Direct Comparison of Subvalent, Polycationic Group 13 Cluster Compounds: Lessons learned on Isoelectronic DMPE Substituted Gallium and Indium Tetracation Salts

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Dedicated to the occasion of the 60th Birthday of Prof. Cameron Jones.

Abstract: The tetracationic, univalent cluster compounds [(M(dmpe)]₃PF⁺ (M = Ga, In; dmpe = bis(dimethylphosphino)ethane) were synthesized as their pF salts ([PF]⁻ = [Al(OR)₃]⁻; R = C(CF₃)₂). The four-membered ring in [(M(dmpe)]₃PF⁺ is slightly puckered for M = Ga and almost square planar for M = In. Yet, although structurally similar, only the gallium cluster is prevalent in solution, while the indium cluster forms temperature dependent equilibria that include even the monomeric cation [In(dmpe)]⁺. This system is the first report of one and the same ligand inducing formation of isoelectronic and isostructural gallium/indium cluster cations. The system allows to study systematically analogies and differences with thermodynamic considerations and bonding analyses, but also to outline perspectives for bond activation using cationic, subvalent group 13 clusters.

Introduction

Subvalent group 13 elements attract increasing interest not only due to their potential in bond activation[1] and catalysis,[2–4] but also due to their rich cluster chemistry. Since group 13 elements M are notoriously electron deficient compounds, the respective ligand supported clusters show a pronounced tendency to accept electrons and thus are often neutral or even anionic.[5–7] Our group demonstrated that the use of a weakly coordinating anion (WCA)[8–9], i.e., [PF]⁻ ([PF]⁻ = [Al(OR)₃]⁻; R = C(CF₃)₂), in combination with weakly coordinating solvents and strongly σ-donating ligands, allowed for formation of cationic, subvalent group 13 clusters.[10] On the one hand, the ligands delocalize the positive charge of M⁺, thereby minimizing Coulomb repulsion within the cluster, and lift the energy of the ns³ lone pair, so that these electron pairs can be used to form the M–M bonds within the cluster. On the other hand, the large volume of WCAs thermodynamically favors the formation of highly charged clusters and disfavors disproportionation of metastable M⁺ into elemental M⁰ and M²⁺.[10]

Employing this strategy, our group synthesized and isolated tricationic, triangular or tetracationic, rhombohedral In clusters with bipy and phenanthroline,[10] a tetracationic, square planar Ga cluster with 'butyldisilazane'[12] (BuNC) and a pentacationic, pentagonal Ga cluster with DMAP (4-dimethylaminopyridine) as ligands.[13] All of these clusters were obtained using [M(PhF)]₁[PF] as the M⁺ starting material.[14,15] Interestingly, Ga⁺, unlike In⁺, disproportionates in the presence of phenanthroline, underlining the differences in the chemistry of subvalent gallium and indium.[12] The stabilizing inert pair effect is more pronounced for the heavier congener, making Ga⁺ more prone to disproportionation.[11,16]

Beyond being chemical curiosities, the cationic gallium and indium clusters [(ML₃)ⁿ⁺]⁺ (M = Ga, In; L = ligand; m = 1 or 2) could possibly be employed in bond activation. Careful ligand design should allow for partial dissociation of the clusters into ligand-supported monomeric species [ML₃]⁻ in solution.[13,16] The metal atom in these fragments possess a ns²np² electron configuration, accounting for their formal carbene[18] or silylene[17,19] like character and amphiphilic nature.[11,13,16] Accordingly, it is well known that neutral or anionic subvalent group 13 complexes efficiently activate covalent bonds.[20]

