Contributions to the Coordination and Structural Chemistry of Gallium(III) and Indium(III) Halides: Complexes with Bi- and Tridentate Tertiary Phosphanes

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The reactions of gallium and indium trihalides with 1,2-bis-(diphenylphosphanyl)benzene (DP) and bis[(2-diphenylphosphanyl)phenyl]phenylphosphane (TP) lead to a variety of molecular and ionic complexes. Treatment of $InCl_3$ with DP results in $[(DP)_2InCl_2]^+[InCl_4]^-$ (**1**). With $InBr_3$ or InI_3 molecular 1:1 complexes $(DP)InX_3$ (**2**: X = Br, **3**: X = I) and ionic 1:2 complexes $[(DP)InX_2]^+[InX_4]^-$ (**4**: X = Br, **5**: X = I) are obtained. With $GaBr_3$ and GaI_3 only the ionic complexes $[(DP)GaX_2]^+[GaX_4]^-$ (**6**: X = Br, **7**: X = I) are generated. According to single-crystal X-ray analyses the environment of the metal center is octahedral in the cation of **1**, square pyramidal in **3**, and tetrahedral in the cations of **5** and **7**. The reactions of TP with GaI_3 or InI_3 afford ionic complexes $[(TP)MI_2]^+[MI_4]^-$ (**8**: M = Ga, **9**: M = In). As shown by ^{31}P-NMR studies and X-ray analyses, TP acts as a bidentate ligand in both complexes. The central phosphorus atom is not engaged in coordinative bonding. The ^{31}P resonances of all compounds appear at higher field as compared to the free ligand. This phenomenon calls for further investigations and a detailed theoretical treatment.

Introduction

Traditional Lewis acid catalysis has been dominated for a long time by the use of boron and aluminium halides.[1] It is only very recently that the analogous compounds of the heavier congeners in group 13, gallium and indium, have also been employed for this purpose.[2] Prominent examples are the $InCl_3$ catalysis of the Mukayama aldol reaction or special variations of the Diels-Alder reaction,[3] but also the $GaBr_3$-mediated methyl transfer of alkylsilanes and -siloxanes.[4] In most of these reactions the anhydrous binary halides EX_3 are employed, but there is growing interest in a mediation of the catalytic effect by the introduction of neutral or cationic donor/acceptor complexes, X_3E-L_n and $[X_2EL_n]^+$, respectively. The soft donor ligand L is expected to be reversibly displaced by the substrate of the reaction. It can also serve as a component which enhances the solubility and stability of the Lewis acid catalyst EX_3.

The formation of donor/acceptor complexes of gallium and indium halides is known for a wide variety of neutral donor ligands L.[5] Among these the cationic species are of special interest, because analogous cationic complexes of boron and aluminium are already well established as active catalysts in the living polymerization of propylene oxide and in Diels-Alder reactions.[6] Structurally characterized ionic species derived from gallium or indium trihalides in previous work are limited to O or N donors like pyridine, bipyridyl, methylpyrazole, or a crown ether, but also dimethyl sulfoxide, triphenylphosphane oxide, dimethylglycol, or hexamethyl phosphoric triamide etc.[7]

Complexes of gallium and indium halides with tertiary phosphanes have been considered only sporadically, and very little information is available on the stoichiometry and structure of such coordination compounds.[8] This is true in particular for complexes with polydentate phosphanes, for which a large variety of structural concepts can be conceived.[8a][8b][8c]

We have therefore initiated a systematic investigation of this chemistry, and in the present paper we report a first set of results obtained for ligands based on a phenylenebis(diphenylphosphane) skeleton.

Preparative Results

In order to secure chelation of the metal trihalides, a bidentate ligand was chosen in which the two donor centers are fixed in a *cis* position at a rigid backbone. 1,2-Bis-(diphenylphosphanyl)benzene (DP) is the most common prototype for this kind of ligands, and in bis[(2-diphenylphosphanyl)phenyl]phenylphosphane (TP) the same structural principle is extended to give a tripodal tertiary phosphane.

Anhydrous $InCl_3$ reacts with equimolar quantities of DP to give almost quantitative yields of an air-stable but moisture-sensitive crystalline product (**1**, 91% yield, m.p. 243°C), soluble in di- and trichloromethane [Eq. (1)]. Solvation in THF causes decomposition indicated by the release of phosphane ligand. The crystal structure analysis has shown that this compound is not a molecular 1:1 complex (below). Instead the reaction is associated with a halide redistribution between two indium atoms to give an ionic product

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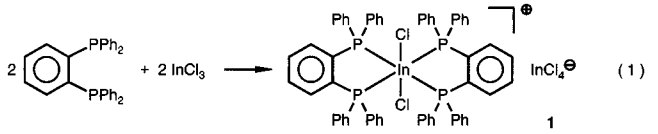
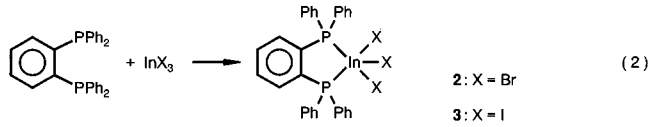
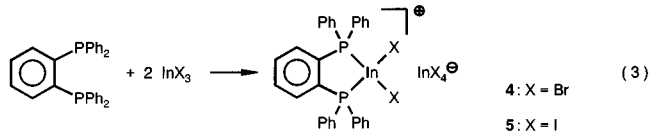
containing an $[InCl_4]^-$ anion and a bis-chelated cation $[(DP)_2InCl_2]^+$ with hexacoordinated indium atoms. Addition of excess $InCl_3$ has no effect regarding the nature of the product, and no complexes of the stoichiometry $(DP)(InCl_3)_2$ or $[(DP)InCl_2]^+$ $[InCl_4]^-$ can be isolated. The NMR spectra of solutions of $[(DP)_2InCl_2]^+[InCl_4]^-$ in $CDCl_3$ are consistent with fully symmetrically bound ligand molecules as suggested by only one set of phenyl and phenylene resonances (^1H,^{13}C). The singlet ^{31}P resonance also supports the proposed molecular symmetry, but the phosphorus nuclei are strongly shielded ($\delta P = -26.6$ in $CDCl_3$) which is very unexpected for tetracoordinated phosphorus atoms.



