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A Novel Soluble In^I Precursor for P$_n$ Ligand Coordination Chemistry

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Dedicated to Professor Henri Brunner on the occasion of his 75th birthday

Over the years low-valent main group element chemistry has been well developed and is now an established field in inorganic chemistry.[1] Furthermore, In^I compounds have proved to be valuable catalysts in organic synthesis.[2] Recently, the preparation and stabilization of monocationic[3] and polycationic[4] species became of great interest and represent very active areas of research. Thereby, the balance between the stabilization and the occurrence of a high reactivity is a general goal.

In the search for Group 13 element cations[5] it appeared to be a challenge to prepare soluble In$^+$ starting materials.[6] Compared to the heavier homologue thallium, indium is less stable in the oxidation state +I and tends to disproportionate in the presence of coordinating solvents and strong Lewis bases.[7] However, a number of different soluble In$^+$ cationic precursors and compounds have recently been reported, for example, the inverse sandwich $[In_2(C_5Me_5)]^+[B(C_6F_5)_4]^-$,[5d] In[BArF] ($BAr^F=[B\{C_6H_3(CF_3)_2\}_4]$),[5g] and $In[SO_3CF_3]$.[8]

One of our main research areas is dedicated to the coordination chemistry of unsubstituted P$_n$ ligand complexes towards Cu^I halides[9] and also transition-metal cations such as Cu$^+$ and Ag$^+$.[10] Recently, we succeeded in the synthesis of a novel coordination polymer of Tl$^+$[11] using $Tl[Al\{OC(CF_3)_3\}_4]$[12] as a starting material in the reaction with $[Cp^*Fe(\eta^5\text{-}P_5)]$. Therefore, we were especially interested to investigate the role of In$^+$ in such chemistry. However, no reactions occurred between P$_n$ ligand complexes and the above-mentioned known In$^+$ sources. This leads to the conclusion that the interaction of In$^+$ with its counterion is stronger than with a weakly nucleophilic P$_n$ ligand complex. To overcome these difficulties, the use of a very weakly coordinating counteranion, such as $[Al\{OC(CF_3)_3\}_4]^-$, seems to be necessary. Up to now the number of M^I salts with this anion is very limited. They are only reported for the transition-metal ions Cu$^+$[13] and Ag$^+$,[14] as well as the alkali-metal ions Li$^+$,[14] K$^+$,[15] and Cs$^+$,[16] for the Group 13 ion Tl$^+$[12] and, very recently, also for Ga$^+$.[17] Usually these salts are synthesized by reaction of $Li[Al\{OC(CF_3)_3\}_4]$ (**1**) with the corresponding M^{I}F salt using LiF elimination (for Ga$^+$ elemental Ga was used). Since InF is not available, a different synthetic route had to be developed. Here, we report on the synthesis, physicochemical properties, and first structural characterization of $In[Al\{OC(CF_3)_3\}_4]$ (**2**)—the missing link within the Group 13 $[Al\{OC(CF_3)_3\}_4]^-$ salts. Moreover, the coordination of a P$_2$ ligand complex leads to an unprecedented tetramer of In, which displays short In···In distances. The reaction product with a *cyclo*-P$_3$ ligand complex shows a novel σ- and π-coordination mode of the *cyclo*-P$_3$ ring in the solid-state and a fluxional process in solution.

The desired In^I precursor can be prepared under strictly inert conditions by a metathesis reaction of $Li[Al\{OC(CF_3)_3\}_4]$ (**1**)[14] with a twofold excess of InCl in CH_2Cl_2 in 87% yield (Scheme 1). The isolated extremely air-sensitive white powder dissolves readily in CH_2Cl_2 and aromatic solvents such as toluene or 1,2-difluorobenzene. Its ^{19}F NMR spectrum in CD_2Cl_2 at room temperature shows a singlet at $\delta=-75.6$ ppm, which is in agreement with the 36 chemically equivalent fluorine atoms of the anion. The ^{27}Al NMR spectrum in CD_2Cl_2 at room temperature exhibits a singlet at $\delta=33.7$ ppm. In the ESI mass spectrum in CH_3CN signals for naked In$^+$ and $[In(CH_3CN)_x]^+$ ($x=1$–3) are found in the positive-ion mode, and one signal for the intact anion $[Al\{OC(CF_3)_3\}_4]^-$ in the negative-ion mode. Single crystals of **2** suitable for single-crystal X-ray diffraction analysis