Since phosphines are electron rich, σ-donating ligands, we rationalized that phosphines may induce cluster formation of univalent gallium and indium cations. Since, most likely, two P-donor atoms have to coordinate to the metal cation in order to promote M–M bond formation, it is crucial to employ a sterically non-demanding phosphine. This is underlined by the fact that P(Bu)₃ and PPh₃ do not induce cluster formation as Ga⁺ or In⁺ complexes.[14,18] Thus, we assumed that a chelating bisphosphine may be a suitable ligand, since ethylene-bridged bisphosphines of the type R₂PCH₂CH₂PR₂ have generally a smaller Tolman cone angle than two molecules of the respective monophosphines PR₂.[21] As a consequence, we chose
Me₃PCH₂CH₂PMMe₂ (bis(dimethylphosphino)ethane = dmpe) as a model ligand. So far, this bisphosphine has allowed for the isolation of unusual transition metal compounds[18] and also of mononuclear group 13 metal complexes[19] but, to the best of our knowledge, has not been employed for the synthesis of main group element clusters.

Results and Discussion

Synthesis

Layering the solutions containing a 1:1 stoichiometric ratio of [M(PhF₄)]₂[pf] (M = Ga, In) and dmpe in oDFB with n-pentane afforded orange-yellow and dark red crystals of [(Ga-dmpe)₄][pf]₄·4oDFB (1) and [(In-dmpe)₄][pf]₄·4oDFB (2), respectively, in almost quantitative yields. Both compounds are stable at room temperature (rt), but readily decompose in air. Equation (1) shows their formation and structural formulae.

\[
P + [M(PhF₄)]₂[pf] \rightarrow 4x_{oDFB, rt} - 2 PhF
\]

1 : 1 ratio

\[
M = Ga (1); \quad M = In (2)
\]

Molecular structure and bonding

To the best of our knowledge, 1⁺⁺ and 2⁺⁺ represent the first two cationic complexes of a chelating bisphosphine and subvalent group 13 metal ions. The molecular structure of the cationic clusters as determined by single crystal X-ray analysis is shown in Figure 1, along with selected structural parameters. Apart from [(Ga(CN)Bu)₃]⁺⁺, the square planar M₄ structure motif has been reported in potassium-stabilized, anionic gallium and indium clusters, i.e., K₃[Ga₄(C₂H₅)₂-2,6-Trip]₂[26] (Trip = 2,4,6-(Pr)₂C₆H₃) and K₃[In₄(BNDippCH)₂] [Dipp = 2,6-(Pr)₂C₆H₅].[27] It is noted that the alkali–metal counter ions can play a crucial role in stabilizing formally anionic group 13 clusters, which is why they are sometimes rather regarded as mixed alkali–metal-group 13 clusters.[26,24,25]

By contrast, in the hitherto prepared subvalent cationic clusters, including 1⁺⁺ and 2⁺⁺, no M–F₄ contact is shorter than the sum of the van-der-Waals radii,[26] indicating that the very weakly coordinating pf anion does not interact with the core of the metal atom cluster.[16,12,13]

The average Ga–Ga bond length in 1⁺⁺ is comparable to those found in [(Ga(CN)Bu)₄]⁺⁺ (246.1–246.6 pm)[12] [Ga(DMAP)]₄⁺⁺ (248.7–250.1 pm)[13] and in the anionic Ga₄ cluster in K₃[Ga₄(C₂H₅)₂-2,6-Trip]₂ (246.2–246.9 pm).[26] As for the In–In bond lengths in 2⁺⁺, they are somewhat longer than most of the In–In bonds in the cationic, rhombic bipy- (259.7–280.8 pm) and phenanthroline-supported (258.1–281.6 pm) clusters[16] but similar to those found in the anionic In₄ cluster in K₃[In₄(BNDippCH)₂] (280.5–283.8 pm).[27]