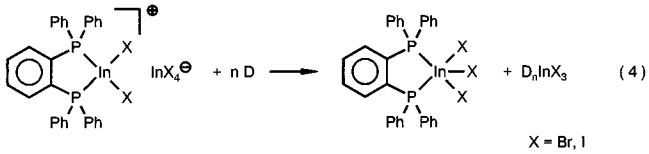
Unlike the results obtained with $InCl_3$, the nature of the product of the reaction of DP with $InBr_3$ and InI_3 depends on the molar ratio between the phosphane and the indium halide [Eq. (2) and (3)]. The 1:1 addition compound of DP with $InBr_3$ is assigned a molecular, non-ionic structure (**2**, 89% yield, m.p. 268°C, $\delta P = -26.9$) with a pentacoordinated indium atom. The compound is stable towards THF and its ^{13}C-NMR spectrum resembles that of $(DP)InI_3$, for which the non-ionic structure was confirmed by a crystal structure analysis (below, **3**, 75% yield, m.p. 239°C, $\delta P = -31.7$). The redistribution of halide anions as observed for **1** is excluded in both cases, because of serious steric congestion of the larger halogen atoms at a hexacoordinated metal center.





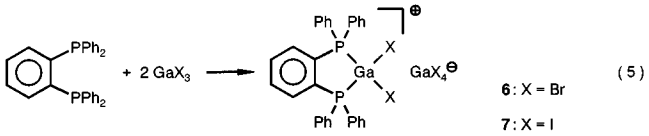
If the same components are allowed to react in the molar ratio of 1:2, ionic products are obtained, in which the $[InX_4]^-$ anion is accompanied by a cation $[(DP)InX_2]^+$ with tetracoordinated indium atoms (**4**, X = Br, 95% yield, m.p. 251°C, $\delta P = -20.0$; **5**, X = I, 87% yield, m.p. 199°C, $\delta P = -27.9$). The structure of **5** has also been determined by X-ray crystallography. The ^{13}C-NMR data of **5** show a distinct similarity with those of the bromo analog **4**.

In order to investigate whether an addition of nucleophiles to the tetracoordinated cationic indium complexes **4** and **5** is possible, reactions with THF, acetone and $OPPh_3$ were carried out. The reaction was found to transform the cationic complexes into the corresponding molecular 1:1 complexes [Eq. (4)].

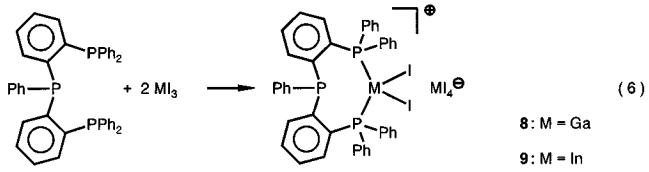


Cationic complexes of the type $[(DP)GaX_2]^+[GaX_4]^-$ with X = Br, I were also obtained with the lighter congener gallium [**6**, X = Br, 81% yield, m.p. 259°C, $\delta P = -22.1$; **7**, X = I, 95% yield, m.p. 219°C, $\delta P = -29.3$; Eq. (5)]. The ionic structure of the iodo compound with tetracoordinated gallium atoms in both the cation and the anion was confirmed in X-ray structure analysis (below).

Attempts to synthesize molecular gallium complexes analogous to **2** or **3** have failed.



Treatment of GaI_3 with TP in the molar ratio of 2:1 gives the ionic complex $[(TP)GaI_2]^+[GaI_4]^-$ in 83% yield [**8**, m.p. 267°C; Eq. (6)]. Earlier work with boron halides and a number of transition-metal salts has shown, that TP represents a potent tripodal ligand.[9] As derived from ^{31}P-NMR studies and X-ray analysis (below), in the present case TP acts only as a bidentate ligand, however, and the central phosphorus atom remains uncoordinated.



The reaction with InI_3 produces the indium analog of **8** in 88% yield (**9**, m.p. 259°C), for which the analytical and structural data (^{31}P NMR, X-ray diffraction) prove tetracoordinated metal centers. No molecular complex $(TP)InI_3$ could be obtained from equimolar quantities of TP and InI_3. The ionic complex **9** was again formed and half of the TP ligand applied (2:1 molar ratio!) remained unaffected.

NMR-Spectroscopic Investigations

The ^1H- and ^{13}C-NMR spectra of the complexes are characterized by complex multiplets and by a large number of phenyl/phenylene resonances, respectively, which were not analyzed any further because the δ and J data are not expected to be relevant to the discussion of structure and bonding in the individual species.