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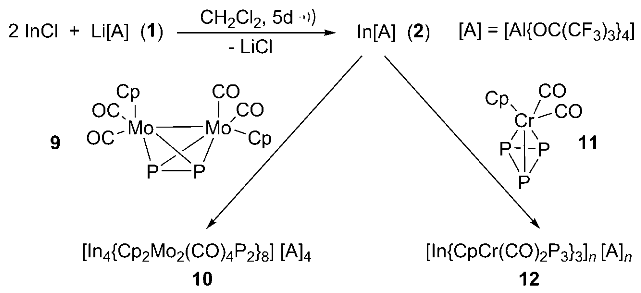

Scheme 1. Synthesis of complexes **2**, **10**, and **12**.

were grown from a concentrated *o*-difluorobenzene solution of **2**. The compound crystallizes in the *Pbca* space group of the orthorhombic crystal system. In the asymmetric unit a bent sandwich complex of two *o*-difluorobenzene solvent molecules weakly coordinated to an In^+ ion is found, together with the $[Al\{OC(CF_3)_3\}_4]^-$ counteranion (Figure 1, see also Figure S1 in the Supporting Information).

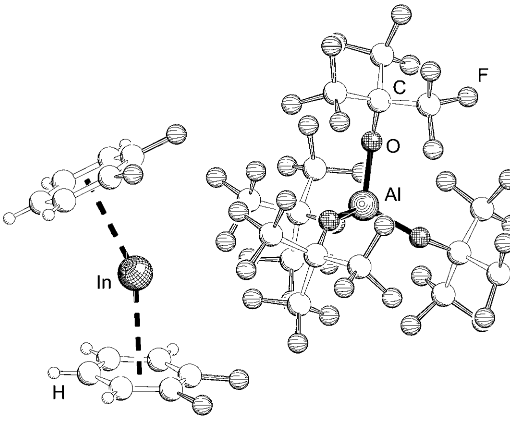

Figure 1. Structure of $\mathbf{2}\cdot 2\,C_6H_4F_2$ in the solid state (SCHAKAL 99).[33] Selected bond lengths [Å] and angles [°]: In–Ctr 2.878(1), In–Ctr' 2.894(1); Ctr-In-Ctr' 154.857(8).

Up to now only a few complexes of low-valent indium with neutral arenes have been structurally characterized.[18] Schmidbaur and co-workers synthesized the mesitylene complex $[In(1,3,5\text{-}Me_3C_6H_3)_2]^+[InBr_4]^-$ (**3**)[19] and the 1D polymer with [2,2]paracyclophane (**4**),[20] both of which show notable cation–anion interactions. Cowley et al. observed In–toluene interactions in the triple-decker complex $[(C_7H_8)_2In_2(C_5Me_5)]^+[(C_6F_5)_6B_2OH]^-$ (**5**).[5c,e] The $[In(C_6D_6)]^+[\{CH_3)_3Si\}_3C{-}InI_3]^-$ (**6**) complex was reported as a side product by Weidlein and co-workers.[21] The distances between In^+ and the centers of the π-coordinating C_6 rings of the solvent molecules (Ctr) in **2** are 2.878(1) Å and 2.894(1) Å with In–C distances ranging from 3.051(3) to 3.329(3) Å. These distances compare well with the In–ring plane distances observed for **3** (2.83 and 2.89 Å) and **4** (2.95 Å), but are considerably shorter than those of **5** (3.490(4), 3.325(4) Å) and **6** (3.255(3) Å). Compared to recently reported Tl^I–centroid distances in $[Tl(C_6Me_6)_2]^+[H_2N\{B(C_6F_5)_3\}_2]^-$ (**7**) (2.789 and 2.855 Å)[22] and $[Tl(C_6Me_6)]^+[H_2N\{B(C_6F_5)_3\}_2]^-$(**8**) (2.723 Å),[23] the distances found in **2** appear to be quite long. This effect reflects the relativistic contraction of the Tl^+ ion (similar M^+ radii for In and Tl) and a stronger bonding interaction with arene ligands compared to those of In^+. Similar tendencies have been observed for paracyclophane complexes.[20] In the Ga^I analogue of **2** expectedly somewhat shorter M–Ctr distances are found (average value 2.684 Å).[17] The interplane angle between the two $C_6H_4F_2$ ligands in **2** is with 32.2(1)° more acute than the related angles in **3** (47.3°) and **4** (61.2°). Two relatively short In–F distances at the open side of the bent sandwich can be identified in the solid-state structure of **2** (3.156(2) and 3.262(2) Å). Interestingly, the *o*-difluorobenzene ligands show a *syn* conformation, whereas in the corresponding Cu^I complex an *anti* conformation is observed.[13c]