However, it is noteworthy that the average P–M distances (Ga: 237.9–244.8, av. 241.1 pm and In: 259.6–262.4, av. 260.5 pm) are significantly shorter than the average P–M bond lengths in the complexes [M(PhF₄)]₂⁻ (271 Ga and 300 In pm) or [M(PhBµ₂)₂]⁺ (277 Ga and 305 In pm). The bond shortening can probably be attributed to stronger P–M bonds, since charge delocalization in the clusters is more crucial than in the mononuclear complexes. Consequently, the calculated AIM charge on the M atoms in 1⁺⁺ and 2⁺⁺ (0.30 and 0.28 for M = Ga and In; Table 1) is not only reduced compared to the free ions, but also compared to that calculated for the hypothetical monomeric [M(dmpe)]⁺ fragments (0.50 and 0.56 for M = Ga and In). Remarkably, the P–M distances are only slightly longer than typical P–M⁺⁺ single bond lengths (235 Ga and 253 In pm)[27]

Interestingly, the In₄ moiety is a nearly perfectly planar square. By contrast, and unlike in the [Ga(CN)Bu)₄]⁺⁺ cluster cation, the Ga₄ ring deviates from planarity, with Ga–Ga–Ga–Ga dihedral angles surpassing 20°. Probably, the distortion of the Ga₄ tetragon is caused by steric repulsion of the methyl groups of the dmpe ligands due to the shorter P–M and M–M bonds and thus the smaller M₄ cluster core for M = Ga. However, the two diagonal, transannular Ga–Ga distances [344.8(1) pm and 346.6(1) pm] are considerably longer than the other intra-molecular Ga–Ga distances, so that a butterfly structure, which has already been observed in an anionic tetragainedide,[26] can be ruled out. This is underlined by AIM calculations, which give a ring critical point, but no bond critical point (BCP) in the middle of the Ga₄ moiety (see Section 8.3 in the Supporting Information). The structure of 1⁺⁺ and 2⁺⁺ is well reproduced by quantum chemical calculations. Selected calculated structural parameters are compared with experimental parameters in Table 1. Additionally, AIM charges on the M atoms, and bond

### Table 1. Calculated structural parameters of 1⁺⁺ and 2⁺⁺ (average structural parameters found in the crystal structure are given in parentheses; the average P–M bond lengths and P–M–P bond angles correspond to the values found in the [M(dmpe)]⁺ fragments. For disordered dmpe ligands, average P–M bond lengths and P–M–P bond angles equal the values found in the majority part of disordered dmpe molecules), along with calculated AIM charges on the metal atoms, bond path ellipticities ε, electron densities on the M–M bond critical points (BCPs) and Wiberg Bond Indices (WBI) of the M–M bonds. Calculations were performed at the RI-BP66D(D3BJ)/def2-TZVPP level of theory.

| Structural/Calculated parameters | 1⁺⁺ (M = Ga) | 2⁺⁺ (M = In) |
|---------------------------------|-------------|-------------|
| M–M bond lengths [pm]           | 250.7–251.1 (248.5) | 291.2 (280.2) |
| M–M–M angles [°]               | 88.3–89.0 (88.2) | 90.0 (90.0) |
| M–M–M–M angles [°]             | 19.3–19.4 (20.4) | 0.0 (0) |
| P–M distances [pm]             | 242.4–242.7 (241.1) | 266.2–267.4 (260.5) |
| P–M–P angles [°]               | 85.0–85.2 (84.9) | 79.3–79.4 (81.0) |
| AIM charge on M [e]             | 0.30         | 0.28        |
| Bond ellipticity ε on M–M–M BCPs [a.u.] | 0.057 | 0.037 |
| Electron density on M–M BCPs [e Å⁻³] | 0.403 | 0.273 |
| WBI of M–M bonds (av.)         | 0.87         | 0.74        |
ellipticities as well as electron densities on the M–M bond critical points and Wiberg Bond Indices (WBI) are given. Both the WBI and the electron density at the M–M BCPs are significantly higher for M = Ga than for M = In, which is indicative of the stronger Ga–Ga bonds compared to the In–In bonds. This agrees with the hypothetical reaction shown in Equation (2),

$$1^+ \rightarrow 4 [\text{In(dmpe)}]^+ \Delta \mu_{H}^{\text{f}} = +171.8 \text{ kJ mol}^{-1} 2^+ \rightarrow 4 [\text{Ga(dmpe)}]^+$$

