Inorganic Chemistry

Article

Diphenyldichlorophosphonium Trichloride–Chlorine Solvate 1:1, [PPh$_2$Cl$_2$]$^+$Cl$_3^-$·Cl$_2$: An Ionic Form of Diphenyltrichlorophosphorane. Crystal Structures of [PPh$_2$Cl$_2$]$^+$Cl$_3^-$·Cl$_2$ and [(PPh$_2$Cl$_2$)$^+$]$_2$[InCl$_5$]$^{2-}$

Jan Taraba and Zdirad Zak*

Department of Inorganic Chemistry, Masaryk University, Kotlarska 2,
611 37 Brno, Czech Republic

An ionic form of diphenyltrichlorophosphorane, namely, diphenyldichlorophosphonium trichloride isolated as a dichlorine solvate (**1**), was obtained by treating PPh$_2$Cl$_3$ with excess chlorine. The identity of this species was established by single-crystal X-ray analysis and ^{31}P, ^{1}H, and ^{35}Cl NMR and Raman spectra. Bis(diphenyldichlorophosphonium) pentachloroindate (**2**) was obtained by the reaction of diphenyltrichlorophosphorane with indium trichloride in dichloromethane for comparison purposes. Its identity was determined by ^{31}P NMR spectra and single-crystal X-ray analysis.

Introduction

The existence of ionic forms of various alkyl and/or aryl chlorophosphoranes has been established by extensive ^{31}P and ^{35}Cl NMR studies of various solutions of appropriate compounds, and/or for the solid state as summarized by Bell, Geib, and Meyer.[1] There are two structures of ionic triorganodichlorophosphoranes known, namely [PPh$_3$Cl]$^+$Cl$^-$·CH$_2$Cl$_2$ and [PPr$^n_3$Cl]$^+$Cl$^-$, both exhibiting short −Cl···Cl$^-$ interactions.[2,3] However, no structural characteristics of ionic forms of diorganotrichlorophosphoranes have been given yet. We became interested in the problem when synthesizing diphenyltrichlorophosphorane as a starting material for further syntheses by the reaction of diphenylchlorophosphine with excess chlorine in chloroform. When checking the identity of the obtained crystals by X-ray structure analysis, we found, to our surprise, that the compound that we believed to be diphenyltrichlorophosphorane was actually diphenyldichlorophosphonium trichloride solvated by elemental chlorine (**1**). However, the salt decomposes at room temperature, and when recrystallized from dichloromethane, chlorine escapes and the salt is converted into the common molecular form of diphenyltrichlorophosphorane, PPh$_2$Cl$_3$. It is obvious

that the stability of the ionic form of diphenyltrichlorophosphorane is closely related to excess chlorine, which was used during the synthesis.

Our findings are interesting also from another point of view: while triiodide and tribromide anions are well-known and can easily be obtained by addition of elemental halogen on the iodide or bromide anions,[4] there are only a few examples[5−8] of structurally characterized trichloride salts. We believe that, at present, [PPh$_2$Cl$_2$]$^+$ is one of the simplest cations known to stabilize the trichloride anion. Herein we present not only its structure but also some new solution ^{31}P NMR and vibrational spectra. We have also prepared bis(diphenyldichlorophosphonium) pentachloroindate (**2**) in order to compare its vibrational spectra and the structure of its [PPh$_2$Cl$_2$]$^+$ cation.

Results and Discussion

Crystal Structures. Perspective views of the molecular structure and of the crystal packing of [PPh$_2$Cl$_2$]$^+$Cl$_3^-$·Cl$_2$ (**1**) are shown in Figures 1 and 2, respectively. Both cations and anions and the Cl$_2$ molecules are situated on a symmetry

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* To whom correspondence should be addressed. E-mail: zak@chemi.muni.cz. Fax: ++420-5-41211214.