With the new soluble In^I source **2** the reaction with the tetrahedrane P_2 ligand complex **9**[24] was carried out (Scheme 1). Indeed, in such a weakly coordinating environment, a coordination of the P_2 complex to In^+ could be achieved. Upon diffusion into an *n*-pentane layer, red single crystals of the new coordination compound **10** suitable for single-crystal X-ray diffraction analysis were formed in 88% yield (Scheme 1). The compound crystallizes in the *Pbcn* space group of the orthorhombic crystal system and consists of an aggregate of four In^+ ions coordinated by eight P_2 complexes **9**, in addition to four $[Al\{OC(CF_3)_3\}_4]^-$ counterions (Figure 2, and Figure S2 in the Supporting Information). Six of the complexes **9** exhibit a bridging $\eta^1{:}\eta^1$-coordination mode, while the other two coordinate in an end-on style. Two of the In^+ ions (In2, In2', Figure 2) show a distorted trigonal-pyramidal coordination environment with In–P bond lengths in the range between 2.832(3) and 3.382(15) Å. The second pair of In^+ ions (In1, In1', Figure 2) is σ-coordinated by only three units of **9** (In–P distances 2.850(3)–3.167(6) Å). The four In^+ ions form a planar rhombic arrangement with the shortest intermetallic distance $d(In1\cdots In1')$ being 3.482(1) Å (sum of the van-der-

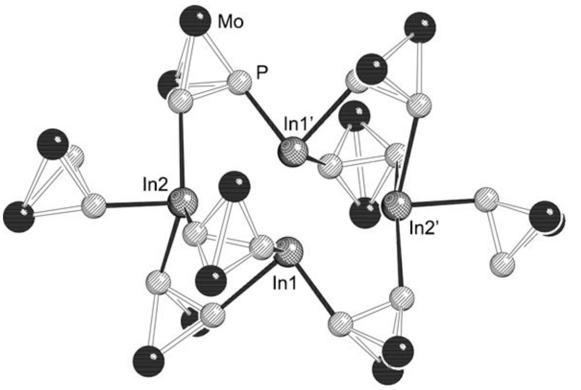

Figure 2. View of the tetracation of **10** in the solid state (one orientation; SCHAKAL 99).[33] Cp and CO ligands are omitted for clarity.

Waals radii: 3.8 Å). Qualitative analysis of molecular orbitals obtained at the DFT level indicates a weak interaction between the 5s orbitals of these ions. However, the topological analysis of the electron density[25] does not indicate a bond critical point between In1 and In1′ (see the Supporting Information). Compared to **10**, significantly shorter In–In distances (2.887(2)–3.18(2) Å) are found in tetrahedral In_4 clusters synthesized in the groups of Uhl, Cowley, and Linti, which definitely show In^I–In^I interactions.[1a,g,26] Even shorter In–In distances (2.696(2) Å) are reported for a trigonal-planar In_4 cluster by Power et al.[27] However, in the compounds $[InC_5R_5]$ (R = H, Me) the intermetallic distances (3.942(1)–3.986(1) Å) are considerably longer than those in **10**.[28] The tetramer of In^+ formed by coordination to the Mo_2P_2 complex **9** contrasts to the obtained dicationic complex of **9** with the Tl^+ analogue of **2**.[11] In comparison with the related Tl^I compound, which reveals an M_2L_6 core, not a M_4L_8 core such as **10**, the average M–P distance in **10** is slightly shorter, but the distance range is similar (3.044(6)–3.380(6) Å for Tl^I).[11] The P–P bond lengths (2.085(5)–2.130(19) Å) resemble the bond length found in the free complex (2.079(2) Å),[24] the P–P bonds of the end-on coordinating complexes **9** being the shortest ones. Owing to the large counteranion **10** is soluble in non-coordinating solvents like CH_2Cl_2. The $^{31}P\{^1H\}$ NMR spectrum of **10** in CD_2Cl_2 at room temperature only shows one singlet at $\delta = -47.1$ ppm ($\omega_{1/2} = 88$ Hz), which is slightly high-field shifted compared to that of free **9** ($\delta = -43.2$ ppm). Recording the spectrum at 183 K, the lowest possible temperature in CD_2Cl_2 (dissociation of the complexes is observed in THF/CD_2Cl_2 mixtures), leads to a significant broadening of the signal ($\omega_{1/2} = 3474$ Hz). The ESI mass spectrum of a solution of **10** in CH_2Cl_2 shows one signal for the anion $[Al\{OC(CF_3)_3\}_4]^-$ in the negative-ion mode, but no assignable signals in the positive-ion mode. In CH_3CN, dissociation takes place and the ESI-MS exhibits signals for naked In^+, $[In(CH_3CN)]^+$, and the free ligand. Thus, the solution data suggest very weak bonding energies and dynamic behavior involving fast equilibria in CH_2Cl_2 solution.