The ^{31}P-NMR spectra of the *DP complexes* show only one resonance with a large half width (ca. 80 Hz) owing to quadrupole broadening originating from interactions with the ^{115}In and $^{71/69}Ga$ nuclei which all have high quadrupole

moments. This line broadening is of course proof for the coordinative bonding of the phosphorus donors to the metal acceptors. It is very surprising, however, that the chemical shifts δP of the complexes are all in the range from −20 to −35 and hence upfield from the resonance of the free DP ligand (δP = −13.1 in $CDCl_3$). It is generally true for most phosphane complexes of main-group as well as transition metals that there is a downfield "coordination shift" between the free ligand and the corresponding complex. In the present cases this "coordination shift" is inverted. There is no straightforward explanation for this phenomenon, although it is tempting to ascribe the effect to the very low electronegativity of the heavy group 13 elements. Further experimental work and − more importantly − theoretical studies are required to clarify this point.

In the two *TP complexes* the resonances of the phosphorus atoms show marked differences: While the signals of the two terminal phosphorus atoms have a severe line broadening with poorly resolved (if any) splitting, the resonance of the central phosphorus atom is rather sharp and has the expected splitting for the A part of an AB_2 spin system (Figures 1 and 2). The implications of the two spectra are threefold:

1) The lack of quadrupole broadening of the signal of the central phosphorus atoms is proof that this atom is not strongly coordinated to indium or gallium, respectively. For the Ga compound this is clearly ruled out completely by the narrow line width, while for In there is discernible broadening, but still much less than for the terminal phosphorus atoms. (The same conclusions can be drawn from the crystal structure studies below.)

2) The *J*(P,P) coupling constants of the complexes are larger than in the free ligand, indicative of the change of hybridization at phosphorus upon complexation (from p to sp^3) as suggested by the Fermi contact mechanism.

3) There is no downfield shift of the resonance of the terminal or central phosphorus atoms upon complexation. On the contrary, all resonances are again (as for DP, above) shifted strongly *upfield* as compared to free TP.

Figure 1. $^{31}P\{^1H\}$-NMR spectrum of **8** in CD_2Cl_2 at 20°C; chemical shifts (δ values)

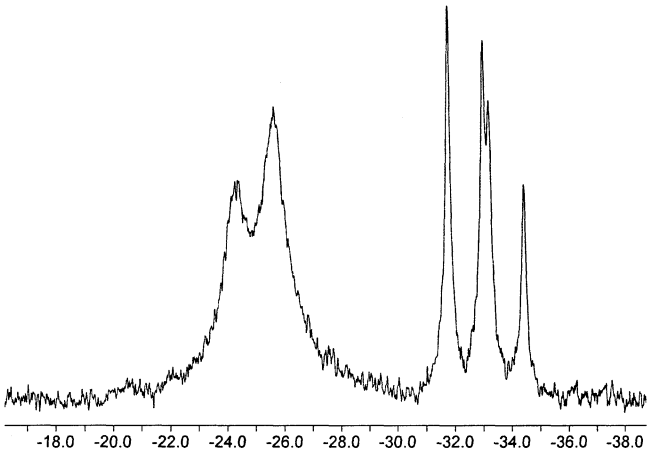
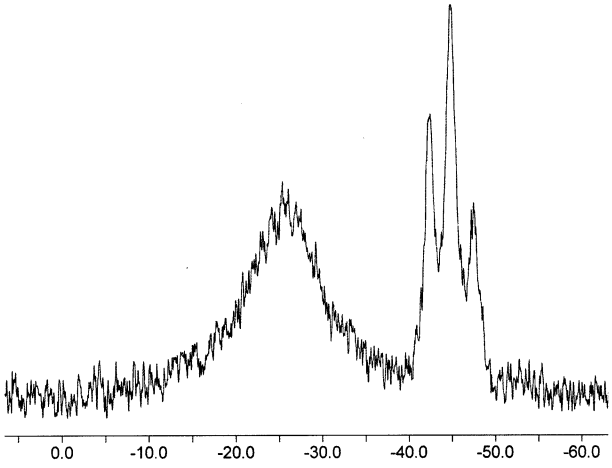


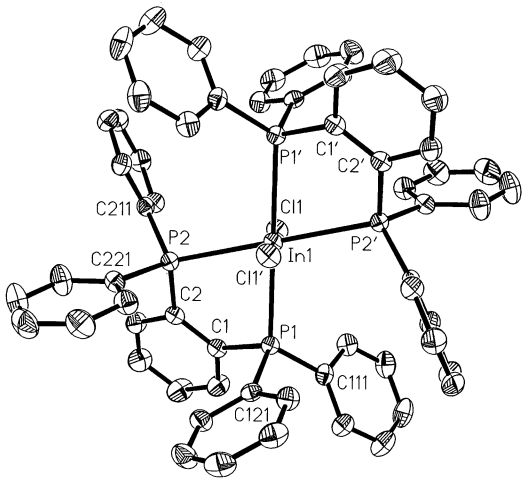
Figure 2. $^{31}P\{^1H\}$-NMR spectrum of **9** in CD_2Cl_2 at 20°C; chemical shifts (δ values)



Structural Investigations

Complexes of 1,2-Bis(diphenylphosphanyl)benzene (DP): The compound with the net formula $(DP)InCl_3$ (**1**) was found to have the ionic structure $[(DP)_2InCl_2]^+[InCl_4]^-$. The complex crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The asymmetric unit contains two crystallographically independent halves of the cation and one anion. The *anion* with In3 as the central atom has a standard tetrahedral structure with bond lengths and angles in the ranges documented in the literature. The two *cation* halves are complemented by their second halves which are related by crystallographic centers of inversion (Figure 3). As shown by a schematic superposition (Figure 4), the two cations are structurally very similar, and in a discussion of the details both cations can be treated together.