which is calculated to be endothermic by more than 170 kJ mol$^{-1}$ in the gas phase (RI–BP86(D3BJ)/def2–TZVPP). As a consequence, every Ga–Ga bond in $1^{+}$ is inherently stronger than the four In–In bonds in $2^{+}$. And this also holds despite the greater steric repulsion of the ligands and greater Coulomb repulsion induced by the shorter Ga–Ga and Ga–P bonds in $1^{+}$ if compared to the respective indium system. The smaller HOMO-LUMO gap in the monomeric Ga-unit [M(dmpe)]$^{-}$ (2.94/3.10 eV for M = Ga/In), qualifies $1^{+}$ for better orbital overlap between the monomeric units, hence its HOMO and LUMO. In addition, the frontier orbitals of Ga are less diffuse than for the heavier congener, ensuring better spatial overlap. The frontier orbitals of $1^{+}$ and $2^{+}$ are depicted in Figure 2.

The HOMO is formed by $p$ orbitals, under mixing of the occupied metal $s$ orbitals, in the ring plane on the M–M bond edge, while the empty $p$ orbitals form a $\pi$ system perpendicular to the ring plane in the LUMO. The shape of the calculated Kohn-Sham frontier orbitals of $1^{+}$ and $2^{+}$ are similar, even though the $s$–$p$ mixing in the LUMO of $1^{+}$ is more pronounced than in the LUMO of $2^{+}$. 

![Molecular structures of the cluster cations $1^{+}$ (a) and b)) and $2^{+}$ (c) and d)]. The second perspective is shown in order to visualize the puckered Ga and the planar In, ring (M–M–M–M angle: ca. 20.4° for M = Ga and 0° for M = In). Average distances [pm] and angles [°]: Ga–Ga: 248.49(6), P–Ga: 241.1(1), Ga–Ga–Ga: 88.15(2), P–Ga–P: 84.9(1), In–In: 280.2(1), P–In–P: 260.5(1), In–In–In: 90.00(2), P–In–P: 81.05(3). The P–M bond lengths and P–M–P bond angles correspond to the values found in the [M(dmpe)]$^{-}$ subunits. For disordered dmpe ligands, the P–M bond lengths and P–M–P bond angles equate the values found in the majority part of disordered dmpe molecules. Counterions, solvent molecules, hydrogen atoms and disordered ligand molecules are not shown for clarity. Thermal ellipsoids are shown at the 50% probability level.

Figure 1. Molecular structures of the cluster cations $1^{+}$ (a) and b)) and $2^{+}$ (c) and d)). The second perspective is shown in order to visualize the puckered Ga and the planar In, ring (M–M–M–M angle: ca. 20.4° for M = Ga and 0° for M = In). Average distances [pm] and angles [°]: Ga–Ga: 248.49(6), P–Ga: 241.1(1), Ga–Ga–Ga: 88.15(2), P–Ga–P: 84.9(1), In–In: 280.2(1), P–In–P: 260.5(1), In–In–In: 90.00(2), P–In–P: 81.05(3). The P–M bond lengths and P–M–P bond angles correspond to the values found in the [M(dmpe)]$^{-}$ subunits. For disordered dmpe ligands, the P–M bond lengths and P–M–P bond angles equate the values found in the majority part of disordered dmpe molecules. Counterions, solvent molecules, hydrogen atoms and disordered ligand molecules are not shown for clarity. Thermal ellipsoids are shown at the 50% probability level.
Clustering in solution and gas phase: DOSY NMR and calculations

NMR spectroscopic measurements confirm that the Ga–Ga bonds are stronger than the In–In bonds in the respective cluster, despite of the weaker Coulomb repulsion in the In₄ cluster with the longer M–M bond lengths. When dissolving crystals of [M(dmpe)]₄·4oDFB in oDFB, the ¹H and ³¹P NMR spectra suggest that only one dmpe-containing species is present in solution. The ¹H chemical shifts of the methylene and the methyl groups are ca. 1.6 and 1.4 ppm downfield, compared to the free ligand in oDFB. Similarly, the ³¹P NMR signal is shifted from −49 ppm for the free ligand to −7 ppm for the Ga/dmpe complex in oDFB (see Section 3.3 in the Supporting Information).

