tertiary phosphines L are substituted by sulfide leading to a cross-linking of the molecular units.

The intermediates of the sulfide substitution reactions, the aforementioned mixed "gallium(III) sulfide hydride chloride complexes" have the hydrogen atom attached to gallium(III) as a hydride and not to sulfur in a gallium(I) hydrogensulfide chloride. It should be noted that there is no literature on a ternary compound of the net composition GaSH or its complexes. Since no gallium(I) compounds have been encountered in the present and previous studies it appears that the "GaSH" involved under the experimental conditions chosen for this work is to be classified as a gallium(III) hydride sulfide Ga(S)(H) and not a gallium(I) hydrogensulfide Ga(SH).

Under more forcing conditions, $(L)GaHCl_2$ complexes (with L = pyridine or phosphine) can undergo reductive elimination of molecular hydrogen to give dinuclear gallium(II) compounds of the formula $(L)Cl_2Ga\text{-}GaCl_2(L)$. To date, no such elimination of molecular hydrogen was observed in the gallium(III) hydride sulfide systems.

Experimental Part

General: All preparative experiments were carried out in an atmosphere of dry, pure nitrogen. Solvents were dried, distilled and saturated with nitrogen, glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. Dichlorogallane was prepared following a published procedure [7, 8]. All other chemicals were commercially available.

(Triethylphosphine)dichlorogallane(III): The molecular structure of $(Et_3P)GaHCl_2$ [8] was calculated with the TURBOMOLE suite of programs on the RI-MP2 level with a SV(P) basis set (split valence quality with a polarization function for all non-hydrogen atoms) [13].

(Tricyclohexylphosphine)dichlorogallane(III): Freshly prepared $(HGaCl_2)_2$ (0.84 g, 2.98 mmol) is dissolved in 15 ml of diethyl ether at −25 °C and Cy_3P is added as a solution in diethyl ether (1.67 g, 5.95 mmol, 40 ml Et_2O) with stirring. A precipitate forms, which is filtered and washed with 2x20 ml of diethyl ether. Remaining solvent is evaporated in a vacuum. Additional crystalline product is obtained by slow cooling of the combined filtrates to −78 °C: Colorless, air-sensitive crystals, m.p. 174 °C (decomposition); 2.33 g (93 % yield). Found C 51.37, H 8.19, Cl 16.57, P 7.11; calcd. for $C_{18}H_{34}Cl_2GaP$ (422.07) C 51.22, H 8.12, Cl 16.80, P 7.34 %. IR (Nujol on KBr): 1920 cm^{-1} (ν Ga-H). NMR (C_6D_6, 25 °C) ^1H: 0.9-2.4, m, 33H, Cy; 5.1, br. s, 1H, Ga*H*. ^{13}C: 26.0, s, *C*-4; 27.2, d, J 10.4 Hz, *C*-3/5; 29.3, s, *C*-2/6; 31.2, d, J 15.6 Hz, *C*-1. ^{31}P: 0.9, br. s.

(Triphenylphosphine)dichlorogallane(III): As described above, from $(HGaCl_2)_2$ (1.67 g, 5.89 mmol, 30 ml Et_2O) and Ph_3P (3.09 g, 11.8 mmol, 30 ml Et_2O); colorless, air-sensitive, triclinic crystals, m.p. 202-205 °C; 4.76 g (97 % yield). Found C 53.25, H 3.96, Cl 17.38, P 7.37; calcd. for $C_{18}H_{16}Cl_2GaP$ (403.92): C 53.52, H 3.99, Cl 17.55, P 7.67 %. IR (KBr): 1940 cm^{-1} (ν Ga-H). NMR (C_6D_6, 25 °C) ^1H: 5.84, br. s, 1H, Ga*H*; 6.87-7.00, m, AA′*BB′C*X, 9H, C*H*-3/4/5; 7.46-7.54, m, *AA′*BB′CX, C*H*-2/6. ^{13}C: 129.6, d, J 10.3 Hz, *C*-3/5; 132.0, d, J 2.6 Hz, *C*-2/6; 134.0, d, J 11.3 Hz, *C*-1; *C*-4 not detected. ^{31}P: −8.8, br. s. [Note: Crystals from diethyl ether are triclinic; crystals from diethyl ether containing excess Ph_3P are monoclinic.]

