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Notes

Ph_2PCl_3: Covalency in Solution and the Solid State

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Introduction

The structure of Ph_2PCl_3 (**1**) both in solution and in the solid state has been the subject of several investigations.[1−6] On the basis of these studies, it is apparent that the compound can exist in two forms, either a 5-coordinate covalent compound or a 4-coordinate cation with a chloride or Lewis-acid-complexed anion. We first became interested in this issue when, in the course of preparing Ph_2PCl_3 as a starting material, we found that the ^{31}P NMR data reported for the compound ranged from −32 to +94 ppm! The confusion was further enhanced by the fact that it was often unclear which sign convention had been used for the assignment of the ^{31}P data vs 85% H_3PO_4. Furthermore, no single-crystal X-ray diffraction studies of **1** or any simple derivatives of it existed in the literature. Therefore a single crystal of Ph_2PCl_3 was isolated and herein we present not only its structure but the correlation of our spectroscopic data with previous reports.

Results and Discussion

Using the protocol of Gates and co-workers,[2] we prepared what we believed was the neutral compound (eq 1).

$$Ph_2PCl + Cl_2 \xrightarrow{\text{toluene}} Ph_2PCl_3 \qquad (1)$$

X-ray-quality crystals were grown from slowly evaporating toluene at room temperature. The resulting colorless plates were extremely hygroscopic and dissolved rapidly in epoxy and Fluorolube such that it was necessary to seal them in glass capillaries. Due to the delicate nature of these crystals—they deteriorated in the capillary with time—it was difficult to obtain a satisfactory data set. Despite the somewhat poor data ($wR_{F^1} = 0.069$, $wR_{F^2} = 0.190$), however, the broad structural features can easily be distinguished.

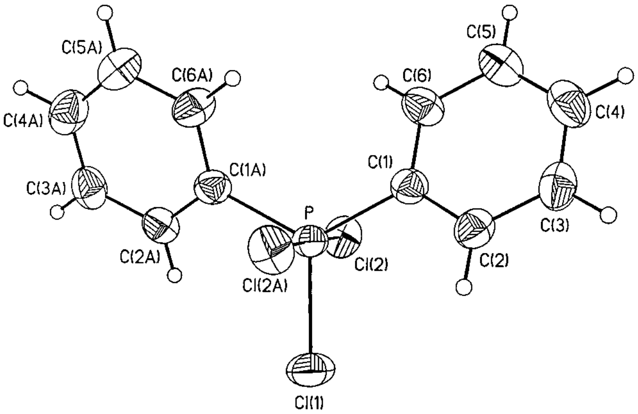

Figure 1. Molecular structure of Ph_2PCl_3 (**1**; 50% probability ellipsoids). Selected bond lengths (Å): P−Cl(1) 2.011 (3); P−Cl(2) 2.227 (2); P−C(1) 1.816. Selected bond angles (°): Cl(1)−P-Cl(2) 89.30 (6); Cl(2)−P-Cl(2A) 178.60 (13); Cl(1)−P-C(1) 118.12 (9); Cl(2)−P-C(1) 90.34 (19); C(1)−P-C(1A) 123.8 (4).

Table 1. Crystallographic Data for Ph_2PCl_3 (**1**)

empirical formula	$C_{12}H_{10}Cl_3P$	Z, Å^3	1253.6(17)
space group	$C2/c$ (monoclinic)	fw	291.52
a, Å	14.565(13)	T, °C	−65(2)
b, Å	10.903(6)	λ	0.710 73
c, Å	7.941(7)	ρ(calcd), g cm^{-3}	1.545
α, deg	90	μ, cm^{-1}	0.0826
β, deg	96.22(7)	wR_{F^2}[a] (1284 data)[b]	0.1900
γ, deg	90	wR_{F^2}[c] (all data)	0.2105

[a] $wR_F^2 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $F_o > 4\sigma(F_o)$. [c] $wR_{F^2} = [\sum w(F_o^2 - F_c^2)/F_o^4]^{1//2}$, $w = [\sigma^2 F_o^2 + (0.1F_o)^2]^{-1}$.