Further results of ¹H and ¹⁹F diffusion ordered spectroscopy (DOSY) investigations are summarized in Table 2. They show that...

![Figure 2. Kohn-Sham frontier orbitals of 1⁺ (a) LUMO and b) HOMO) and 2⁺ (c) LUMO and d) HOMO) as well as their energies (RI–BP86(D3BJ)/def2–TZVP, iso value = 0.04).](image)

### Table 2. Diffusion coefficients, ¹H and ³¹P NMR shifts and tentative assignments of different species in oDFB solutions of [M(dmpe)]₄·4oDFB (M = Ga, In). Diffusion coefficients were determined with ¹H DOSY NMR experiments at rt.

| Assignment for [M(dmpe)]₄⁺ | ¹H shift [ppm] | ³¹P shift [ppm] | Diffusion coefficient [m²·s⁻¹] |
|---------------------------|----------------|----------------|-------------------------------|
| M = Ga; x = 4             | 2.93 and 2.31  | −7.1           | (3.285 ± 0.002) × 10⁻¹⁰       |
| M = In; x = 5             | 2.88 and 2.28  | −16.7          | (2.747 ± 0.001) × 10⁻¹⁰       |
| M = In; x = 4             | 2.68 and 2.09  | −13.4          | (3.112 ± 0.001) × 10⁻¹⁰       |
| M = In; x = 1             | 1.83 and 1.27  | −7.4           | (8.879 ± 0.001) × 10⁻¹⁰       |
the diffusion coefficient of the Ga/dmpe species ($D = (3.285 \pm 0.002) \times 10^{-10}$ m$^2$/s) is smaller than the diffusion coefficient of the [pf]$^-$ anion ($D = (4.737 \pm 0.001) \times 10^{-10}$ m$^2$/s) in the same sample. Hence, the cluster volume has to be larger than that of the [pf]$^-$ anion, which agrees well with their thermochromic volumes found in the solid state: from the volume of the [pf]$^-$ anion (727 Å$^3$), [Ga(dfB)], [pf] (971 Å$^3$), [Ga(pf)] (734 Å$^3$) and of dfB (119 Å$^3$ as calculated from the latter two values) follows that the volume of $1^{+\text{f}}$ is ca. 1055 Å$^3$. This clearly implies that the intact cluster $1^{+\text{f}}$ also exists in solution.

By contrast, three main species were detected via $^1$H and $^31$P NMR spectroscopy when dissolving $2$[pf]$_4$·4dfB in dfB. The exact nature of the species corresponding to the low field NMR signals is unclear. However, since these two species display similar, and comparatively low, diffusion coefficients ($D = (2.747 \pm 0.001) \times 10^{-10}$ m$^2$/s and (3.112 \pm 0.001) \times 10^{-10}$ m$^2$/s), we tentatively assign the two signals to $\text{In}^{+\text{f}}$/dmpe clusters, for example $2^{+\text{f}}$, and [In(dmpe)]$^{3+}$. In line with this and according to DFT calculations, the pentamer is only slightly less stable than the tetramer $2^{+\text{f}}$ in solution (see below).

