On the Chemistry of Gallium, 9[◇]

Monomeric Phosphanylgallanes – Synthesis and Structural Characterization☆

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The monomeric phosphanylgallanes $R_2GaPR'R''$ (R = tmp, Mes; R' = H, *t*Bu; R'' = Mes, *t*Bu), the diphosphanylgallane $MesGa(PtBu_2)_2$, and diphosphandiylbisgallane $[tmp_2GaP(tBu)]_2$ have been synthesized from alkali metal phosphides and substituted gallium chlorides. Low-temperature NMR studies of the phosphanylgallanes reveal no barrier to rotation about the gallium–phosphorus bond. Analysis of the crystal structures of $tmp_2GaPtBu_2$, $Mes_2GaPtBu_2$, $MesGa(PtBu_2)_2$, and $[tmp_2GaP(tBu)]_2$ confirms the monomeric nature of these molecules. The gallium–phosphorus bond lengths are found to be 237.5, 233.5, 235.4 pm (averaged), and 242.3 pm, respectively, with all phosphorus atoms being pyramidally coordinated.

Gallium pnicogen compounds $R_2Ga-ER'_2$ have attracted considerable attention in recent years for several reasons. Primarily, such compounds are of interest because of their possible use as MOCVD precursors for gallium pnictides GaE (E = N, P, As)[1,2], which are versatile semiconductor materials. In addition, further interest arises because of the nature of the bonding in such compounds, specifically whether there is π-bonding between gallium and atoms of the elements E. Multiple bonding between atoms of main-group-13 and -15 elements has been the subject of widespread interest for many years. These investigations have been mainly concerned with boron-nitrogen compounds and multiple bonding between boron and atoms of the heavier group-15 elements has only recently been established[3]. Information regarding π-bonding between heavier group-13 and group-15 element atoms is rare. In the following, we will confine ourselves to the combination of gallium and phosphorus atoms. Phosphanylgallanes are normally oligomeric; four-membered ring structures with tetracoordinated gallium and phosphorus atoms are most commonly encountered[4]. Monomeric phosphanylgallanes have only recently been characterized. Like **1**, most of them bear bulky silyl groups at the phosphorus atom[5]. Such compounds exhibit barriers of more than 40 kcal/mol for rotation about the gallium–phosphorus bond. The gallium–phosphorus bond length in these compounds seems to be a function of the torsion angle between the vacant p-orbital at the gallium center and the lone pair at the phosphorus atom[6]. The monomeric all-*tert*-butyl-substituted phosphanylgallane $tBu_2Ga-PtBu_2$[7] has yet to be structurally characterized, but in the heterocyclic derivatives **2**[8] and **3**[9] the phosphorus atoms are known to be coordinated pyramidally. In contrast to the compounds described above, the phosphorus atom in digallylphosphane $MesP[Ga(trip_2)]_2$ is coordinated in a trigonal planar fashion[10]. However, in several boron-phosphorus compounds large and electropositive substituents at the phosphorus atom are known to lower the inversion barrier and induce multiple bonding[11]. Therefore, it is desirable to collect structural data on diorganylphosphanylgallanes. Several examples of new gallium phosphorus compounds incorporating the di-*tert*-butylphosphanyl group are reported in this work. Information concerning group-13-substituted diphosphanes is also rather limited. The only example of a acyclic boryl-substituted derivative **4** allowed some insight as to whether shortening of P–P bonds can be attributed to p-p(π) overlap[12]. A single attempt to prepare a gallium compound with a P–P unit resulted in the isolation of the cage compound **5**[13].

Reactions

The lithium phosphides LiP(H)R (R = Mes, *t*Bu) react with tmp_2GaCl (tmp = 2,2,6,6-tetramethylpiperidino) **6** to afford the monomeric, oily bis(amino)phosphanylgallanes **7a, b** (eq. 1). On combining tmp_2GaCl with $LiPtBu_2$, **8** crystallizes in orange needles. Analogously, $K_2P_2tBu_2$ reacts with tmp_2GaCl to afford the diphosphandiylbisgallane $[tmp_2GaP(tBu)]_2$ **9** as yellow crystals (eq. 2). The reaction of dimesitylgallium chloride with $LiPtBu_2$ yields the mono-

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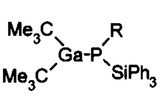
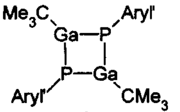


1



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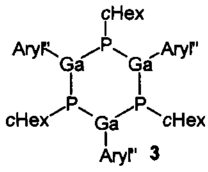
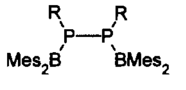


3

R = *t*Bu, adamantyl Aryl' = 2,4,6-*t*Bu$_3$C$_6$H$_2$ Aryl'' = 2,4,6-Ph$_3$C$_6$H$_2$