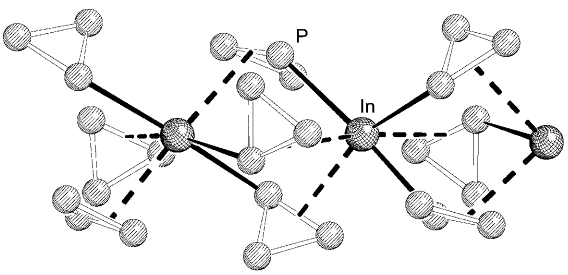

Figure 3. Section of the polycationic chain in **12** (SCHAKAL 99).[33] [Cp(CO)$_2$Cr] fragments are omitted for clarity.

Moreover, **2** was allowed to react with three equivalents of the *cyclo*-P_3 complex $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ (**11**)[29] in CH_2Cl_2 (Scheme 1). Upon addition of *n*-pentane, compound **12** could be isolated as a bright red powder in 76 % yield. Single crystals of **12** crystallize in the $P6_5$ space group of the hexagonal crystal system. The asymmetric unit contains one In^+ ion, three molecules **11**, and one aluminate anion. The application of all symmetry operations reveals a 1D polymeric chain of In^+ ions bridged by the *cyclo*-P_3 ligand complexes (Figure 3, see Figure S3 in the Supporting Information). Each *cyclo*-P_3 ligand thereby forms one σ-bond to one In^+ ion and coordinates the neighboring In^+ ion in a π-style coordination through one of the P–P bonds. The overall coordination mode of the P_3-ligand complexes towards the In^+ ions can hence be described as $\mu\text{-}1\kappa P_A{:}1\kappa P_B{:}2\kappa P_B$—a coordination mode, which is unprecedented for a *cyclo*-P_3 ligand complex. Unlike **12**, the recently published Ag^I coordination polymers with *cyclo*-P_3 ligand complexes exhibit $\mu\text{-}1\kappa P_A{:}1\kappa P_B{:}2\kappa P_C$ and $\mu\text{-}1\kappa P_A{:}2\kappa P_B$ coordination modes.[10c] The geometry around the In^+ centers in **12** can be described as a distorted octahedron including three σ-bonds and three π-bonds, the maximum coordination number so far observed for the In–P system. This coordination environment is reminiscent of the structure of the mixed-valent salt $[In_4(SO_3CF_3)_6]$, exhibiting a distorted octahedral InO_6 core.[30] The bond lengths of the σ-bonds in **12** are between 3.188(2) and 3.302(2) Å. The distances between the In^+ ions and the centers of the π-coordinating P–P bonds are in the range between 3.192(1) and 3.253(1) Å. All bond lengths of the latter show an elongation compared to the other P–P distances in the *cyclo*-P_3 rings (average distances: 2.151(6) vs. 2.134(12) Å). The polycationic $[In\{CpCr(CO)_2P_3\}_3]^+_n$ strands are oriented along the crystallographic *c* axis and are separated from each other by the large aluminate counterions. No short contacts between the anions and the In^+ ions are present. Except for the half-sandwich complexes $[In(tBu_2C_2P_3)]$[31] and $[In(tBu_3C_3P_2)]$,[31b] compounds **10** and **12** represent, to the best of our knowledge, the only examples of complexes with P-donor atoms coordinated to In^I. In the $^{31}P\{^1H\}$ MAS solid-state NMR spectrum of **12** at room temperature a singlet at $\delta = -287.3$ ppm is observed. This leads to the conclusion that the *cyclo*-P_3 rings show dynamic behavior in the solid state: a fast rotation renders all P nuclei chemically equivalent on the NMR timescale. The $^{31}P\{^1H\}$ NMR spectrum of **12** in CD_2Cl_2 at room temperature also shows one singlet at a similar chemical shift ($\delta = -287.9$ ppm). Compared to free **11** ($\delta = -288.3$ ppm), this signal is slightly shifted to lower field. In the ESI mass spectra of a CH_2Cl_2 solution of **12** a species $[In\{CpCr(CO)_2P_3\}]^+$ $[Al\{OC(CF_3)_3\}_4]^-$ is detected. The solution data suggest fast dynamics in solution. To clarify which processes and energy differences are involved, DFT calculations have been carried out. Table 1 shows the calculated free enthalpies of $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ and CH_2Cl_2 ligand-exchange reactions