[Bis(diphenylphosphino)ethane]-P,P′-bis[dichlorogallane(III)]: As described above, from $(HGaCl_2)_2$ (1.70 g, 6.00 mmol, 20 ml Et_2O) and $(CH_2PPh_2)_2$ (dppe) (2.39 g, 6.00 mmol, 20 ml Et_2O); colorless, air-sensitive crystals, m.p. 202-205 °C; 3.80 g (93 % yield). Found: C 45.93, H 3.91, Cl 20.45, P 8.95; calcd. for $C_{26}H_{26}Cl_4Ga_2P_2$ (681.69): C 45.81, H 3.84, Cl 20.80, P 9.09 %. IR (KBr): 1951 cm^{-1} (ν Ga-H). NMR (C_6D_6, 25 °C) ^1H: 2.48, br. s, 2H, C*H*$_2$; 6.17, br. s, 1H, Ga*H*; 6.96, m, AA′*BB′C*X, 6H, C*H*-3/4/5; 7.36, m, *AA′*BB′CX, 4H, C*H*-2/6. ^{13}C: 22.3, br. s, *C*H$_2$; 129.2, br. s, *C*-3/5; 130.2, br. s, *C*-2/6; 133.1, m, AXX′, *C*-1. *C*-4 not detected. ^{31}P: −10.4, br. s.

Reaction of trivinylphosphine with dichlorogallane(III): As described above, $(HGaCl_2)_2$ (0.70 g, 2.47 mmol) is treated with Vi_3P (0.56 g, 5.00 mmol) in 20 ml of diethyl ether at −78 °C. On warming the reaction mixture a colorless precipitate is formed which cannot be redissolved in organic solvents and decomposes upon heating without melting; 0.98 g (78 % yield). Found: C 28.71, H 4.30, Cl 27.27, P 10.36; calcd. for $C_6H_{10}Cl_2GaP$ (253.75): C 28.40, H 3.97, Cl 27.94, P 12.21 %. The IR spectrum (Nujol on KBr) shows no absorption for a ν Ga-H stretching vibration.

Tetrakis(4-dimethylamino-pyridine)tetragallium(III) hexasulfide: (4-Dimethylamino-pyridine)dichlorogallane (1.04 g, 3.92 mmol) [12] is reacted with bis(trimethylsilyl)sulfide (0.70 g, 3.94 mmol) in 30 ml of acetonitrile at −25 °C for 3 h. The reaction mixture is allowed to warm to room temperature over a period of 12 h and kept at 20 °C for another 24 h. The colorless precipitate is filtered off, washed with 2x20 ml of hexane and dried in a vacuum. The solid product melts and decomposes over a broad temperature interval (0.72 g, 78 % yield). Found: C 34.95, H 4.62, N 11.42, S 13.88, Cl 5.46, Ga 29.49; calcd. for $(C_7H_{10}N)GaSCl_{0.36}H_{0.64}$: C 35.42, H 4.52, N 11.80, S 13.51, Cl 5.38, Ga 29.37 %. IR (Nujol on KBr): 1890 cm^{-1} (ν Ga-H).

0.502 g (2.11 mmol) of this product is suspended in 25 ml of a saturated solution of 4-dimethylamino-pyridine in acetonitrile and heated to reflux for 8 h. The reaction mixture is filtered at 70 °C and the solvent removed from the filtrate in a vacuum. The residue is dissolved in 40 ml of dichloromethane and the solution cooled to −30 °C for crystallization of the colorless product, 0.105 g, 21 % yield. Found: C 35.56, H 4.50, N 11.60; calcd. for $C_{28}H_{40}N_4Ga_4S_6$ (959.9) C 35.03, H 4.02, N 11.67 %. MS (FAB): m/e 959.9 [M^+]. NMR (CD_2Cl_2, 20 °C) ^1H: 3.01, s, 6H, *Me*; 6.55 and 8.45, m, AA′BB′, 2H each, C*H*-2/6 and C*H*-3/5. Upon thermolysis a sublimate of 4-dimethylamino-pyridine is obtained and X-ray amorphous gallium sulfide (containing no carbon, nitrogen or hydrogen, and with a correct gallium and sulfur analysis) remains.

(4-Dimethylamino-pyridine)trichlorogallium(III): Anhydrous $(GaCl_3)_2$ (1.80 g, 5.11 mmol) is dissolved in dichloromethane (20 ml) and L′ (1.25 g, 10.22 mmol) is added. The reaction mixture is stirred for 2 h and subsequently the volume of the solution is reduced to one half in a vacuum. Cooling of the remainder solution to −78 °C leads to the deposition of the colorless, crystalline product; 2.96 g (98 % yield, m.p. 103-104 °C). Found: C 28.28, H 3.30, N 9.29, Cl 35.66; calcd. for $C_7H_{10}Cl_3GaN_2$ (298.25): C 28.19, H 3.38, N 9.39, Cl 35.66 %. NMR (C_6D_6, 25 °C) ^1H: 2.07, s, 6H, Me; 5.55 and 7.38, m, AA′BB′, 2H each, C_6H_4. ^{13}C: 38.7, s, Me; 107.0, 143.6 and 155.9, all s, for C-3/5, -2/6 and -4, respectively.