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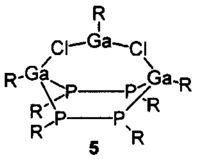
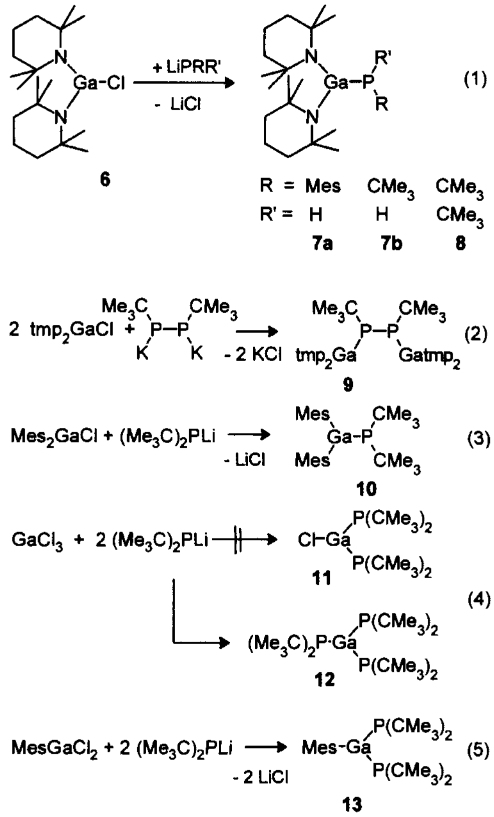


5

R = adamantyl R = *t*Bu



meric phosphanylgallane **10**, which crystallizes in pale-yellow prisms (eq. 3). When gallium trichloride is treated with LiP*t*Bu$_2$ in a molar ratio of 1:2 the product is not **11**, which would be a valuable starting material for other bis(phosphanyl)gallanes, but only the tris(phosphanyl)gallane **12** is isolated (eq. 4). The intensely red compound has previously been characterized[14], but in contrast to the corresponding indium compound[15], structural investigations have not been undertaken. The bis(phosphanyl)gallane **13** is prepared by an alternative route, in which both chloride functions in mesitylgallium dichloride are substituted by reaction with LiP*t*Bu$_2$ (eq. 5). Mesitylgallium dichloride and dibromide **14** are easily synthesized from trimethylsilylmesitylene and gallium halides. The preparation of arylboron dihalides from trimethylsilyl-substituted aryl compounds is well-known[16], as is the cleavage of tetramethylsilane with gallium chloride to form methylgallium dichloride[17].

NMR-Spectroscopic Characterization

The ^{1}H- and ^{13}C-NMR spectra of the (di-*tert*-butylphosphanyl)gallanes **8**, **9**, **10**, and **13** show doublets for the *tert*-butyl groups. This is indicative of the monomeric nature of these compounds, because in the case of phosphorus-bridged dimers more complicated patterns would be expected[4]. Free rotation about the gallium–nitrogen and gallium–phosphorus bonds, even at −60 °C, is verified by the observation of single sets of signals for all substituents. In the ^{31}P-NMR spectra of all compounds under investigation only one singlet is observed. In the case of **13**, this is further evidence of its monomeric nature. A dimeric compound or a monomer/dimer equilibrium would give rise to two signals or at least a concentration dependent shift. The ^{31}P-NMR shifts of these di-*tert*-butylphosphanyl compounds are found in the region of $\delta \approx 50$. This is approximately 30 ppm downfield compared to the shift of di-*tert*-butylphosphane ($\delta^{31}P = 20.1$)[18] and 20 ppm downfield compared to the signals of dimeric di-*tert*-butylphosphanylgallanes such as [Me$_2$GaP*t*Bu$_2$]$_2$ ($\delta^{31}P = 28.4$) and [*n*Bu$_2$GaP*t*Bu$_2$]$_2$ ($\delta^{31}P = 32.9$)[4]. The coordination number cannot, however, be unambiguously assigned on the basis of these shifts, because monomeric *t*Bu$_2$Ga–P*t*Bu$_2$[7] has a reported chemical shift of $\delta^{31}P = 23.9$ and [*t*Bu(Me$_3$SiC≡C)GaP*t*Bu$_2$]$_2$[19], dimeric in solution, one of $\delta^{31}P = 51.5$. This is contrary to the overall trend. Comparable downfield shifts of 30 to 40 ppm relative to the corresponding phosphanes are observed for **7a**, **b**, and **9**. The phosphorus nuclei in dimeric [*t*Bu$_2$GaP(H)*t*Bu]$_2$[20] [$\delta^{31}P = -68.3$ (*anti* isomer) and $\delta^{31}P = -74.4$ (*syn* isomer)] are deshielded only by 6 to 12 ppm compared to *tert*-butylphosphane ($\delta^{31}P = -80.2$)[18]. The ^{31}P resonance of [(tmp)$_2$Ga]$_2$PMes [$\delta^{31}P = -69.0$][21] is found 50 ppm further downfield than that of **7a**. This is suggestive of an increasing planarity of the coordination sphere at the phosphorus atom. Thus, MesP[Ga(trip$_2$)]$_2$, with a trigonal planar coordinated phosphorus atom shows a chemical shift of $\delta^{31}P = -58$[10].