The structure of **1**, as shown in Figure 1, is trigonal bipyramidal with axial chlorines (Table 1). A crystallographically imposed 2-fold axis of symmetry coincides with the $P-Cl_{eq}$ bond. The axial P−Cl bonds at 2.227(2) Å are significantly longer than the equatorial P−Cl bond at 2.011(3) Å. Both bond distances lie within the normal range for P−Cl bonds for similar compounds.[7,8] To accommodate the phenyl groups, the structure is slightly deformed from ideal trigonal bipyramidal geometry. The angle between the phenyl rings, for example, is slightly larger at 123.8(11)° than the phenyl−P−Cl(1) angle of 118.1(19)°. The axial chlorines are also slightly bent away from the phenyl groups with a Cl−P−Cl angle of 178.60(13)°. The phenyl rings do not lie in the equatorial plane but are rotated 51.7° out of the plane.[9]

In a search of the Cambridge Crystallography Database,[10] only one structure for any neutral compound of the general formula R_2PCl_3 was located. The compound $(Cl_3C)_2PCl_3$ is also

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(9) Theory predicts that planarity correlates with the π-donor characteristics of the aryl ligand. Hoffman, R.; Howell, J. M.; Muetterties, E. L. *Inorg. Chem.* **1972**, *9*, 3047−3058. See also ref 12 for a comparison of the angles of fluorinated and unfluorinated phenyl groups in isostructural molecules.

(10) Cambridge Structural Database, Version 5.15; Cambridge Crystallographic Data Centre: Cambridge, UK.

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trigonal bipyramidal, but in contrast with **1**, the Cl ligands are equatorial, leaving the axial sites for the electronegative CCl_3 groups.[11] A more informative context for this structure, given the scarcity of homologues, is the closely related R_3PX_2 (X = F, Cl) class of complexes. Within this family, the structure of **1** closely matches those of Ph_3PF_2,[12] Ar_3PF_2,[13] and the recently reported chloride derivatives Ph_3PCl_2,[8] Ph_2ArPCl_2,[7] and Ar_3PCl_2[7] ($Ar = C_6F_5$). All of these complexes have been isolated in the molecular form and have been shown to be trigonal bipyramidal with axial chlorines. Interestingly, Ph_3PCl_2 can also be isolated from polar solvents in an ionic form with a unique Cl···Cl···Cl bridge.[7] Godfrey and co-workers have surveyed the X-ray structures for a variety of other derivatives of R_3EX_2, (E = P, As, Sb; $X_2 = Cl_2, Br_2, I_2$, IBr) and have found that the solid-state structures are very sensitive to the identity of E and the electronic nature of the ligands.[14] Wiley and Stine proposed that the tendency to form covalent structures follows the pattern: F > Cl > Br > I, Ph > alkyl. Furthermore, nonpolar solvents favor the covalent isomers.[15]

Prior to our work, the solid-state structure for neutral Ph_2PCl_3 had been determined using Raman and ^{37}Cl NQR spectroscopies. Gates and co-workers assigned the solid-state Raman spectra for both neutral and ionic isomers of Ph_2PCl_3.[2] The accuracy of their assignments for the neutral complex is confirmed by our study since Raman data obtained for complex **1** matched their reported spectrum. Svergun *et al.*[16] and Dillon *et al.*[3a] likewise concluded accurately, based on solid state ^{37}Cl NQR spectra, that the structure of **1** should be trigonal bipyramidal with equatorial phenyl groups.

Given the assurance from the X-ray structure and Raman spectrum that the solid compound **1** was in fact the neutral species, dissolution in nonpolar solvents should also give neutral complexes. The ^{31}P NMR spectra, in dry toluene solvent, showed for **1** a single resonance at δ −32.[17] Solutions in other hydrocarbon solvents showed shifts of only 1−2 ppm. In contrast, the resonance occurs at δ −11 to +70 in more polar solvents (Table 2). Addition of CH_2Cl_2 to a solution of **1** in C_6D_6 causes a shift in the ^{31}P NMR resonance from δ −32 to −11. Examination of the previously reported NMR data showed that, after normalizing all data to the same shift convention, there was a consensus. Ph_2PCl_3 prepared in the absence of chloride-abstracting Lewis acids and dissolved in nonpolar solvents has a ^{31}P shift of $\sim\delta$ −30. The shift of Ph_2PCl_3 in the presence of Lewis acids, such as $AlCl_3$ or PCl_5, ranged from δ +67 to 94. Intermediate shifts such as those observed in $CDCl_3$ and CD_2Cl_2 solvents are likely to correspond to an intermediate stage of ionization attained when the neutral compound is dissolved in these ion-supporting solvents.[1a,15,18]

Table 2. ^{31}P Chemical Shifts for Ph_2PCl_3

compound or synthetic method	^{31}P NMR/ppm[a]	solvent	reference
	Neutral		
$Ph_2PCl + Cl_2$	−25	nitrobenzene	4
Ph_2PCl_3, method unknown	−32.7	benzene	1
compound **1**	−31	benzene	this work
	−32	toluene	this work
	−30	CCl_4	this work
	Ionic		
$Ph_2PCl + 2Cl_2$	+67	nitrobenzene	4
$Ph_2PCl_3 + HCl$	+67	$CHCl_3$	5
$Ph_2PCl + PCl_5$	+73	1,1,2,2-tetrachloroethane	6
$[PPh_2Cl_2][BCl_4]$	+93.6	solid state	3a
$[PPh_2Cl_2][SbCl_6]$	+92	solid state	3a
$[PPh_2Cl_2][PCl_6]$	+89.7	solid state	3a
Ph_2PCl_3, method unknown	+42.8	solid state	1
compound **1**	+70	CH_3CN	this work
compound **1**	−11	CD_2Cl_2	this work
compound **1**	+25−37[b]	$CDCl_3$	this work

