**Bis[(2-diphenylphosphino)phenyl]phenylphosphine as an Inflexible Tridentate Ligand for Indium Trichloride**

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Anhydrous indium trichloride reacts with [2-(Ph$_2$P)$_2$C$_6$H$_4$]$_2$PPh (TP) in the molar ratio 2:1 to give an ionic complex [(TP)InCl$_2$]$^+$ InCl$_4^-$ in almost quantitative yield. The structure of the product has been determined by a single crystal X-ray diffraction study. In the cation the TP molecule acts only as a bidentate ligand via its two terminal phosphorus atoms [In-P 2.5956(8), In-P2 2.5799(7) Å]. Although the central phosphorus atom is also rather close to the metal atom [2.8259(8) Å], the In-P3 interaction is inefficient because of an adverse orientation of the lone pair of electrons at P3 owing to the steric inflexibility of the ligand. Accordingly, the $^{31}$P NMR spectra of the compound in CD$_2$Cl$_2$ show large contact shifts and quadrupole broadening only for the signals of the two terminal phosphorus atoms, whereas the lines of the central phosphorus atom are less shifted and well resolved (AB$_2$ spin system at -60°C).

**Introduction**

There is currently growing interest in the coordination chemistry of the heavier Group III (13) Elements with Group V (15) Element donor centers. Complexes of this type not only contain the III/V element combination relevant to semiconductor components, but are also important as moderately strong Lewis acids in catalysis [1 - 3]. In the presence of sensitive functional groups or under other more specific conditions the catalytical properties of gallium and indium halides are superior to those of the standard boron or aluminium halide reagents [4].

This is true in particular with ambidentate ligands, which can open and close reaction sites at the catalytically active metal depending on the reaction conditions and the relative affinities of ligand donor centers and substrates.

Ligands with an inflexible skeleton may offer such advantages if not all the donor centers can be perfectly oriented towards the metal acceptor. As a case study we have chosen bis[2-(diphenylphosphino)phenyl]phosphine (TP), which is known to have highly hindered intramolecular motions [5,6]. Rotations around critical linkages between the phenyl rings and the phosphorus atoms are only possible if a certain concertedness is followed in such motions. The general literature on phosphine complexes of indium(III) has been summarized in a preceding paper [5].

**Preparation, Analysis, Spectroscopy and Structure**

The reaction of anhydrous indium trichloride and the TP ligand in the molar ratio 2:1 in toluene at room temperature affords a colourless crystalline product (in 90% yield) which melts at 246°C. It is only slightly sensitive to air and moisture. Its elemental analysis is in agreement with the proposed stoichiometry. The compound is soluble in di- and trichloromethane, but only sparingly soluble in tetrahydrofuran, dioxane, or diethyl ether, and insoluble in hydrocarbons.

Solutions in dichloromethane-d$_2$ show two groups of signals with the relative intensity 2:1. At -60°C the more intense signal is a very broad double-hump (at ~15 ppm) indicating broadened doublet splitting. The less intense signal is a well resolved, sharp triplet (at ~44 ppm) with a fine-structure typical of the B-part of an A$_2$B spin system [J(P,P) 242 Hz]. At room temperature the line broadening is increased further probably owing to ligand exchange. This behaviour resembles that of the analogous gallium and indium iodide compounds [5].
Crystals of the complex are monoclinic, space group $P\overline{2}_1/c$ with $Z = 4$ formula units in the unit cell. The lattice is composed of fully separated $[\text{InCl}_3]^-$ anions and $[\text{TP}\text{InCl}_2]^+$ cations. There are no solvent molecules included. The crystals are not isomorphous with those of the corresponding Ga$^+$ and In$^+$ complexes [5].

The anions have a standard tetrahedral structure with all Cl-In2-Cl angles in the narrow range between 106.08(4) and 112.07(6)$^\circ$ and all In2-Cl distances between 2.3321(12) and 2.3493(10) Å (Fig. 1).