In the mass spectrum of **8**, the molecular peak ($m/z = 494$) is observed at very low intensity. The base peak can be assigned to the species [tmp$_2$Ga]$^+$. Likewise, the mass spectrum of **10**, which shows relatively few fragments, exhibits besides the weak molecular peak ($m/z = 452$) the cation [Mes$_2$Ga]$^+$ as the signal of highest intensity. The mass spectrum of **13** is dominated by the loss of a P*t*Bu$_2$ fragment from the molecular peak ($m/z = 478$) to afford [MesGaP*t*Bu$_2$]$^+$ ($m/z = 333$) with subsequent elimination of one and two isobutene molecules, respectively. A second, less promiment, fragmentation pathway is the elimination of an isobutyl radical following by elimination of two isobutene molecules.

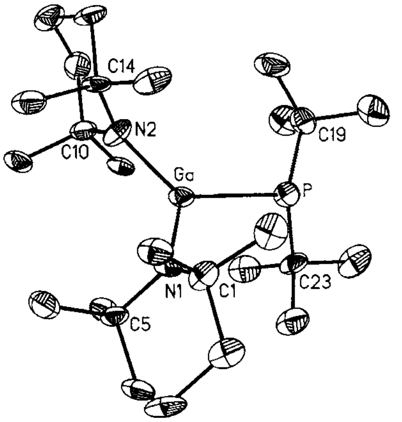
X-ray Structure Analysis

The gallium atom in **8** is bonded to three atoms of group-15 elements (Figure 1). **8** crystallizes in the monoclinic system, with space group $P2_1/c$. Within the esd's, both gallium–nitrogen bonds are equal (190.8 pm). The two nitrogen atoms and the gallium atom are each coordinated in a distorted trigonal planar fashion. The N(1)–Ga–N(2)-bond angle [121.8(3)°] is close to the ideal value of 120°. Clearly, the molecule **8** cannot release steric strain by increasing the angle between the tmp groups, as is the case in tmp_2GaOPh[22]. In the latter, the N–Ga–N angle is wide (134°) and the gallium–nitrogen bonds are 7 pm shorter than in **8**. This is due to the space-filling nature of the phosphanyl ligand. Other compounds bearing bulky groups, such as bis(2,2,6,6-tetramethylpiperidino)gallanes tmp_2GaR [R = $Si(SiMe_3)_3$[23], $Gatmp_2$[24]] also have long gallium–nitrogen bonds and N–Ga–N angles of about 120°. The N(2)–Ga–P angle in **8** [126.0(2)°] is very wide. This is a consequence of the nearly eclipsed conformation of one of the *tert*-butyl groups and the tmp group of N2; the torsion angle N(2)–Ga/P–C(19) is only 4.2°. Together with the torsion angle N(2)–Ga/P–C(23) (−118.7°), the twist of the lone pair at the phosphorus atom and the p_z orbital at the gallium atom can be estimated as 30°. The phosphorus atom is coordinated pyramidally (sum of angles 331.8°), and the gallium–phosphorus bond length is 237.5(3) pm. Dimeric compounds, such as $[Me_2GaP\mathit{t}Bu_2]_2$[4], have gallium–phosphorus distances which are approximately 10 pm longer. The gallium–phosphorus distance in **8** is 8 pm larger than in monomeric (silylphosphanyl)gallanes $\mathit{t}Bu_2GaP(SiPh_3)R$ [R = trip: d_{GaN} = 229.5(1) pm; R = 2,4,6-$\mathit{t}Bu_3C_6H_2$: d_{GaN} = 229.6(1) pm][6] and 11 pm larger than in the digallylphosphane $MesP[Ga(trip_2)]_2$[10]. The latter is the only known gallium-phosphorus compound containing a planar-coordinated phosphorus atom. In these compounds a geometrically ideal overlap between the phosphorus lone pair and the p orbital of the gallium atom is possible. Shorter gallium–phosphorus bonds are found in cyclic phosphanylgallanes with tricoordinated gallium and phosphorus atoms such as **4**[8] [d_{Ga-P} = 227.4(4) pm] and **5**[9] [d_{Ga-P} = 227.9(4)–233.8(5) pm].