[a] The signs of ^{31}P chemical shifts have been changed as necessary to conform to the sign convention that assigns PPh_3 at δ −6 relative to 85% H_3PO_4. [b] The shift was sensitive to the source/purity of the $CDCl_3$. Small amounts HCl, a common impurity in $CHCl_3$ apparently stabilize the ionic form.

Only one reported shift does not fit these parameters. Timokhin et al. reported that the solid state ^{31}P NMR spectrum of **1** was δ +42.8, but that the same material in solution gave a single ^{31}P NMR resonance of δ −32.7.[1] It is probable, that although they isolated the ionic compound, it reverted to the neutral form upon dissolution in benzene. Unfortunately, we have not been able to isolate X-ray quality crystals of a material that we believe to be the ionic isomer to test this hypothesis. In this context, it is important to note that we screened several crystals of **1** from two different preparations. In all cases, the same unit cell was found suggesting that the complex did not crystallize in two different forms from toluene solution.

In conclusion the covalent isomer of Ph_2PCl_3 adopts a trigonal bipyramidal structure with axial chlorines in the solid state. This structure is in accord with previously reported Raman and NMR spectroscopic data.

Experimental Section

Solvents, Reagents, and General Data. Solvents were freshly distilled under nitrogen prior to use. Toluene and benzene were distilled from benzophenone/sodium. Chloroform, methylene chloride, and acetonitrile were dried over CaH_2 and vacuum transferred. All deuterated solvents used were purified in the same manner as the nondeuterated equivalent after being received from Cambridge Isotope Laboratories. Chlorine gas was purified by passing it through concentrated sulfuric acid and then over a 4:1 mixture of activated carbon/silica. The Ph_2PCl was used as received from Aldrich (reagent grade).

Spectroscopy and Magnetic Measurements. ^1H and ^{31}P NMR spectra were recorded on a Bruker AF300 NMR spectrometer. Raman spectra were recorded as powders on a Nicolet 950 Spectrometer ($Nd:YVO_4$ source, $\lambda = 1064$ nm) at 1 cm^{-1} resolution. The Raman signal was detected with an Applied Detector Corp. high-purity germanium-diode detector (model 203NR). Frequencies were calibrated using acetonitrile as an external reference.

Synthesis of Ph_2PCl_3. Chlorine gas (130 mL at 1 atm, 5.34 mmol) was injected via syringe into a Schlenk flask containing toluene (15 mL) under a nitrogen atmosphere. Ph_2PCl (1.00 mL, 5.34 mmol) was added over a period of 5 min to the stirred solution. A white precipitate formed within a few minutes. After 4 h, the mixture was filtered, and the precipitate was collected and recrystallized from a slowly evaporating toluene solution. Yield 55.4%. Raman (powder, frequency range

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(17) The modern sign convention is used for all ^{31}P NMR data. According to this convention the ^{31}P NMR resonance of PPh_3 occurs at −6 ppm referenced to external 85% H_3PO_4.

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700−0 cm^{-1}) ν/cm^{-1} 620 (w), 575 (w), 338 (s), 302 (w), 277 (s), 267 (m), 241 (m), 137 (s).

X-ray Diffraction Study of Ph_2PCl_3. Single-crystal X-ray diffraction experiments were performed on a Siemens P3 diffractometer with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Diffraction data were refined using the Siemens SHELXTL PLUS (version 5.02) software package on a Silicon Graphics Indigo system. Lattice parameters were determined from a least-squares fit of the angular settings of 24 reflections in the range $20° \leq 2\theta \leq 25°$. The intensities of 3 representative reflections were measured every 197 reflections to check for decay of the crystals; none was observed. An empirical absorption correction, based on azimuthal scans of 6 reflections, was performed. All data were corrected for Lorentz and polarization effects. The heavy atoms of the complex were located using direct methods; remaining atoms were located from subsequent difference Fourier syntheses and refined anisotropically. Hydrogen-atom positions were computed by fixing the C−H distance to 0.96 Å.

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Supporting Information Available: Raman spectrum for compound **1** and one X-ray crystallographic file, in CIF format, are available free of charge via the Internet at http://pubs.acs.org.

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