Table 1. Calculated free enthalpies (kJ mol^{-1}) of ligand-exchange reactions in the gas phase (ΔG_g) and CH_2Cl_2 solution (ΔG_s) at 293.15 K ($P_3 = CpCr(CO)_2P_3$).

Reaction	ΔG_g	ΔG_s
$In(P_3)_3^+ + CH_2Cl_2 \rightarrow In(P_3)_2(CH_2Cl_2)^+ + P_3$	13.9	2.8
$In(P_3)_2(CH_2Cl_2)^+ + CH_2Cl_2 \rightarrow In(P_3)(CH_2Cl_2)_2^+ + P_3$	15.5	2.2
$In(P_3)(CH_2Cl_2)_2^+ + CH_2Cl_2 \rightarrow In(CH_2Cl_2)_3^+ + P_3$	16.3	−2.4

in the gas phase and in CH_2Cl_2 solution. In the gas phase, the exchange of ligand **11** is an endothermic process and the most stable species is $[In\{CpCr(CO)_2P_3\}_3]^+$. The small values of free energies in solution (about 2 kJ mol^{-1}) indicate dynamic behavior and strong concentration-dependent equilibria. Assuming an overall concentration of $[In(CH_2Cl_2)_{3-n}\{CpCr(CO)_2P_3\}_n]^+$ ($n=0$–3) of 10^{-5} mol L^{-1}, the calculations suggest $[In(CH_2Cl_2)_3]^+$ to be the predominant species present in solution (see the Supporting Information).[32] In comparison to the Tl^+–[Cp*Fe(η^5-P_5)] system, in which the Tl surrounded by three *cyclo*-P_5 ligand complexes was found to be stable in solution, the present data for the In^+–[CpCr(CO)$_2$(η^3-P_3)] system reveal much weaker interactions of the *cyclo*-P_3 ligand complex with In^+ in solution.

In summary, the previously missing link of the Group 13 cations containing the weakly coordinating counterion $[Al\{OC(CF_3)_3\}_4]^-$, the In^+ salt, could be synthesized and reveals a high reaction potential. Thus, the first coordination compounds of P_n-ligand complexes with indium have been prepared. With compound **10** containing the $[Cp_2Mo_2(CO)_4(\mu,\eta^2\text{-}P_2)]$ ligand an unprecedented tetrametallic aggregate has been synthesized, which features a short In···In distance. Moreover, the coordination of a *cyclo*-P_3 ligand to a main group metal as present in **12** is unique and reveals a novel coordination mode of a *cyclo*-P_3 unit. The extensive characterization of the structural and dynamic properties of **12** offers new insights in a field of coordination chemistry, which is still unexplored. The newly developed $In[Al\{OC(CF_3)_3\}_4]$ precursor provides a valuable novel source of highly soluble and reactive 'naked' In^+, and will therefore find its way into many other areas of coordination chemistry.

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Keywords: coordination polymers · Group 13 elements · indium · phosphorus · weakly coordinating anions

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[32] We note however, that this is only a qualitative result since the accuracy needed for precise calculation of equilibrium constants for systems of this size is beyond the reach of our computational resources. Further computational details are given in the Supporting Information.

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