9 (Figure 2) crystallizes in the triclinic system, with space group $P\bar{1}$. The gallium–phosphorus bond in this centrosymmetric molecule [d_{Ga-P} = 242.25(8) pm] is even longer than that in **8**. This is consistent with a pyramidally coordinated phosphorus atom (317.7°) with more acute bond angles than those in **8**. The gallium–nitrogen bond lengths and the bond angles at the gallium centre are very similar to those in **8**. The phosphorus–phosphorus bond length [d_{P-P} = 225.4(1) pm] is in the normal range found for P–P single bonds. However, compared to **9**, the phosphorus–phosphorus bond between the trigonal planar coordinated phosphorus atoms in **4** is some 15 pm shorter[12]. Clearly, in **9** no gallium–phosphorus pp(π) overlap can force the phosphorus atom into an sp^2-like situation, which is responsible for the shortening of the phosphorus–phosphorus bond length.

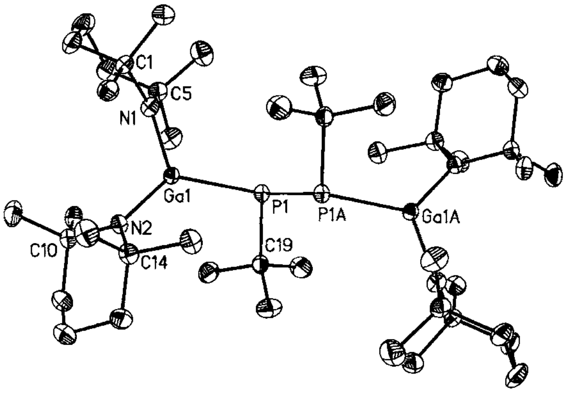
10 (Figure 3) crystallizes in the monoclinic system, with space group $P2_1/c$, Z = 8. The structure suffers from a severe disorder of the $P\mathit{t}Bu_2$ group in one of the two independent molecules, which is equal to an inversion of the phosphorus pyramid[25]. The average gallium–phosphorus distance is 233.5 pm with the phosphorus atoms being pyramidally coordinated [sum of bond angles P(1): 333.3°, P(2): 326.9°, P(2)A: 329.8°]. This is smaller than in **8** and **9** but longer than in **1**. The stereochemistry of **10** is similar to that of **8** in terms of the eclipsed orientation of one of the *tert*-butyl groups in relation to one of the gallium–carbon bonds. Consequently, the angle C(1)–Ga(1)–P(1) is wide, as is the corresponding N–Ga–P angle in **8**. The torsion angle between the P lone pair and the Ga-p_z orbital in **10** is approx. 25° and the planes of the mesityl substituents form angles of 60° and 80° to the C(1)/P(1)/C(10) plane.

Figure 1. View of a molecule of **8**; the thermal ellipsoids represent 30% probability. Hydrogen atoms have been omitted for clarity[a]



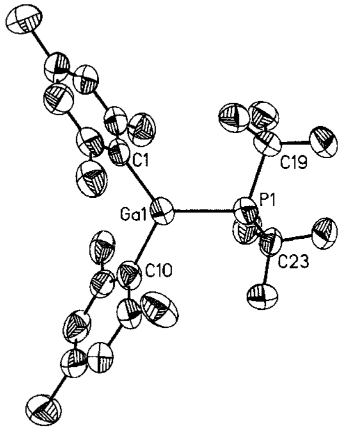
[a] Selected bond lengths [pm] and angles [°]: Ga–P 237.5(3), Ga–N(1) 191.2(6), Ga–N(2) 190.4(6); N(1)–Ga–N(2) 121.8(3), N(1)–Ga–P 111.5(2), N(2)–Ga–P 126.0(2), C(1)–N(1)–Ga 124.2(5), C(1)–N(1)–C(5) 118.1(6), C(5)–N(1)–Ga 117.3(5), C(10)–N(2)–Ga 123.7(5), C(10)–N(2)–C(14) 116.8(6), C(14)–N(2)–Ga 119.3(5), C(19)–P–C(23) 110.8(4), C(19)–P–Ga 113.5(3), C(23)–P–Ga 107.5(3).

Figure 2. View of a molecule of **9**; the thermal ellipsoids represent 50% probability; hydrogen atoms have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ga(1)–P(1) 242.25(8), Ga(1)–N(1) 189.4(2), Ga(1)–N(2) 189.5(2), P(1)–P(1)A 225.4(1); N(1)–Ga(1)–N(2) 120.38(8), N(1)–Ga(1)–P(1) 110.60(6), N(2)–Ga(1)–P(1) 128.48(6), C(1)–N(1)–Ga(1) 121.4(1), C(1)–N(1)–C(5) 116.3(2), C(5)–N(1)–Ga(1) 122.3(1), C(10)–N(2)–Ga(1) 122.4(1), C(10)–N(2)–C(14) 116.7(2), C(14)–N(2)–Ga(1) 120.9(1), C(19)–P(1)–P(1)A 103.61(7), C(19)–P(1)–Ga(1) 105.21(7), P(1)A–P(1)–Ga(1) 108.87(4).