Crystal Structure Determinations:

Specimens of suitable quality and size of $[(4\text{-}Me_2N\text{-}Py)_4Ga_4S_6]$, $(4\text{-}Me_2N\text{-}Py)GaCl_3$, $(Cy_3P)GaHCl_2$, $(Ph_3P)GaHCl_2$ (one monoclinic and one triclinic polymorph), $[(dppe)(GaHCl_2)_2](C_6H_6)$ and $[(dppe)(GaHCl_2)_2](Et_2O)_2$ were mounted on the ends of quartz fibers in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo K_α radiation. 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. After an initial structure solution and refinement of $(Cy_3P)GaHCl_2$ and $[(dppe)(GaHCl_2)_2](C_6D_6)$ high residual electron densities in appropriate distances and angles suggested a disorder of the $HGaCl_2$ groups over two sites in both structures. The subsequent refinement of split atom models gave satisfactory results for both structures with site occupation factors of 87.6 and 91.3 % for the major components in $(Cy_3P)GaHCl_2$ and $[(dppe)(GaHCl_2)_2](C_6D_6)$ respectively. To prevent closely neighbouring atoms from becoming non positive definite, all Ga-Cl distances were restrained to be equal within a standard deviation of 0.01 Å. The Ga-*H* hydrogen atoms of the major components in both structures were attributed to residual electron densities. The refined Ga-*H* distances are in good agreement with reference data. The Ga-*H* hydrogen atoms of the minor components were calculated in ideal positions with Ga-*H* distances derived from the corresponding major components. In the structure refinements of both polymorphs of $(Ph_3P)GaHCl_2$ and of $[(dppe)(GaHCl_2)_2](Et_2O)_2$ also relatively high residual electron densities occurred, roughly in the space segments where the hydride ligands were expected. Together with significantly unequal anisotropic thermal displacement parameters for Cl1 and Cl2 in the triclinic polymorph of $(Ph_3P)GaHCl_2$ this indicated a disorder similar to the one discussed above. The Ga-*H* hydrogen atoms of both polymorphs of $(Ph_3P)GaHCl_2$ and of $[(dppe)(GaHCl_2)_2](Et_2O)_2$ therefore were calculated in ideal positions with a mean Ga-*H* distance based on information held in the *Cambridge Structural Database* (version 5.25, April 2004 release) [15]. The search fragment used consisted of a four-coordinate gallium atom attached to a singly-coordinate hydrogen atom. The 138 data listed in this compilation gave a mean Ga-*H* distance of 1.51 Å. The C-*H* hydrogen atoms were located and refined with isotropic displacement parameters in all structures except $[(4\text{-}Me_2N\text{-}Py)_4Ga_4S_6]$ where they were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions. The Flack parameter for $(Cy_3P)GaHCl_2$ is 0.006(10). The structure of $[(4\text{-}Me_2N\text{-}Py)_4Ga_4S_6]$ contains disordered solvent molecules, which were partially taken into account by the SQUEEZE method [16] (Solvent Accessible Volume: 970.7 Å^3 containing 35 electrons per cell). Absorption corrections for $[(dppe)(GaHCl_2)_2](Et_2O)_2$, $(Cy_3P)GaHCl_2$ and $(4\text{-}Me_2N\text{-}Py)GaCl_3$ were carried out using DELABS, as part of the PLATON [16] suite of programms. Further information on crystal data, data collection and structure refinement are summarized in Tables 1 and 2, CCDC reference numbers 225439 and 244202−244207.

Acknowledgement. This work was generously supported by Fonds der Chemischen Industrie (FCI) and by Deutscher Akademischer Austauschdienst (DAAD). *Professor P. Pyykkö* (University of Helsinki) and *Dr. U. Monkowius* (TUM) are thanked for assistance with the quantum chemical calculations.

Table 1 Crystal Data, Data Collection, and Structure Refinement of $[(4\text{-}Me_2N\text{-}Py)_4Ga_4S_6]$, $(4\text{-}Me_2N\text{-}Py)GaCl_3$ and $(Cy_3P)GaHCl_2$.