Figure 3. Molecular structure of the cation in **1** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, only one of the two crystallographically independent cations is shown, hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: In1−Cl1 2.4822(5) [2.4838(6)], In1−P1 2.6648(6) [2.6849(6)], In1−P2 2.7133(6) [2.7374(6)]; Cl1−In1−Cl1′ 180.0 [180.0], Cl1−In1−P1 85.35(2) [85.50(2)], Cl1−In1−P2 82.77(2) [85.39(2)], P1−In1−P2 76.14(2) [73.29(2)]. The data in brackets refer to the second independent cation accordingly.

Figure 4. Superposition of the two crystallographically independent cations in **1**

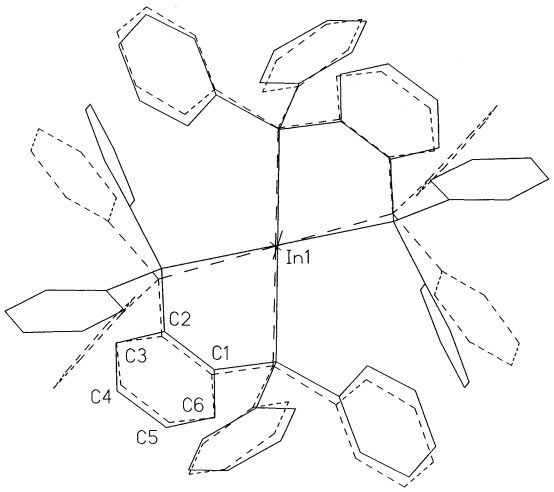
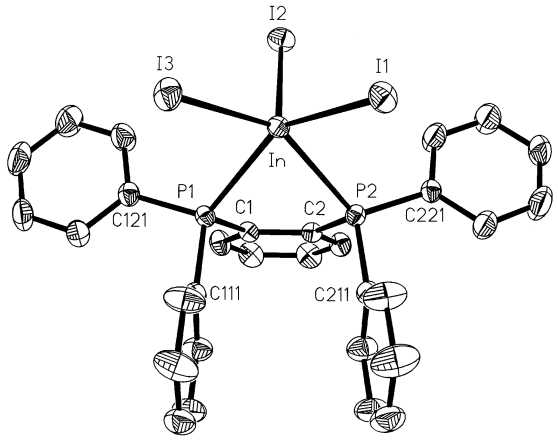


Figure 5. Molecular structure of **3** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: In−I2 2.7134(4), In−I1 2.7729(4), In−I3 2.7875(5), In−P1 2.7140(9), In−P2 2.7569(9); I3−In−I1 95.306(13), I1−In−I2 109.336(14), I2−In−I3 108.045(14), I1−In−P2 89.66(2), I3−In−P1 89.37(2), I2−In−P1 99.82(2), I2−In−P2 97.99(2), P1−In−P2 71.44(3).

The indium atoms in the cations are in an octahedral environment with two chloride ligands in the apical positions and two chelate ligands spanning equatorial edges. The angles at In1 and In2 are all close to 90 or 180°. The In1/In2−Cl bond lengths in the octahedra [average 2.4830 Å] are significantly longer than the In3−Cl bond lengths [average 2.3487 Å] in the tetrahedral anion. This result is in agreement with previous observations for two different polyhedra with a common central element having the same ligands.

The four chelate rings are in envelope conformations with the metal atoms out of the plane containing the phenylene rings and the phosphorus atoms. In both cases the geometry of the rings and their substituents is very close to mirror symmetry, the individual mirror planes passing through Cl1−In1−Cl1′/Cl2−In2−Cl2′ and bisecting the phenylene rings (Figures 3 and 4).

The compound with the net formula $(DP)InI_3$ (**3**) was found to be a molecular, non-ionic species. It crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The individual molecules have no crystallographically imposed symmetry, but the molecular geometry follows very closely mirror symmetry as related to a plane passing through the In−I2 unit and bisecting the phenylene ring (Figure 5).

The indium atom is pentacoordinated in a quasi square-pyramidal environment, where I2 occupies the apical position and the ligand spans one edge of the basal square plane and with the other two iodine atoms at the remaining basal vertices. The chelate ring has an envelope conformation as already noted for $[(DP)_2InCl_2]^+$. The In−I2 distance (apical) is significantly shorter [2.7134(4) Å] than the In−I1/I3 distances [basal, average 2.7802 Å]. This deviation corresponds to two different sets of I−In−I angles, a smaller one for I1−In−I3 [95.306(13)°] and two larger ones for I1−In−I2 [109.336(14)°] and I2−In−I3 [108.045(14)°].

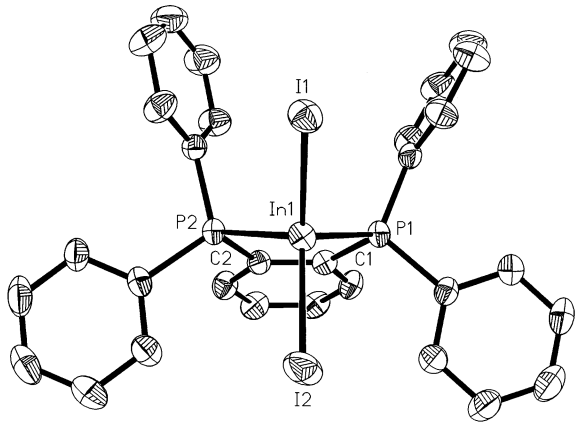
The compound of the stoichiometry $(DP)(InI_3)_2$ (**5**) has an ionic structure $[(DP)InI_2]^+[InI_4]^-$. It crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The anion has a slightly distorted tetrahedral geometry at the central indium atom (In2) with standard bond lengths. The geometry of the cation (Figure 6) deviates only slightly from mirror symmetry. The indium atom In1 is in a tetrahedral environment and part of a chelate ring with an envelope conformation. Following a very general rule, the In−I distances are significantly shorter in the cation [average 2.6570 Å] than in the anion [average 2.6993 Å]. Both distances are shorter, however, than the bond lengths for pentacoordinate indium (above), and this reduction also applies to the In−P bonds in the tetra- as compared to the pentacoordinate species (see captions to figures).