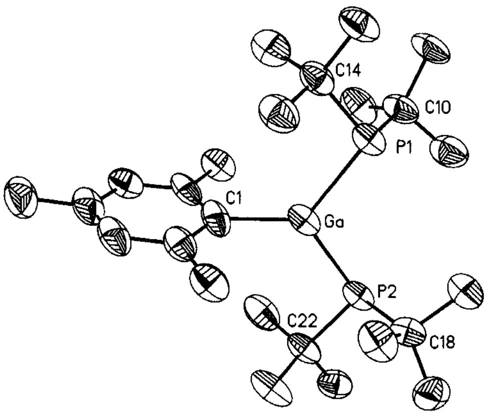
Figure 3. View of a non-disordered molecule of **10**; the thermal ellipsoids represent 50% probability; hydrogen atoms have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ga(1)–P(1) 232.1(2), Ga(1)–C(1) 199.0(6), Ga(1)–C(10) 197.6(6), P(1)–C(19) 189.1(6), P(1)–C(23) 189.9(6); C(1)–Ga(1)–C(10) 116.9(2), C(1)–Ga(1)–P(1) 124.5(2), C(10)–Ga(1)–P(1) 117.4(2), C(19)–P(1)–C(23) 112.4(3), C(19)–P(1)–Ga(1) 108.4(2), C(23)–P(1)–Ga(1) 102.5(2).

Relatively long gallium–phosphorus bonds [d_{GaP} = 236.3(3), 234.5(3) pm] and pyramidally coordinated phosphorus atoms [sum of bond angles P(1): 323.1°, P(2): 322.6°] are also present in the bis(phosphanyl)gallane **13** (Figure 4). It crystallizes in the triclinic system, with space group $P\bar{1}$. The small P(1)–Ga–P(2) angle of 111.7(1)° is remarkable. This is possible, because the *tert*-butyl groups are oriented to the outside of the molecule. Thus, a molecule of **13** possesses almost C_2 point group symmetry. The plane of the aromatic carbon atoms is almost orthogonal to the Ga/C(1)/P_2 plane, which minimizes steric repulsion in the molecule.

Figure 4. View of a molecule of **13**; the thermal ellipsoids represent 50% probability; hydrogen atoms have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Ga–P(1) 236.3(3), Ga–P(2) 234.5(3), Ga–C(1) 197.7(11); P(1)–Ga–P(2) 111.7(1), C(1)–Ga–P(1) 123.5(3), C(1)–Ga–P(2) 124.8(3).

The monomeric bis- and tris(phosphanyl)gallanes *t*Bu-Ga[P(H)aryl']$_2$[8] (d_{Ga-P} = 232.4 pm) and Ga[P(H)Aryl']$_3$[4] (d_{Ga-P} = 234 pm) have comparably large gallium–phosphorus distances. The terminal gallium–phosphorus bond in [*t*Bu(*i*Pr$_2$P)Ga(μ-P*i*Pr$_2$)$_2$(Cl)*t*Bu] is longer [$d_{Ga-P_{term.}}$ = 238.9(3) pm][26]. The gallium–carbon distances in **10** and **13** are typical for arylgallium compounds, for example in GaMes$_3$, d_{Ga-C} = 196 pm[27].

Table 1. Results of ab initio (SCF) calculations on phosphanylgallanes (base set: LANL2DZ)

	$(H_3C)_2GaPH_2$	$(H_3C)_2GaPH_2$	$H_3CGa(PH_2)_2$
Symmetry	C_{2v}	C_1	C_1
*d*GaP [pm]	227.4	237.2	236.2, 236.3
*d*GaC [pm]	197.1	197.5, 197.6	197.0
C–Ga–C [°]	126.8	125.5	PGaP: 117.4°
C–Ga–P [°]	116.6	117.1, 117.1	CGaP:120.6, 122.0°
sum of angles P [°]	360	305.4	301.5, 303.6
$\tilde{\nu}$ GaP	375.0	328.0	307.7(as), 362.5(s)

Conclusions

The observed stereochemistry in compounds **8**, **9**, **10**, and **13** precludes any possible gallium–phosphorus pp(π) interactions in these molecules. This is in accordance with low-temperature NMR studies, which show no measurable rotational barrier about the Ga–P bond. Ab initio (SCF) calculations on model compounds Me$_2$GaPH$_2$ and MeGa(PH$_2$)$_2$ support the experimental results. These revealed pyramidally coordinated phosphorus atoms as minimum-energy structures (Table 1). A planar Me$_2$GaPH$_2$ represents a saddle point on the potential energy surface. The calculated gallium–phosphorus distances for Me$_2$GaPH$_2$ and MeGa(PH$_2$)$_2$ are close to the experimental values found in **10** and **13**.