(1) Bell, S. A.; Geib, S. J.; Meyer, T. Y. *Inorg. Chem.* **1999**, *38*, 2524−2526 and references therein.

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(7) Jansen, M.; Strojek, S. *Z. Naturforsch. B* **1995**, *50*, 1171−1174.

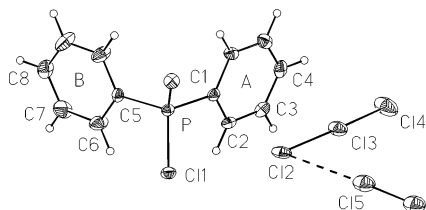(8) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1985**, *24*, 2453−2458.

Figure 1. Perspective view of the molecular structure of **1**. Thermal ellipsoids are drawn with 50% probability.
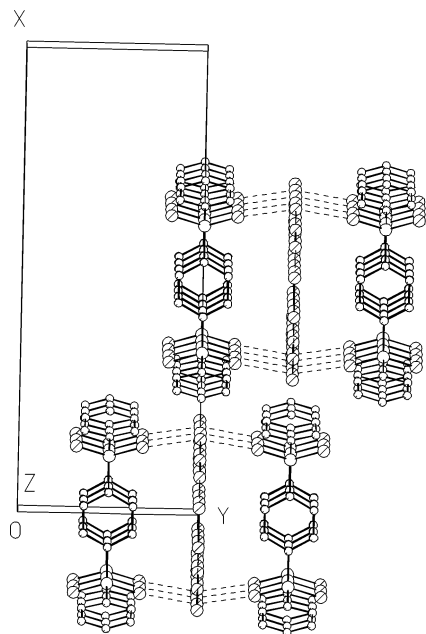

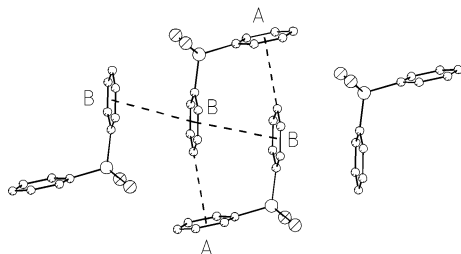**Figure 2.** Crystal packing of the structure of **1**.

Figure 3. Cation—cation interactions in the structure of **1**.

plane. The crystal structure of **1** is composed of layers parallel to the (100) plane with no apparent contacts between adjacent layers, which are mutually shifted by $^1/_2b$. Each layer is formed by alternating cationic and anionic ribbons propagating along the *c*-axis and stacked along the *b*-axis (Figure 2).

Two levels of cation—cation interactions can be distinguished in the cationic ribbons (Figure 3). First, the cations are arranged by "face-to-face/center-to-edge" (rings B—B) and "face-to-edge" [9,10] (rings A—B) $\pi-\sigma$ interactions into dimers, which are further stacked by "face-to-face/center-to-edge" (rings B—B) $\pi-\sigma$ interactions into the cationic ribbons. All phenyl rings of type B, involved in this latter type of interaction, are parallel and equidistant (*d* ap-

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(10) Ponzini, F.; Zagha, R.; Hardcastle, K.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 2323—2325.
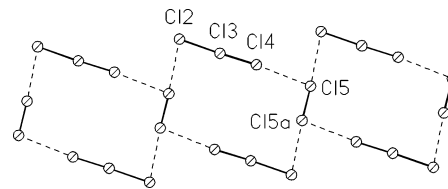
Figure 4. Anionic layer in the structure of **1**.

proximately 3.89 Å). However, the offsets of centroids of interacting B rings within the dimers and between the dimers are different (approximately 0.69 and 1.03 Å, respectively). The angle between the rings involved in the "face-to-edge" (A—B) interaction is 77.7°; the distance of the corresponding hydrogen atom, H(8), from the best plane of ring A is approximately 5.4 Å, and that from the centroid of ring A is approximately 2.46 Å. Similar intermolecular stacking interactions were observed in other structures having aromatic ligands, e.g., bis(4,5-diazafluorene-9-one thiosemicarbazone) palladium.[11]