In agreement with the smaller diffusion coefficients compared to $1^{+\text{f}}$, $2^{+\text{f}}$ has a calculated volume of ca. 1150 Å$^3$ in the solid state, which is slightly greater than the volume of $1^{+\text{f}}$. The high field $^1$H NMR signal corresponds to the species with the highest diffusion coefficient ($D = 8.879 \pm 0.001) \times 10^{-10}$ m$^2$/s). It decreases in intensity upon lowering the temperature and disappears at $-20\degree$C (Figure 3) but increases in intensity, relative to the cluster signals, upon dilution (see Section 3.6 in the Supporting Information). The exact nature of the species corresponding to the high field $^1$H NMR spectra is unclear. However, since these two species display similar, and comparatively low, diffusion coefficients ($D = (2.747 \pm 0.001) \times 10^{-10}$ m$^2$/s and (3.112 \pm 0.001) \times 10^{-10}$ m$^2$/s), we tentatively assign the two signals to $\text{In}^{+\text{f}}$/dmpe clusters, for example $2^{+\text{f}}$, and [In(dmpe)]$^{3+}$. In line with this and according to DFT calculations, the pentamer is only slightly less stable than the tetramer $2^{+\text{f}}$ in solution (see below).

![Figure 3. $^1$H NMR spectra (400.17 MHz, dfB) of crystalline ([In- (dmpe)]$_x$)[PF]$_4$·4dfB measured at 253 K, 263 K, 273 K, 283 K and 298 K (from bottom to top). The signals are tentatively assigned to [In(dmpe)]$^{3+}$, [In(dmpe)]$^{2+}$ and [In(dmpe)]$^{+}$.](image)

Reactions with excess DMPE

Obviously, the In cluster partly disaggregates in solution, and the position of the dynamic chemical equilibrium between clusters and monomer is altered by temperature change, clearly underlining the weaker M–M bonds in the indium cluster relative to the gallium analogue. Consequently, from solutions of [In(PhF)$_2$]$_x$(pf) and a two-fold excess dmpe, we obtained crystals of the pf salt of [In(dmpe)]$^{3+}$ (see section 6.3 in the Supporting Information). This cation can probably be considered as a trapping product of [In(dmpe)]$^{3+}$ with dmpe and is observed by NMR spectroscopy as the only species in solution in 1:2 mixtures of [In(PhF)$_2$]$_x$(pf) and dmpe. In contrast to this, crystals of [In(PhF)$_2$]$_x$(pf)/dmpe mixtures, even when employing a two-fold excess of dmpe. Additionally, in solutions of Ga$^{2+}$ and excess dmpe, the cluster $1^{+\text{f}}$ is still detected and decreases only very slowly over weeks. Since the formation of [M(dmpe)]$^{3+}$ from dmpe and $1^{+\text{f}}$ or $2^{+\text{f}}$ is thermodynamically favorable for both M$_x$ clusters in dfB (Δ$G_{\text{obs}} = -81$ and $-207 \text{kJ mol}^{-1}$ for $1^{+\text{f}}$ and $2^{+\text{f}}$, respectively; RI-BP86(D3BJ)/def2–TZVPP), these findings underline that $1^{+\text{f}}$ is not only thermodynamically, but also kinetically more stable than $2^{+\text{f}}$.

Thermodynamics of disaggregation

The different dissociation tendencies of both clusters as shown in Equation (3) are well described by DFT calculations.

\[
\begin{align*}
\text{M}_x \rightarrow \text{M}_x^{3+} + \text{dmpe}^{-} \\
\frac{4}{x} \rightarrow \text{M}_x^{3+} + \text{dmpe}^{-}
\end{align*}
\]

Hence, Table 3 delineates that the dissociation of gaseous ([M(dmpe)]$_x$)$_{3+}$ is always both, highly exothermic and exergonic.

| Product | Δ$H^\ddagger$ (gas) | Δ$G^\ddagger$ (gas) | Δ$G^\ddagger$ (dfB) |
|---------|------------------|------------------|------------------|
| M=Ga; x=1 | -756.2 | -745.7 | +193.8 |
| M=In; x=1 | -748.0 | -909.8 | -12.5 |
| M=In; x=2 | -469.1 | -562.5 | +33.7 |
| M=In; x=3 | -224.2 | -257.8 | +19.4 |
| M=In; x=5 | +241.4 | +254.8 | +6.2 |
| M=In; x=6 | +485.1 | +508.2 | +8.4 |