The calculations also pointed to an almost eclipsed orientation of one of the gallium–carbon bonds in relation to a phosphorus–hydrogen bond, thus modelling the X-ray data results. In the case of the bis(phosphanyl)gallane MeGa(PH$_2$)$_2$, the P–Ga–P angle was calculated to be smaller than 120°, as is indeed found in the *tert*-butyl derivative **13**. Even the calculated orientation of the pyramidal PH$_2$ residues with respect to the GaCP$_2$ plane in MeGa(PH$_2$)$_2$ resemble those observed in **13**.

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Experimental Section

General: All compounds were handled under purified nitrogen or in vacuo using Schlenk techniques. – NMR: Bruker ACP 200 and 250. – MS: Atlas CH7 or Varian MAT 711 machines with direct inlet. – Elemental analyses: Microanalytical laboratory of the Institut für Anorganische Chemie (München). – Melting points (uncorrected): sealed capillaries. – X-ray crystallographic study[28]: Suitable crystals were mounted with a perfluorinated polyether oil on the tip of a glass fibre and cooled immediately on the goniometer head, or were sealed under argon in a Lindemann capillary. Data collections were performed in ω-scan with Mo-K_α radiation (graphite monochromator) on Syntex P3 (**8**), STOE IPDS (**9**), or STADI4 (**10**, **13**) diffractometers using commercial software. Structures were solved using the program XS from Siemens

SHELXTL (PC) and refined against F^2 (full-matrix) with SHELXL93. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms were included as a riding model with fixed isotropic *U*'s in the final refinement. For further details see Table 2. – Quantum-chemical calculations: GAUSSIAN94 (Windows PC version)[29], base set LANL2DZ[30] for all atoms. – Gallium halides were prepared from the elements[31]; Mes_2GaCl, tmp_2GaCl[22], $MesPH_2$[32], $t$$BuPH_2$[33], $t$$Bu_2PH$[33], and $t$$Bu_2P_2K_2(THF)_x$[34] as described in the literature. Other chemicals were used as purchased.

Table 2. Details of crystal-structure investigations

	8	**9**	**10**	**12**
Formula	$C_{26}H_{54}GaN_2P$	$C_{44}H_{90}Ga_2N_4P_2$	$C_{26}H_{40}GaP$	$C_{25}H_{47}GaP_2$
Mol. mass	495.4	876.6	453.3	479.3
Temperature [K]	223	200	213	213
Crystal size [mm^3]	0.40×0.35×0.25	0.15×0.20×0.25	0.30×0.25×0.20	0.40×0.30×0.20
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [pm]	794.4(7)	8.429(2)	2371.4(5)	883.1(1)
b [pm]	1746.9(12)	10.191(2)	1256.7(3)	1048.9(1)
c [pm]	2058.7(12)	14.852(3)	1834.2(4)	1574.7(6)
α [°]		89.80(2)		87.40(4)
β [°]	99.24(6)	73.68(2)	108.99(3)	74.34(2)
γ [°]		75.05(2)		75.71(2)
V [nm^3]	2.820(4)	1179.7(4)	5.169 (2)	1.3607(6)
Z	4	1	8	2
μ (Mo-K_α) [mm^{-1}]	1.05	1.234	1.14	1.14
$\rho_{calcd.}$ [gcm^{-3}]	1.17	1.243	1.17	1.17
2Θ-Range	3 – 44	5 – 52	5 – 46	4 – 45
Refl. measured (in)	3725 ($h,k,\pm l$)	8317 ($\pm h,\pm k,\pm l$)	8993 ($\pm h,k,\pm l$)	3026 ($\pm h,\pm k,l$)
Unique reflections	3464	4301	7180	3026
Observed [with $F > n\sigma(F)$]	2311 (4)	3886 (4)	3514 (4)	2195 (4)
Structure solution	direct methods	direct methods	heavy atom method	heavy atom method
$R1$ [$4\sigma(F)$]	0.067	0.0338	0.050	0.082
$wR2$ (all data)	0.189	0.0915	0.158	0.245
Weighting scheme x/y [a]	0.0668/11.260	0.0561/0.2809	0.0816/0.00	0.0988/ 6.3089
Data/parameters	12.1	17.5	12.4	11.3
GOOF	1.085	1.065	0.937	1.273
Largest residual electron density [eÅ^{-3}]	0.64	0.533	0.29	0.92

[a] $w^{-1} = \sigma^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2\,F_c^2)/3$.