The anionic layers contain both Cl_3^- anions and solvating molecules of Cl_2 arranged in a system of parallelograms (Figure 4). There are several Cl···Cl contacts (3.171—3.300 Å) shorter than the sum of van der Waals radii (3.5 Å)[12] both within the anionic ribbon and between the anionic and cationic ribbons (Figure 2, Table 2), with the shortest being between Cl(2) of the trichloride anion and Cl(5) of the chlorine molecule (3.171(2) Å). The distance 3.225 Å between Cl(2) of the trichloride anion and Cl(1) of the cation compares well with $-Cl···Cl^-$ distances in $[PPh_3Cl]^+Cl^-·CH_2Cl_2$ (3.279 Å) and $[PPr^n_3Cl]^+Cl^-$ (3.207 Å).[2,3] Short Cl···Cl contacts are not unusual; they have already been observed in other chlorine containing molecules, e.g., Cl_3PNSO_2Cl.[13]

There is an apparent shortening of all bonds formed by P in the $[PPh_2Cl_2]$ cation (mean P—C 1.787 Å, P—Cl 1.966 Å) as compared with neutral PPh_2Cl_3 which can be easily explained by increased attractive forces between the positively charged phosphorus and its ligands and the lower coordination number.

The Cl(2)—Cl(3) and Cl(3)—Cl(4) distances, 2.419(2) and 2.144(2) Å, respectively, of the trichloride anion differ significantly from the corresponding distances found in other trichloride salts which are in the range 2.249—2.394 Å for the longer bond and 2.182—2.262 Å for the shorter bond.

We attribute this to the instability of the salt, which decomposes at temperatures above the boiling point of chlorine. This fact is further supported by a significant residual electron density $\Delta\rho$ (4.94 e Å^{-3}) in the vicinity of Cl(3) and Cl(4). We believe that in the first step the trichloride anion decomposes to free chlorine and a chloride anion, whose presence is manifested by this residual electron density (for details, see the Experimental Section). The distance Cl—Cl 2.025(5) Å in the solvating molecule of Cl_2

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(13) Zák, Z.; Růžička, A. *Z. Kristallogr.* **1997**, *212*, 855—858 and references therein.
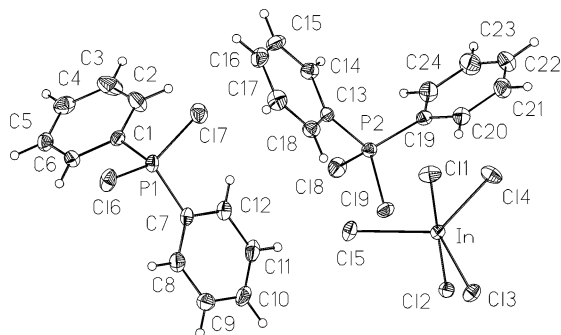
Figure 5. Molecular structure of **2**. Thermal ellipsoids are drawn with 50% probability.

is a little longer than that found in the solid structure of elemental chlorine, 1.984(4) Å.[14]

A perspective view of the structure of $[(PPh_2Cl_2)^+]_2[InCl_5]^{2-}$ (**2**) is shown in Figure 5. The crystal structure is formed by interdispersed cations and anions. While the overall geometries of the cations of **1** and **2** are the same, there are significant (almost 10σ) differences in the corresponding bond lengths and angles, which can be attributed to the different environments of the cations in the crystals and to different anion−cation interactions. The $InCl_5^{2-}$ anion forms a fairly regular trigonal bipyramid with bond distances and angles comparable to those found in $[PPh_4]_2InCl_5$[15] (Table 2). There are also rather short Cl···Cl contacts between $InCl_5$ anions and PPh_2Cl_2 cations, the shortest being 3.140, 3.205, and 3.307 Å.