Table 3. Calculated standard Gibbs free energies and enthalpies for the dissociation of $1^{+\text{f}}$ and $2^{+\text{f}}$ into mono- or oligomeric ([M(dmpe)]$_x$)$_{3+}$ according to Equation (3) in the gas phase and an dfB solution at 298 K (ε = 13.38 [218] COSMO model, RI-BP86(D3BJ)/def2–TZVPP). Note that the formation of the dimer is less favored than the formation of the higher clusters, due to the presence of a non-classical, double dative double bond, which is weaker than the o bonds in the higher cluster compounds (see sections 8.5 and 8.7.15 in the Supporting Information) [219].
The notion that $1^{+}$ exists exclusively as tetramer in solution, but $2^{+}$ dissociates with monomer formation is further supported by two reactions of $1^{+}$ and $2^{+}$ with one equivalent of $P_4$ in oDFB each. Quantum chemical calculations suggest that

\[ 1^{+} + P_4 \xrightarrow{oDFB, 60 \degree C} \text{no reaction} \]

(4)

\[ 2^{+} + P_4 \xrightarrow{oDFB, 60 \degree C} \text{?} \]

(5)

Hence, no substantial amounts of the monomer appear in an equilibrium in solution, in line with the results of the thermodynamic calculations (cf. Table 3). By contrast, a mixture of $P_4$ in oDFB even at 60°C.

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Table 4. Experimentally determined reaction enthalpy, entropy and Gibbs free energy for the tetramer-monomer conversion by means of a van’t Hoff analysis of the variable temperature NMR spectra in oDFB.

| Reaction | $\Delta H^\circ$ [kJ mol$^{-1}$] | $\Delta S^\circ$ [J K$^{-1}$ mol$^{-1}$] | $\Delta G^\circ$ [kJ mol$^{-1}$] |
|----------|-----------------|-----------------|-----------------|
| $[\ln (dmppe)]^{1+}$ | 220.6 ± 16.3 | 668.6 ± 59.9 | 21.3 ± 24.2 |

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It was also observed that $[2][Pf]_4-4$ partially decomposes in solution and that a small amount of a precipitate, consisting of elemental indium and other crystalline and amorphous compounds, formed, which adds uncertainty to the exact concentration of the three species. For the van’t Hoff analysis of this system, it was postulated that for the time the measurements took, these decomposition reactions do not affect the result of the analysis significantly. See Section 3.6 in the Supporting Information for a detailed discussion of the decomposition reactions.
However, cationic, subvalent gallium in non-coordinating environments towards silanes was recently demonstrated as being higher ligand. The salts \([\text{M(dmpe)}]^{+}\) display interesting reactivity, and, after careful ligand design, may be employed in bond activation reactions. Phosphonium cations \([\text{see Equation (5) and Section 3.7 in the Supporting Information}]\) are detected, again in accordance with the DFT calculations. For M = Ga and In, \([\text{M(PhF)}_2]^{+}\) \([\text{M} = \text{Ga}, \text{In})\) can vary, depending on the vacuum applied when drying the product. Thus, the formula \([\text{M(PhF)}_2]^{+}\) \([\text{M} = \text{Ga}, \text{In})\] was determined via \[^{19}F\text{NMR}\] spectroscopy.  