(Mesitylphosphanyl)bis(2,2,6,6-tetramethylpiperidino)gallane (**7a**): A solution of tmp_2GaCl (1.59 g, 4.12 mmol) in 10 ml of hexane was added dropwise to a stirred suspension of lithium mesitylphosphide (0.65 g, 4.12 mmol) in 20 ml of hexane at −78 °C. After stirring for 16 h, the precipitate was filtered off and all volatiles were removed from the solution. The remaining yellow oil was repeatedly dissolved in pentane and the solvent was evaporated. The product **7a** was clean on the basis of its NMR spectra, but did not crystallize from pentane, diethyl ether, toluene, or mixtures of these solvents; yield: 1.80 g (87%) of **7a**. – ^{1}H NMR (C_6D_6): δ = 6.81 (*m*-H), 3.77 (d, $^1J_{PH}$ = 210 Hz, PH), 2.46 (*o*-CH_3), 2.13 (*p*-CH_3), 1.62 (4-CH_2), 1.30 (3,5-CH_2), 1.38 (CH_3). – ^{13}C NMR (C_6D_6): δ = 141.0 (d, $^4J_{PC}$ = 11 Hz, *p*-C), 136.0 (*o*-C), 129.2 (d, $^3J_{PC}$ = 9 Hz, *m*-C), 54.5 (C-2,6), 40.7 (C-3,5), 34.7 (C-7–10), 25.0 (d, $^3J_{PC}$ = 11 Hz, *o*-CH_3), 21.1 (*p*-CH_3), 18.7 (C-4). – ^{31}P NMR (C_6D_6): δ = −124 (d, $^1J_{PH}$ = 210 Hz). – MS (70 eV, EI, ^{69}Ga); *m/z* (%): 349 (100) $[(tmp)_2Ga]^+$.

(tert-Butylphosphanyl)bis(2,2,6,6-tetramethylpiperidino)gallane (**7b**): The preparation was carried out analogously to that of **7a** using 1.69 g (4.38 mmol) of tmp_2GaCl and 0.42 g (4.38 mmol) of lithium *tert*-butylphosphide; yield: 1.58 g (84%) of **7b** as a yellow oil. – ^{1}H NMR (C_6D_6): δ = 6.81 (*m*-H), 3.77 (d, $^1J_{PH}$ = 210 Hz, PH), 2.46 (*o*-CH_3), 2.13 (*p*-CH_3), 1.77 (4-CH_2), 1.63 (d, $^3J_{PH}$ = 6 Hz, C-CH_3), 1.42 (3,5-CH_2), 1.49 (CH_3). – ^{13}C NMR (C_6D_6): δ = 54.7 (C-2,6), 41.3 (C-3,5), 35.0 (C-7–10), 34.3 (d, $^2J_{PC}$ = 9 Hz, C-CH_3), 35.8 (d, $^1J_{PC}$ = 13 Hz, *C*-CH_3), 18.9 (C-4). – ^{31}P NMR (C_6D_6): δ = −38 (d, $^1J_{PH}$ = 210 Hz). – MS (70 eV, EI, ^{69}Ga); *m/z* (%): 349 (13) $[(tmp)_2Ga]^+$, 126 (100) $[tmpH - Me]^+$.

(Di-tert-butylphosphanyl)bis(2,2,6,6-tetramethylpiperidino)gallane (**8**): A solution of lithium di-*tert*-butylphosphide (0.76 g, 5.0 mmol) in 15 ml of diethyl ether was treated at −78 °C with a solution of tmp_2GaCl (1.93 g, 5.0 mmol) in 15 ml of hexane. During slow warming to room temperature an orange-red colored solution was formed, from which a colorless precipitate deposited. After stirring for 20 h, all volatiles were removed in vacuo and the residue was redissolved in 10 ml of hexane. After filtration, repeated crystallization at −30 °C afforded 1.35 g (55%) of **8** as orange prisms; m.p. 122–123 °C. – Mol. mass: 494 (MS, ^{69}Ga). – ^{1}H NMR (C_6D_6): δ = 1.76 (4-CH_2), 1.60 (CH_3), 1.53 (d, $^3J_{PH}$ = 12 Hz, C-CH_3), 1.42 (3,5-CH_2). – ^{13}C NMR (C_6D_6): δ = 54.1 (C-2,6), 40.9 (C-3,5), 35.6 (C-7–10), 34.5 (d, $^2J_{PC}$ = 19 Hz, C-CH_3), 35.1 (d, $^1J_{PC}$ = 31 Hz, *C*-CH_3), 19.0 (C-4). – ^{31}P NMR (C_6D_6): δ = 48.6. – MS (70 eV, EI, ^{69}Ga); *m/z* (%): 494 (1) $[M]^{+\bullet}$, 354 (28) $[tmpGaP$*t*$Bu_2]^+$, 349 (100) $[M - P$*t*$Bu_2]^+$. – $C_{26}H_{54}N_2PGa$ (495.5): calcd. C 63.03, H 10.99, N 5.65; found C 61.31, H 10.39, N 5.07.