The cations have a very irregular structure with no crystallographically imposed symmetry (Fig. 1). The geometry cannot be described using any of the standard geometries for pentacoordinate atoms (the trigonal bipyramid and the square pyramid). The two terminal phosphorus atoms of the ligand are closer to the indium atom than the central phosphorus atom: In1-P1 2.5956(8), In1-P2 2.5799(7); In1-P3 2.8259(8) Å. The two chlorine-indium distances in the cation differ significantly [In1-Cl1 2.4172(8), In1-Cl2 2.3547(9) Å], and are longer than any of the In2-Cl distances in the anion. If the phosphorus atom P3 is ignored as a donor site, the coordination geometry at the indium atom In1 is not representing a tetrahedron, as shown by a set of very different P/Cl-In-P/Cl angles in the broad range between 94.36(3) and 119.82(3)$^\circ$.

The coordination geometry is thus clearly a compromise in the interplay between the coordination potential and requirements of the central acceptor atom and the inflexible donor ligand. As judged by the bond lengths, only two of the three phosphorus atoms can be used efficiently as donor atoms (P1, P2). An inspection of the C-P3-In1 angles in the cation [99.90(10), 106.10(9), 130.31(11)$^\circ$] shows that the lone pair of electrons at P3 is not directed towards the indium atom at all.

These geometrical findings are in agreement with the NMR observations: Only the nuclei of P1 and P2 experience a large coordination shift as compared to the free ligand, while the nucleus of P3 is much less affected. Its signals are also sharp and show no sign of quadrupole broadening by the In isotopes, whereas the resonances of P1 and P2 are very broad.

In summary therefore the cation of the title compound should be considered an eight-membered ring with very weak, almost negligible transannular In1–P3 interactions (Fig. 2). The compound is a remarkable example where a potential tridentate ligand is limited in its functions to a bidentate action
by its intrinsic structural inflexibility: It cannot be wrapped around a metal in such a way as to fully exploit its donor capacity.

Experimental Part

All experiments were carried out routinely in an atmosphere of purified dry nitrogen. Solvents were dried and kept under nitrogen. Glassware was oven-dried and filled with nitrogen. TP was prepared following a literature procedure [7]. InCl₃ was commercially available and handled in a dry-box. Standard equipment was used throughout.

Preparation

The TP ligand (110 mg, 0.17 mmol) was dissolved in toluene (10 ml) and InCl₃ was added in small portions (77 mg, 0.35 mmol) at room temperature. The mixture was stirred for 2 h at 80 °C. After cooling the precipitate was collected and crystallized from dichloromethane/pentane (168 mg, 90% yield; m.p. 246 °C). ^{1}H NMR (CD₂Cl₂, -60°C): δ -15, broad d, 2P; -44, t, 7(P,P) 242 Hz, 1P (A₂B).

C₄₂H₃₃In₂Cl₆P₃ (1072.93)
Calcd. C 47.01, H 3.10 %,
Found C 46.76, H 3.02 %.

Crystal structure determination

A specimen of suitable quality and size was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo-Kα radiation, λ(Mo-Kα) = 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. Lp correction was applied and intensity data were corrected for absorption effects [μ(Mo-Kα) = 15.52 cm⁻¹; T_mín/ máximo = 0.837/0.999]. The structure was solved by direct methods and completed by full-matrix least-squares techniques on Fᵢ. The thermal motion of all non-hydrogen atoms was treated anisotropically. All C-H atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions (Uₐₙiso = 1.5·Ueq of the attached atom).

Crystal data for C₄₂H₃₃In₂Cl₆P₃: Mᵣ 1072.93, colourless crystals (0.5x0.4x0.25 mm³), monoclinic, a = 9.205(1), b = 29.779(2), c = 16.207(1) Å, β = 94.88(1)°, space group P2₁/c, Z = 4, V = 4426.6(6) Å³, ρcalcd 1.1610 g cm⁻³, F(000) 2120; T = 74 °C. 13339 measured and 9625 unique reflections [(sin θ/λ)max = 0.64 Å⁻¹; Rint = 0.0199]; 478 refined parameters, wR² = 0.0741, R = 0.0338 for 9582 reflections used for refinement. Residual electron densities: ±0.98/-0.67. The function minimized was: wR² = [(w(F₀²-Fc²)/2)]/[(w(F₀²))²]¹/²; w = 1/[σ²(F₀²) + (ap)² + bp]; p = (F₀² + 2Fc²)/3; a = 0.0272, b = 5.14. Important interatomic distances and angles are shown in the figure caption. Anisotropic thermal parameters and tables of distances and angles have been deposited with the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk. The data are available on request on quoting CCDC-135360.

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