NMR Measurements. In order to determine if the intermolecular stacking interactions of the phenyl rings as found in the solid state structure are also present in solution, we measured the ^1H NMR spectra of a $CHCl_3/Cl_2$ solution of **1**. We did not observe any upfield/downfield shift of the center of phenyl hydrogen multiplet (7.8 ppm) with respect to a molecular form, which suggests there are no phenyl rings interactions.[11,16]

No sharp signal belonging to simple Cl^- ions was observed in the ^{35}Cl NMR, which would indicate a fast exchange:

$$Cl_3^- \leftrightarrow Cl_2 + Cl^-$$
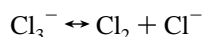
As can be seen from Table 3, the chemical shift of **1** does not depend on the solvent but on the amount of chlorine added. If a sufficient amount of chlorine is used, molecular PPh_2Cl_3 is completely transformed into its ionic form, $[PPh_2Cl_2]^+Cl_3^-$. These results are in full agreement with those obtained from studies in nitromethane solutions of diphenylchlorophosphino−chlorine mixtures, where increased amounts of chlorine led to upfield shifts (after appropriate change in sign convention).[17] In those experiments, however, the ratio of chlorine/phosphine never exceeded 2:1, and thus, full ionization of phosphorane was never achieved. Our

results agree also (after the appropriate change in sign convention) with solid state ^{31}P NMR studies of BCl_4^-, $SbCl_6^-$, and PCl_6^-[18] (93.6, 92, 89.7 ppm, respectively) and $AlCl_4^-$[17] (92 ppm, CH_3NO_2 solution) salts of the $[PPh_2Cl_2]^+$ cation. The chemical shift of the dichloromethane solution of **2** is 94.6 ppm.

Raman Spectra. Comparing the Raman spectra of a $CHCl_3/Cl_2$ solution and the solid state of **1**, we were able to identify a distinct Raman line at approximately 286 cm^{-1} (solution) and 273 cm^{-1} (solid) belonging to the symmetric stretching vibration of the Cl_3^- ion, which agrees well with those observed in the acetonitrile solution (275 cm^1) and solid state (268 cm^{-1}) of tetrapropylammonium trichloride.[19] Moreover, in $CHCl_3/Cl_2$ solution of **1**, we also observed an intensive broad Raman line with its center at 466 cm^{-1}. A similar band (482 cm^{-1}) was also observed in $(NPr_4)Cl_3/Cl_2$ solution[19] and assigned to the stretching mode of the Cl_5^- ion. The presence of molecular Cl_2 was evidenced by two Raman lines at 536 and 543 cm^{-1}.

Experimental Section

Synthesis. PPh_2Cl_3. The synthesis of the molecular form of diphenyltrichlorophosphorane was performed by the reaction of PPh_2Cl with an equimolar amount of gaseous chlorine. Thus, 2.00 g (28.2 mmol) of gaseous chlorine was added to 6.20 g (28.2 mmol) of PPh_2Cl dissolved in 20 mL of CCl_4. A white crystalline precipitate was formed during the reaction. After all the chlorine was added, the crystalline slush was stirred for an hour at ambient temperature and then filtered and the precipitate washed twice by 2 mL of CCl_4 and dried in vacuo. Yield: 5.90 g (19.6 mmol), i.e., 69.5%. Anal. Calcd for PPh_2Cl_3: P, 10.62%; Cl, 36.48%. Found: P, 10.51%; Cl, 36.89%.

$[PPh_2Cl_2]Cl_3·Cl_2$. Chlorine [7.00 g (98.7 mmol)] was condensed onto a solidified solution of 2.20 g (7.5 mmol) of PPh_2Cl_3 dissolved in 5 mL of chloroform in a 50 mL Schlenk pressure vessel immersed in liquid N_2. After all the chlorine had been added, the vessel was closed and left to warm to ambient temperature. When the contents of the vessel melted, a yellow precipitate was formed. The vessel was then heated to 55 °C in a water bath for an hour, and then, the mixture was allowed to cool slowly to ambient temperature. During the heating, the yellow precipitate dissolved, and on cooling, transparent yellow crystals were formed. When separated from the mother liquid, the crystals rapidly decomposed at room temperature releasing gaseous chlorine.