The gallium analog of the composition $(DP)GaI_3$ (**7**) has the same structure $[(DP)GaI_2]^+[GaI_4]^-$ like its indium counterpart (Figure 7). The crystals are also triclinic, space group $P\bar{1}$, $Z = 2$, but are not isomorphous with the indium compound. The general description can be adopted from $[(DP)InI_2]^+$ $[InI_4]^-$. Where variations appear, these are only associated with the difference in the covalent radii of gallium and indium.

Complexes of Bis[(2-diphenylphosphanyl)phenyl]phenylphosphane (TP): The complexes $(TP)(InI_3)_2$ (**9**) and $(TP)(GaI_3)_2$ (**8**) have ionic structures $[(TP)MI_2]^+[MI_4]^-$ with M = In, Ga. The crystals are isomorphous (space group $P\bar{1}$, $Z = 2$) with very similar cell dimensions (Table 2). The anions are tetrahedral tetraiodometallate moieties with structural details closely comparable to those of the DP complexes (above).

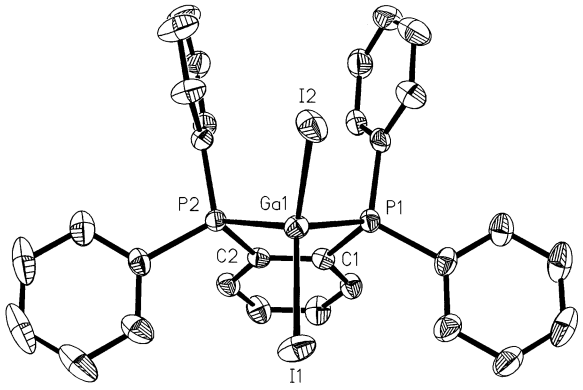
The metal atoms of the cations are also tetracoordinated with bond angles I−M−I and P−M−P at 103.02(2)/

Figure 6. Molecular structure of the cation in **5** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: In1−I1 2.6644(6), In1−I2 2.6497(5), In1−P1 2.5862(11), In1−P2 2.5635(11); I1−In1−I2 118.12(2), I1−In1−P1 116.22(3), I1−In1−P2 113.78(3), I2−In1−P1 111.02(3), I2−In1−P2 110.47(3), P1−In1−P2 81.61(4).

Figure 7. Molecular structure of the cation in **7** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms omitted for clarity)[a]

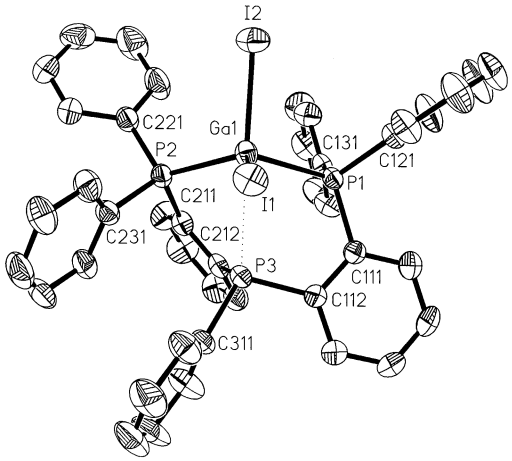


[a] Selected bond lengths [Å] and angles [°]: Ga1−I1 2.4904(6), Ga1−I2 2.4912(7), Ga1−P1 2.3976(13), Ga1−P2 2.4085(12); I1−Ga1−I2 115.02(2), I1−Ga1−P1 110.84(4), I1−Ga1−P2 110.05(4), I2−Ga1−P1 112.64(4), I2−Ga1−P2 119.90(4), P1−Ga1−P2 84.49(4).

113.11(3)° for In and 103.43(3)/113.71(5)° for Ga, respectively (Figures 8 and 9). Deviations from the regular tetrahedral angle are thus very small and not indicative of *tri*-podal action of the ligand. Bond lengths M−I and M−P are also similar to those in the DP complexes (above).

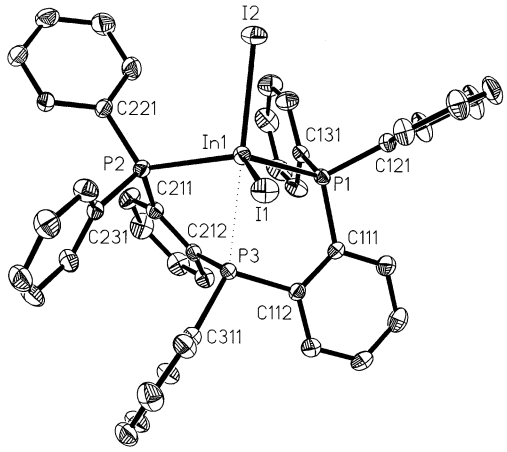
Closer inspection of the structural diagrams shows, however, that the distance In1−P3 [2.8933(10) Å] in the indium compound is not that much larger (about 10%) than the distances In−P1 [2.6239(10) Å] and In1−P2 [2.5982(10) Å]. This observation suggests that coordinative bonding of the middle phosphorus atom (P3) of the TP ligand to In1 cannot a priori be ruled out. In fact, the rather rigid geometry of the ligand leaves no choice and virtually forces the third phosphorus atom into the bonding region of the metal atom.