	$[(4\text{-}Me_2N\text{-}Py)_4Ga_4S_6](CH_2Cl_2)_{3.86+x}$	$(4\text{-}Me_2N\text{-}Py)GaCl_3$	$(Cy_3P)GaHCl_2$
Empirical formula	$C_{31.88}H_{47.73}Cl_{7.73}Ga_4N_8S_6$	$C_7H_{10}Cl_3GaN_2$	$C_{18}H_{34}Cl_2GaP$
M	1288.04	298.24	422.05
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C*2/*c*	*Pnma*	*Cc*
a/Å	10.3839(2)	7.3898(1)	16.7490(5)
b/Å	39.335(1)	28.6487(4)	9.5296(3)
c/Å	14.4037(5)	16.6420(2)	13.0925(4)
β/°	94.821(1)	90	98.212(2)
V/Å^3	5862.5(3)	3523.25(8)	2068.28(1)
ρ_{calc}/g cm^{-3}	1.459	1.687	1.355
Z	4	12	4
F(000)	2585	1776	888
μ (Mo-K_α)/cm^{-1}	24.14	29.84	16.62
T/K	143	143	143
Refls. measured	159925	72813	30932
Refls. Unique	3603	3284	3759[R_{int} = 0.056]
Refined parameters /restraints	287 / 12	244 / 0	364 / 10
$R1$ [I≥2σ(I)]	0.0521	0.0270	0.0370
$wR2$[a)]	0.1298	0.0695	0.0871
Weighting scheme	a = 0.451 b = 61.7951	a = 0.0332 b = 4.0385	a = 0.0000 b = 1.0445
σ_{fin}(max/min)/eÅ^{-3}	0.744 / −0.731	1.612 / −0.460	0.452 / −0.502

[a)] $wR2 = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2 + 2F_c^2)/3$.

Table 2 Crystal Data, Data Collection, and Structure Refinement of $(Ph_3P)GaHCl_2$, $(Ph_3P)GaHCl_2$, $[(dppe)(GaHCl_2)_2](C_6H_6)$ and $[(dppe)(GaHCl_2)_2](Et_2O)_2$.

	$(Ph_3P)GaHCl_2$	**$(Ph_3P)GaHCl_2$**	**$[(dppe)(GaHCl_2)_2]$ (C_6H_6)**	**$[(dppe)(GaHCl_2)_2]$ $(Et_2O)_2$**
Empirical formula	$C_{18}H_{16}Cl_2GaP$	$C_{18}H_{16}Cl_2GaP$	$C_{32}H_{32}Cl_4Ga_2P_2$	$C_{34}H_{46}Cl_4Ga_2O_2P_2$
M	403.90	403.90	759.76	829.89
Crystal system	monoclinic	triclinic	Monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	12.5720(1)	9.3578(4)	15.5980(2)	8.9950(2)
b/Å	11.1633(2)	9.8923(4)	12.3725(2)	10.7604(3)
c/Å	12.9621(2)	10.3752(5)	18.2083(3)	11.9444(4)
α/°	90	107.468(2)	90	88.321(2)
β/°	90.270(1)	95.163(2)	107.767(1)	68.165(2)
γ/°	90	93.847(2)	90	68.287(2)
V/Å^3	1819.15(5)	907.94(7)	3346.35(9)	989.12(5)
ρ_{calc}/g cm^{-3}	1.475	1.477	1.508	1.393
Z	4	2	4	1
$F(000)$	816	408	1536	426
μ (Mo-K$_\alpha$)/cm^{-1}	18.87	18.91	20.46	17.41
T/K	143	143	143	143
Refls. measured	39424	27871	38753	21949
Refls. Unique	3176 [R_{int} = 0.035]	3137 [R_{int} = 0.063]	2910 [R_{int} = 0.038]	3388[R_{int} = 0.031]
Refined parameters /restraints	259 / 0	260 / 0	264 / 7	288 / 0
$R1$ [I≥2σ(I)]	0.0318	0.0480	0.0258	0.0404
$wR2$$^{a)}$	0.0816	0.1049	0.0695	0.1091
Weighting scheme	a = 0.0380 b = 1.9075	a = 0.0170 b = 2.5972	a = 0.0277 b = 3.6298	a = 0.0573 b = 1.0010
σ_{fin}(max/min)/eÅ^{-3}	1.229 / −0.496	1.125 / −0.568	0.460 / −0.317	1.390 / −0.711

$^{a)}$ $wR2 = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2 + 2F_c^2)/3$.

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