For the X-ray structure analysis, the vessel containing the crystals in the mother liquid was cooled to approximately 0 °C, the mother liquid was decanted, and the crystals were rapidly transferred to a drop of perfluoropolyether oil cooled to approximately −25 °C on a microscope stage. A suitable crystal was rapidly chosen, extracted from the oil on a glass needle, and mounted on the diffractometer equipped with a low-temperature device.

$[(PPh_2Cl_2)^+]_2[InCl_5]^{2-}$. To the 2.5 g (8.3 mmol) of PPh_2Cl_3 dissolved in 15 mL of CH_2Cl_2 was added 0.95 g (4.3 mmol) of solid $InCl_3$. The mixture was stirred for 2 h until a clear solution was formed. The crystals were grown from the solution after partial evaporation of the solvent in vacuo. Yield: 84.6% related to PPh_2-Cl_3.

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Table 1. Crystal Data and Structure Refinement of **1** and **2**

	1 [PPh$_2$Cl$_2$$^+$]Cl$_3$$^-$·Cl$_2$	**2** [PPh$_2$Cl$_2$$^+$]$_2$[InCl$_5$]$^{2-}$
formula	C$_{12}$H$_{10}$Cl$_{5.73}$P	C$_{24}$H$_{20}$Cl$_9$InP$_2$
fw	388.30	804.21
T [K]	120	120
space group	$C2/m$	$P2_1/n$
a [Å]	22.689(5)	10.957(2)
b [Å]	8.800(2)	21.295(4)
c [Å]	7.994(2)	13.893(3)
α [deg]	90	90
β [deg]	93.09(3)	110.26(3)
γ [deg]	90	90
V [Å]	1593.8(6)	3041.1(10)
Z	4	4
D [Mg/m^3]	1.618	1.757
R-indices [$I > 2s(I)$]	R1 = 0.0480^a	R1 = 0.0188^a
R-indices (all data)	R1 = 0.0567	R1 = 0.0213

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

X-ray Structure Analysis. The intensity data of both compounds were collected on a KUMA KM-4 CCD κ-axis diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) equipped with an Oxford Cryosystem LT-device at 120 K and corrected for absorption effects using ψ-scan. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were inserted in calculated positions and isotropically refined assuming a "ride-on" model. The crystal data for compounds **1** and **2** and other pertinent information are summarized in Table 1, and a list of interatomic distances and angles is in Table 2. The programs used included the SHELX-97[20] program package for the structure determination and structure refinement and tables, and the drawings were made using the XP program of the Bruker SHELXTL V5.1[21] program package.[22]

Routine refinement of structure **1** assuming a composition [PPh$_2$-Cl$_2$]Cl$_3$·Cl$_2$ yielded a significant residual $\Delta\rho$ 4.94 e Å^{-3} in the neighborhood of Cl(3) and Cl(4). Since we suspected that this belongs to a Cl$^-$ anion formed by partial decomposition of the trichloride, we performed a refinement taking into account both trichloride and chloride anions with variable ratios of their occupancy factors. The best results were achieved when the ratio Cl$_3$$^-$/Cl$^-$ was 5.25:1 and the structure refined to significantly lower esd's, R1 and wR2 indices, and a reasonable residual $\Delta\rho$ value of 1.341 e Å^{-3}. However, this refinement had no influence on a general geometry of the structure, and the changes in bond lengths and angles were only minor. Especially, the refinement resulted only

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(21) Sheldrick, G. M. *SHELXTL*, V 5.1; Bruker AXS GmbH.