Figure 8. Molecular structure of the cation in **8** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: Ga1−I1 2.5473(8), Ga1−I2 2.5818(8), Ga1−P1 2.435(2), Ga1−P2 2.420(2), Ga1−P3 2.905(2); I1−Ga1−I2 103.43(3), I1−Ga1−P1 113.05(4), I1−Ga1−P2 118.84(4), I2−Ga1−P1 100.36(4), I2−Ga1−P2 104.55(4), P1−Ga1−P2 113.71(5), Ga1−P3−C112 103.3(3), Ga1−P3−C212 96.6(2), Ga1−P3−C311 137.2(3).

Figure 9. Molecular structure of the cation in **9** with atomic numbering (ORTEP drawing, 50% probability ellipsoids, hydrogen atoms omitted for clarity)[a]



[a] Selected bond lengths [Å] and angles [°]: In1−I1 2.7092(5), In1−I2 2.7376(5), In1−P1 2.6239(10), In1−P2 2.5982(10), In1−P3 2.8933(10); I1−In1−I2 103.02(2), I1−In1−P1 115.35(2), I1−In1−P2 119.96(2), I2−In1−P1 98.19(2), I2−In1−P2 102.94(2), P1−In1−P2 113.11(3), In1−P3−C112 106.13(12), In1−P3−C212 98.36(12), In1−P3−C311 132.91(13).

A simple geometrical calculation of the orientation of the lone pair of electrons at P3 (taking this atom as a pseudo-tetrahedral center) leads to the conclusion, however, that this vector is not pointing towards the metal atom, but into a direction where In1−P3 interaction is rather poor. This is e.g. borne out by the large spread of the angles from In1−P3−C212 = 98.36(12)° and In1−P3−C112 = 106.13(12)° to In1−P3−C311 = 132.91(13)°. The difference of the In−I distances in the cation and the anion of **9** are surprisingly small (only a few percent).

Table 1. Crystal data, data collection, and structure refinement for compounds **1**, **3**·2 $CHCl_3$, and **5**·CH_2Cl_2

	1	**3**·2 $CHCl_3$	**5**·CH_2Cl_2
crystal data			
formula	$C_{60}H_{48}Cl_6In_2P_4$	$C_{32}H_{26}Cl_6I_3InP_2$	$C_{31}H_{26}Cl_2I_6In_2P_2$
M_r	1335.20	1180.69	1522.40
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.146(1)	9.651(1)	10.611(1)
b [Å]	13.514(1)	12.455(1)	13.103(1)
c [Å]	20.782(1)	17.311(1)	17.522(1)
α [°]	77.48(1)	107.97(1)	68.94(1)
β [°]	81.98(1)	90.35(1)	75.58(1)
γ [°]	70.99(1)	99.00(1)	69.76(1)
V [Å^3]	2881.2(4)	1951.7(3)	2121.3(3)
$\rho_{calcd.}$ [gcm^{-3}]	1.539	2.009	2.383
Z	2	2	2
$F(000)$	1336	1116	1384
μ(Mo-K_α) [cm^{-1}]	12.28	34.94	56.75
absorption corr.	ψ scans	ψ scans	ψ scans
T_{min}/T_{max}	0.96/0.99	0.74/0.99	0.70/0.99
data collection			
T [°C]	−74	−74	−74
scan mode	ω	ω-Θ	ω
hkl range	−13→14, −17→15, −25→26	−12→12, −15→15, 0→22	−12→13, 0→16, −20→22
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.64	0.64	0.64
measured refl.	16992	8232	8800
refls. used for refinement	12467	8199	8766
solution	direct methods	Patterson	Patterson
refinement			
refined parameters	652	397	388
H atoms (found/calcd.)	0/48	0/26	0/26
final R values [$I > 2\sigma(I)$]			
$R1$[a]	0.0249	0.0277	0.0305
$wR2$[b]	0.0571	0.0689	0.0717
$GOOF$	1.073	1.092	1.131
$(\text{shift/error})_{max}$	<0.001	<0.001	<0.001
ρ_{fin}(max/min) [eÅ^{-3}]	0.865/−0.610	2.738/−1.809[c]	1.294/−1.782

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. − [b] $wR2 = \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2+2F_c^2)/3$; a = 0.0210 (**1**), 0.0322 (**3**·2 $CHCl_3$), 0.0303 (**5**·CH_2Cl_2); b = 2.62 (**1**), 5.04 (**3**·2 $CHCl_3$), 6.60 (**5**·CH_2Cl_2). − [c] Residual electron densities located around solvent $CHCl_3$.

Table 2. Crystal data, data collection, and structure refinement for compounds **7**, **8**, and **9**