1,2-Di-tert-butyl-1,2-bis[bis(2,2,6,6-tetramethylpiperidino)gallyl]diphosphane (**9**): A solution of tmp_2GaCl (0.93 g, 2.4 mmol) in 6 ml of hexane was added to a stirred suspension of $t$$Bu_2P_2K_2(THF)_{0.5}$ (0.34 g, 1.2 mmol) in 30 ml of THF at room temperature. The mixture was stirred for 24 h, filtered, and the yellow filtrate was reduced to dryness in vacuo. The residue was dissolved in 3 ml of hot hexane. At room temperature, yellow prisms of **9** crystallized; yield: 0.83 g (78%). – ^{1}H NMR ([D_8]THF, T = 323 K): δ = 1.67 (4-CH_2), 1.60 [d, N = 14 Hz, $PC(CH_3)_3$], 1.55 (CH_3), 1.42 (3,5-CH_2). – ^{13}C NMR ([D_8]THF, T = 323 K): δ = 55.7 (C-2,6), 41.3 (C-3,5), 35.3 (C-7–10), 36.4 (t, N = 14.8 Hz, C-CH_3), 19.3 (C-4). – ^{31}P NMR ([D_8]THF, T = 323 K): δ = –5.5. – MS (70 eV, EI, ^{69}Ga); m/z (%): 349 (100) [tmp_2Ga]$^+$.

Di-tert-butylphosphanylbis(mesityl)gallane (**10**): Lithium di-*tert*-butylphosphide (0.34 g, 2.3 mmol) was stirred in 20 ml of pentane. A suspension of Mes_2GaCl (0.81 g, 2.3 mmol) in 30 ml of pentane was added quickly at –78 °C. After slow warming to ambient temperature, the yellow mixture was filtered and the filtrate was reduced to a volume of 10 ml. At –30 °C, 0.89 g of **10** (84%) crystallized in pale-yellow prisms; m.p. 86–92 °C (dec.). – Mol. mass: 452 (MS, ^{69}Ga). – ^1H NMR (C_6D_6): δ = 6.74 (s, 4H, CH), 2.52 (s, 12H, o-CH_3), 2.14 (s, 6H, p-CH_3), 1.39 (d, $^3J_{PH}$ = 12.5 Hz, $PCMe_3$). – ^{13}C NMR (C_6D_6): δ = 149.7 (d, $^2J_{PC}$ = 8.5 Hz, i-C), 141.7 (o-C), 138.1 (p-C), 127.7 (m-C), 34.8 (d, $^1J_{PC}$ = 26.5 Hz, $PCMe_3$), 34.3 (d, $^2J_{PC}$ = 13.0 Hz, $PC\mathit{Me}_3$), 25.8 (o-CH_3), 21.2 (p-CH_3). – ^{31}P NMR (C_6D_6): δ = 48.6. – MS (70 eV, ^{69}Ga); m/z (%): 452 (3) [M]$^{+\bullet}$, 307 (100) [M – P(tBu)$_2$]$^+$. – $C_{26}H_{40}GaP$ (453.3): calcd. C 68.89, H 8.89; found C 67.92, H 8.87.

Bis(di-tert-butylphosphanyl)mesitylgallane (**13**): The preparation was carried out analogously to that of **10**, using tBu$_2$PLi (0.57 g, 3.8 mmol) and $MesGaCl_2$ (0.49 g, 1.9 mmol); yield: 0.83 g (92%) of **13** as yellow plates, m.p. 92–98 °C. – Mol. mass: 478 (MS, ^{69}Ga). – ^1H NMR (C_6D_6): δ = 6.70 (s, 4H, CH), 2.37 (s, 6H, o-CH_3), 2.17 (s, 3H, p-CH_3), 1.46 (d, $^3J_{PH}$ = 11.4 Hz, $PCMe_3$). – ^{13}C NMR (C_6D_6): δ = 140.7 (p-C), 138.2 (o-C), 128.1 (m-C), 34.7 (d, $^1J_{PC}$ = 15.3 Hz, $PCMe_3$), 31.7 (d, $^2J_{PC}$ = 13.0 Hz, $PC\mathit{Me}_3$), 29.9 (o-CH_3), 26.2 (p-CH_3). – ^{31}P NMR (C_6D_6): δ = 51.7. – MS (70 eV, ^{69}Ga); m/z (%): 478 (10) [M]$^{+\bullet}$, 421 (2) [M – Bu]$^+$, 365 (2) [M – Bu – iC_4H_8]$^+$, 333 (100) [M – P(tBu)$_2$]$^+$, 309 (7) [M – Bu – 2 iC_4H_8]$^+$, 277 (9) [M – P(tBu)$_2$ – iC_4H_8]$^+$, 221 (49) [M – P(tBu)$_2$ – 2 iC_4H_8]$^+$. – $C_{25}H_{47}GaP_2$ (479.3): calcd. C 62.65, H 9.88; found C 61.18, H 9.05.

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