(22) Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 197932 (**1**) and CCDC 200824 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1** and **2**

[PPh$_2$Cl$_2$$^+$]Cl$_3$$^-$·Cl$_2$			
P−C(5)	1.780(4)	C(5)−P−C(1)	112.0(2)
P−C(1)	1.788(5)	C(5)−P−Cl(1)#1^a	108.54(9)
P−Cl(1)	1.9662(11)	C(5)−P−Cl(1)#1	109.07(8)
P−Cl(1)#1	1.9662(11)	C(5)−P−Cl(1)	108.54(9)
C(arom)−C(arom)^b	1.380(3)	C(1)−P−Cl(1)	109.07(8)
Cl(2)−Cl(3)	2.419(2)	C(1)−P−Cl(1)	109.31(7)
Cl(2)−Cl(5)	3.171(2)	Cl(1)#1−P−Cl(1)	109.59(7)
Cl(2)−Cl(1)#2	3.2254(12)	Cl(4)−Cl(3)−Cl(2)	178.09(10)
Cl(2)−Cl(1)#3	3.2254(12)		
Cl(3)−Cl(4)	2.144(2)		
Cl(4)−Cl(5)#4	3.300(2)		
Cl(5)−Cl(5)#5	2.025(3)		

[PPh$_2$Cl$_2$$^+$]$_2$[InCl$_5$]$^{2-}$			
In−Cl(1)	2.4863(9)	Cl(3)−In−Cl(4)	120.09(2)
In−Cl(2)	2.5074(8)	Cl(3)−In−Cl(5)	118.95(2)
In−Cl(3)	2.4095(7)	Cl(4)−In−Cl(5)	120.93(2)
In−Cl(4)	2.4140(6)	Cl(3)−In−Cl(1)	89.31(3)
In−Cl(5)	2.4212(7)	Cl(4)−In−Cl(1)	90.36(2)
P(1)−C(1)	1.768(2)	Cl(5)−In−Cl(1)	91.80(3)
P(1)−C(7)	1.774(2)	Cl(3)−In−Cl(2)	90.74(3)
P(2)−C(19)	1.767(2)	Cl(4)−In−Cl(2)	89.00(2)
P(2)−C(13)	1.779(2)	Cl(5)−In−Cl(2)	88.79(3)
P(1)−Cl(6)	1.9577(8)	Cl(1)−In−Cl(2)	179.294(18)
P(1)−Cl(7)	1.9694(9)	C(1)−P(1)−C(7)	114.44(10)
P(1)−Cl(8)	1.9525(8)	C(1)−P(1)−Cl(6)	110.15(8)
P(1)−Cl(9)	1.9597(8)	C(7)−P(1)−Cl(6)	108.36(8)
C(arom)−C(arom)^b	1.381(3)	C(1)−P(1)−Cl(7)	108.54(8)
		C(7)−P(1)−Cl(7)	107.33(8)
		Cl(6)−P(1)−Cl(7)	107.80(4)

^{a} Symmetry transformations used to generate equivalent atoms: #1 x, $-y$, z; #2 $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 2$; #3 $-x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + 2$; #4 x, y, $z - 1$; #5 $-x$, $-y$, $-z + 2$. ^{b} Average bond lengths.

Table 3. ^{31}P Chemical Shifts for Chlorine Containing Solutions of PPh$_2$Cl$_3$

Cl$_2$/PPh$_2$Cl	solvent	^{31}P NMR
2:1	CCl$_4$	83.4
10:1	CCl$_4$	93.5
10:1	CHCl$_3$	93.3
liquid Cl$_2$	liquid Cl$_2$	93.7

in insignificant changes of Cl−Cl bond lengths of the trichloride anion.

The numerical data for **1** presented in Tables 1 and 3 and in the Supporting Information come from the refinement comprising both Cl$_3$$^-$ and Cl$^-$ anions with their occupancy ratios 5.25:1.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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