	7	**8**	**9**
crystal data			
formula	$C_{30}H_{24}Ga_2I_6P_2$	$C_{42}H_{33}Ga_2I_6P_3$	$C_{42}H_{33}I_6In_2P_3$
M_r	1347.27	1531.43	1621.63
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.832(1)	10.432(1)	10.435(1)
b [Å]	11.107(1)	14.676(1)	14.583(1)
c [Å]	16.929(1)	16.260(2)	16.394(2)
α [°]	89.93(1)	82.04(1)	80.96(1)
β [°]	72.36(1)	79.48(1)	79.17(1)
γ [°]	88.24(1)	81.35(1)	82.02(1)
V [Å^3]	1940.0(3)	2403.9(4)	2404.5(4)
$\rho_{calcd.}$ [gcm^{-3}]	2.306	2.116	2.240
Z	2	2	2
$F(000)$	1228	1420	1492
μ(Mo-K_α) [cm^{-1}]	62.64	51.01	49.39
absorption correction	ψ-scans	ψ-scans	ψ-scans
T_{min}/T_{max}	0.52/0.99	0.70/0.99	0.63/0.99
data collection			
T [°C]	−74	+23	−74
scan mode	ω	ω-Θ	ω-Θ
hkl range	−13→12, −13→13, −17→0	0→12, −17→18, −19→19	−12→13, −18→18, 0→20
$\sin(\theta/\lambda)_{max}$ [Å^{-1}]	0.62	0.62	0.64
measured reflections	6984	8648	10144
refls. used for refinement	6973	8624	10089
solution	direct methods	solution of **9** was used	Patterson
refinement			
refined parameters	361	478	478
H atoms (found/calcd.)	0/24	0/33	0/33
final R values [$I > 2\sigma(I)$]			
$R1$[a]	0.0304	0.0433	0.0279
$wR2$[b]	0.0739	0.1072	0.0671
$GOOF$	1.089	1.083	1.203
$(\text{shift/error})_{max}$	< 0.001	< 0.001	< 0.001
ρ_{fin}(max/min) [eÅ^{-3}]	3.368/−1.927[c]	3.125/−2.012[c]	1.082/−1.585[c]

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$. − [b] $wR2 = \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2+2F_c^2)/3$; a = 0.0316 (**7**), 0.0600 (**8**), 0.0296 (**9**); b = 8.92 (**7**), 7.93 (**8**), 5.43 (**9**). − [c] Residual electron densities located around iodine atoms.

The situation is very similar in the structure of the gallium analog **8**, where the distance Ga1−P3 is 2.905(2) Å and thus almost equal to In1−P3 (above), but much larger as compared to Ga1−P1 [2.435(2) Å] and Ga1−P2 [2.420(2) Å]. The angles Ga1−P3−C112/ C212/C311 vary over a range of 40°, with individual values of 103.3(3)/ 96.6(2)/137.2(3)°, respectively, and are not in agreement with tetrahedral coordination of the phosphorus atom P3.

From the structural data it thus appears that neither the indium nor the gallium atom in the $[(TP)MI_2]^+$ cations of **8** and **9** (M = In, Ga) is pentacoordinated by the two halogen atoms and the potentially tripodal ligand. Although the inflexibility of the TP ligand holds the central phosphorus atom in close proximity of the metal atom, the bonding interaction is poor in spite of the sub-van-der-Waals distance of only ca. 2.90 Å. It is gratifying that this result is in full agreement with the essence of the NMR data regarding in particular the line widths and the coupling pattern of the ^{31}P-NMR resonances, although the chemical-shift parameters are much more difficult to evaluate. More comprehensive data sets are clearly needed in order to allow a deeper understanding of the chemical-shift increments responsible for non-classical signal displacements in the NMR spectra of main-group metal complexes.

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Experimental Section

General: All experiments were carried out routinely in purified dry nitrogen. Solvents were dried and kept under nitrogen, and glassware was oven-dried and filled with nitrogen. 1,2-Bis(diphenylphosphanyl)benzene[10] and bis[(2-diphenylphosphanyl)phenyl]-phenylphosphane[9a] were prepared according to literature procedures, all other starting materials were commercially available. Gallium and indium trihalides were stored and handled in a glove box.

[1,2-Bis(diphenylphosphanyl)benzene]$_2$InCl$_2^+$ InCl$_4^-$ (**1**): Indium trichloride (99 mg, 0.45 mmol) is added to a solution of 1,2-bis(diphenylphosphanyl)benzene (202 mg, 0.45 mmol) in 10 ml of toluene and stirred for 2 h at 80°C. The white precipitate is collected and recrystallized from chloroform/pentane. Yield 273 mg (91%), colorless crystals, m.p. 243°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.78–7.11 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 128.8, 132.1, 135.3 (AXX′, phenylene); 125.8, 129.2, 131.6, 134.2 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −26.6 (br. s). – $C_{60}H_{48}Cl_6In_2P_4$ (1335.30): calcd. C 53.97, H 3.62; found C 53.31, H 3.65.

[1,2-Bis(diphenylphosphanyl)benzene]InBr$_3$ (**2**): As described for compound **1**, with indium tribromide (95 mg, 0.268 mmol) and 1,2-bis(diphenylphosphanyl)benzene (120 mg, 0.268 mmol). Yield 191 mg (89%), colorless crystals, m.p. 268°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.74–7.09 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 131.9, 135.2, 135.4 (AXX′, phenylene); 126.3, 129.1, 131.4, 134.3 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −26.9 (br. s). – $C_{30}H_{24}Br_3InP_2$ (801.00): calcd. C 44.99, H 3.02; found C 44.53, H 3.05.

[1,2-Bis(diphenylphosphanyl)benzene]InI$_3$ (**3**): As described for compound **1**, with indium triiodide (126 mg, 0.255 mmol) and 1,2-bis(diphenylphosphanyl)benzene (114 mg, 0.255 mmol). Yield 180 mg (75%), colorless crystals, m.p. 239°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.65–7.12 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 131.7, 135.4, 135.8 (AXX′, phenylene); 127.1, 129.0, 131.1, 134.2 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −31.7 (br. s). – $C_{30}H_{24}I_3InP_2$ (942.00): calcd. C 38.25, H 2.57; found C 37.63, H 2.81.

[1,2-Bis(diphenylphosphanyl)benzene]InBr$_2^+$ InBr$_4^-$ (**4**): As described for compound **1**, with indium tribromide (190 mg, 0.536 mmol) and 1,2-bis(diphenylphosphanyl)benzene (120 mg, 0.268 mmol). Yield 293 mg (95%), colorless crystals, m.p. 251°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.94–7.30 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 131.6, 134.9, 136.8 (AXX′, phenylene); 121.3, 130.5, 133.9, 134.2 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −20.0 (br. s). – $C_{30}H_{24}Br_6In_2P_2$ (1155.53): calcd. C 31.18, H 2.09; found C 30.89, H 2.02.