Experimental Section  
All manipulations were carried out under exclusion of moisture and air through usage of a MBraun glovebox filled with nitrogen \((\text{O}_2/\text{H}_2\text{O} < 1 \text{ ppm})\) and standard Schlenk techniques. All glassware used in reactions have been stored overnight in an oven at 180°C and were additionally dried with a heat gun prior to use. All solvents were stored under an atmosphere of argon or nitrogen in sealed vessels. Fluorobenzene and ortho-difluorobenzene \((\text{oDFB})\) were dried over \(\text{CaH}_2\) for two days, distilled and degassed prior to use. The water content of the solvents was below 10 ppm, as determined by Karl Fischer titration. Bis(dimethylphosphino)ethane \((\text{dmpe})\) was used as received. \[^{1}H\text{NMR}\] \([\delta = \text{Al(O)}\text{R}]^{1+}, \text{R} = \text{CF}_3\text{J}]^{18}\) and \[^{19}F\text{NMR}\] \([\delta = \text{In(PhF)}_2]\] \([\text{In} = \text{Ga}, \text{In})\] were prepared according to literature protocols. Note that the number of fluorobenzene molecules coordinated to \(\text{M}^{+}\) in \([\text{M(PhF)}_2]^{+}\) \([\text{M} = \text{Ga}, \text{In})\] can vary, depending on the vacuum applied when drying the product. Thus, the formula \([\text{M(PhF)}_2]\) \([\text{M} = \text{Ga}, \text{In})\] is used for the sake of simplicity instead of \([\text{M(PhF)}_2]^{+}\) \([1 < x < 3]\). The exact ratio \(x\) was determined via \[^{19}F\text{NMR}\] spectroscopy.  

Synthesis of \([1][\text{PhF}]_4\cdot 4\text{C}_8\text{H}_8\text{F}_2\).  
Layering a solution of \(\text{dmpe (0.225 M in oDFB, 0.8 mL, 180 \text{ mol}) and [Ga(PhF)}_2]\) \([204 \text{ mg, 180 mol, 1.0 equiv.) with pentane at rt and or heptane at −25 °C (ca. 8 mL, respectively) afforded yellow-orange crystals after 1 d. After removal of the solvent, the crystalline \([1][\text{PhF}]_4\cdot 4\text{C}_8\text{H}_8\text{F}_2\) was obtained in very good yield \((214 \text{ mg, 164 mol, 91%})\). Employing a two-fold excess of \(\text{dmpe also yielded crystals of [1][PhF}_4\cdot 4\text{C}_8\text{H}_8\text{F}_2\).  

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Synthesis of [2][PF6]4 · C4H4F2: Layering a solution of dmpe (0.225 M in oDFB, 0.8 mL, 180 µmol) and [In(PhF2)][PF6] (212 mg, 180 µmol, 1.0 equiv) with pentane at rt or with heptane at -25 °C (ca. 8 mL, respectively) afforded dark red crystals after 1 d. After removal of the solvent, crystalline [2][PF6][PF] was obtained in very good yield (223 mg, 166 µmol, 92%). 1H NMR (400.17 MHz, oDFB, 298 K): δ = 2.88 (m, 20 H, Ch2, x ≈ 5), 2.09 (m, 48 H, Ch2, x ≈ 5), 1.83 (m, 4 H, Ch2, y = 1). 13C{1H} NMR (100.62 MHz, oDFB, 298 K): δ = 26.0 (2 C, x = 1), 25.5 (10 C, x ≈ 5), 25.1 (8 C, x ≈ 4), 12.8 (20 C, x ≈ 5), 12.5 (16 C, x ≈ 4), 8.3 (4 C, y = 1). 19F NMR (376.54 MHz, oDFB, 298 K): δ = -75.3 [s, 36 F, [Al(OCCF3)]4] ppm. 27Al NMR (104.27 MHz, oDFB, 298 K): δ = -35.0 (1 Al, [Al(OCCF3)]4) ppm. 31P{1H} NMR (161.99 MHz, oDFB, 298 K): δ = -7.4 (2 P, x = 1), -13.4 (8 P, y = 4), -16.7 (10 P, x ≈ 5) ppm. 119In NMR (122.04 MHz, oDFB, 298 K): δ = -1324 (1 In, [Influoroarene]4) ppm, ν3 = 3300 Hz ppm.

Deposition Numbers 2157680 (for [1][PF6]4 · C4H4F2), 2157681 (for [2][PF6]4 · C4H4F2) and 2157682 (for [mdpe][PF]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

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