[1,2-Bis(diphenylphosphanyl)benzene]InI$_2^+$ InI$_4^-$ (**5**): As described for compound **1**, with indium triiodide (394 mg, 0.795 mmol) and 1,2-bis(diphenylphosphanyl)benzene (178 mg, 0.40 mmol). Yield 495 mg (87%), colorless crystals, m.p. 199°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.02–7.28 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 131.2, 135.2, 136.9 (AXX′, phenylene); 120.9, 130.4, 133.8, 134.1 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −27.9 (br. s). – $C_{30}H_{24}I_6In_2P_2$ (1437.53): calcd. C 25.07, H 1.68; found C 25.20, H 1.73.

[1,2-Bis(diphenylphosphanyl)benzene]GaBr$_2^+$ GaBr$_4^-$ (**6**): As described for compound **1**, with gallium tribromide (151 mg, 0.448 mmol) and 1,2-bis(diphenylphosphanyl)benzene (109 mg, 0.224 mmol). Yield 210 mg (81%), colorless crystals, m.p. 259°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.76–7.14 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 133.9, 135.9, 136.9 (AXX′, phenylene); 119.0, 130.6, 134.2, 134.5 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −22.1 (br. s). – $C_{30}H_{24}Br_6Ga_2P_2$ (1065.33): calcd. C 33.82, H 2.27; found C 33.48, H 2.14.

[1,2-Bis(diphenylphosphanyl)benzene]GaI$_2^+$ GaI$_4^-$ (**7**): As described for compound **1**, with gallium triiodide (201 mg, 0.446 mmol) and 1,2-bis(diphenylphosphanyl)benzene (100 mg, 0.223 mmol). Yield 285 mg (95%), colorless crystals, m.p. 219°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 8.02–7.28 (m, Ph). – ^{13}C{^{1}H} NMR (v. s.): δ = 131.2, 135.2, 136.9 (AXX′, phenylene); 120.9, 130.4, 133.8, 134.1 (AXX′, Ph). – ^{31}P{^{1}H} NMR (v. s.): δ = −29.3 (br. s). – $C_{30}H_{24}I_6Ga_2P_2$ (1347.33): calcd. C 26.74, H 1.80; found C 26.48, H 1.75.

{Bis[(2-diphenylphosphanyl)phenyl]phenylphosphane}GaI$_2^+$-GaI$_4^-$ (**8**): As described for compound **1**, with gallium triiodide (219 mg, 0.485 mmol) and bis[(2-diphenylphosphanyl)phenyl]phenylphosphane (153 mg, 0.243 mmol). Recrystallization of the white precipitate from methylene chloride/pentane yielded 309 mg (83%) of colorless crystals, m.p. 267°C. – ^{31}P{^{1}H} NMR (CD_2Cl_2, 20°C): δ = −33 (A_2B, J = 213 Hz, $P^{cent.}$), −25 (A_2B, $P^{term.}$). – $C_{42}H_{33}Ga_2I_6P_3$ (1531.51): calcd. C 32.94, H 2.17; found C 32.58, H 2.09.

{Bis[(2-diphenylphosphanyl)phenyl]phenylphosphane}InI$_2^+$-InI$_4^-$ (**9**): As described for compound **8**, with indium triiodide (253 mg, 0.511 mmol) and bis[(2-diphenylphosphanyl)phenyl]phenylphosphane (161 mg, 0.255 mmol). Yield 364 mg (88%), colorless crystals, m.p. 259°C. – ^{31}P{^{1}H} NMR (CD_2Cl_2, 20°C): δ = −45 (A_2B, J = 282 Hz, $P^{cent.}$), −26 (A_2B, $P^{term.}$). – $C_{42}H_{33}Ga_2I_6P_3$ (1621.71): calcd. C 31.11, H 2.05; found C 30.78, H 2.04.

Reactions of **4** *and* **5** *with Oxygen Donors:* [(DP)$InBr_2$]$^+$ [$InBr_4$]$^-$ (**4**, 100 mg, 0.086 mmol) is dissolved in 5 ml of THF and layered with pentane. The colorless crystals obtained show the same analytical data (mp, EA, NMR) as compound **2**. [(DP)InI_2]$^+$[InI_4]$^-$ (**5**, 100 mg, 0.069 mmol) is dissolved in 10 ml of $CHCl_3$ and 0.1 ml of acetone is added. After heating to reflux, a colorless solid is precipitated with pentane. The product shows the same analytical data as compound **3**. Similar results are obtained with $OPPh_3$ (50 mg, 0.18 mmol).

Crystal Structure Determinations: Specimens of suitable quality and size of compounds **1**, **3**·2 $CHCl_3$, **5**·CH_2Cl_2, **7**, **8**, and **9** were mounted in glass capillaries and used for measurements of precise cell constants and intensity-data collection on an Enraf Nonius CAD4 diffractometer [Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å]. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Lp correction was applied and intensity data were corrected for absorption effects. The structures were solved by direct and Patterson methods (SHELXS-86), respectively, and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)}$ = 1.5 × U_{eq} of the attached C atom). Further information on crystal data, data collection, and structure refinement are summarized in Tables 1 and 2. Important interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD-407907 (**1**), -407908 (**3**), -407905 (**5**), -407906 (**7**), -407904 (**8**), -407903 (**9**).

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