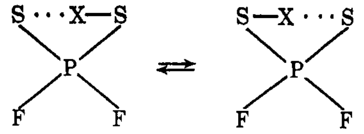
firmed by the observed shift to 1889 cm^{-1} upon deuteration.[8] Colthup, *et al.*,[16] have reported a frequency range of 835–865 cm^{-1} for S–H bending vibrations in dithiophosphoric acid. The strong band observed in the HPS_2F_2 spectrum at 840 cm^{-1} is present as a low intensity absorption in the spectrum of DPS_2F_2. A new band is observed in the DPS_2F_2 spectrum at 607 cm^{-1}. The intensity of this band does not compare with that of the 840-cm^{-1} band, but decreased intensity is often encountered in the same bands of an isotopic derivative. The frequency shift is approximately that which is expected, and therefore the 840-cm^{-1} band is assigned to the S–H bending vibration of the hydrogen-bonded molecule.[17] A second band in this region at 813 cm^{-1} also decreases in intensity in the DPS_2F_2 spectrum. The band cannot be assigned as an overtone or combination of any observed fundamental and therefore may be associated with the S–H bending mode of a nonhydrogen-bonded species.

In conclusion, the physical data support the structure where X = H or D for the difluorodithiophosphoric acid gaseous molecule. In the liquid state, the acid



is also highly associated; however, the present data do not distinguish between intra- and intermolecular hydrogen bonding.

Acknowledgment. This work was carried out in part under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, under Contract DAAH-01-67-C-0655.

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(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 350–352.

(16) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 304.

(17) See ref 16, p 189.

Structures of Several Phenylchlorophosphoranes in Solution[1]

Donald B. Denney, Dorothy Z. Denney, and Bennie C. Chang

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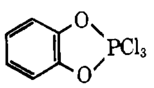
Abstract: The ^{31}P nmr spectra of the reaction products of chlorine with triphenylphosphine, diphenylchlorophosphine, and phenyldichlorophosphine have been determined in nitrobenzene. The results indicate these products exist in this solvent as the pentacoordinated materials. Addition of excess chlorine promotes dissociation to a phosphonium cation trichloride anion ion pair. Hydrogen chloride also promotes dissociation of triphenyldichlorophosphorane to triphenylchlorophosphonium bichloride. Ionization by chlorine becomes less facile as the number of chlorines bonded to phosphorus is increased.

It has long been recognized that phosphorus pentachloride can exist as pentachlorophosphorane or as tetrachlorophosphonium hexachlorophosphate.[2] The structures of pentacoordinate chloroalkyl, chloroaryl, and chloroaryloxy phosphorus compounds have received some study.[3] Compound **1** has been studied by Jones and Katritzky[3a] who have reported that it has a ^{31}P nmr chemical shift of +26 ppm relative to 85% phosphoric acid. The relatively large positive chemical shift suggests that the material exists as the phosphorane rather than as the phosphonium chloride. It is not possible, however, to rule out a rapidly equilibrating mixture of these two substances with an equilibrium constant which highly favors **1**.



1

$(C_6H_5)_3PCl_2 \rightleftharpoons (C_6H_5)_3P^+\text{—}Cl + Cl^-$

2 3

Recently, Wiley and Stine[4] have investigated the structures of the products obtained by adding chlorine to triphenylphosphine and tributylphosphine. The tributylphosphine–chlorine adduct exhibited large negative, *ca.* −105 ppm, chemical shifts in the ^{31}P nmr spectra in either acetonitrile or nitrobenzene. These shifts were not changed when antimony pentachloride was added. The authors concluded that the tributylphosphine–chlorine reaction product exists as tributylchlorophosphonium chloride in these solvents.

The triphenylphosphine–chlorine adduct in acetonitrile in the presence of 1 equiv of antimony pentachloride or in its absence had ^{31}P nmr spectra with one absorption at −66 and −62 ppm, respectively. It was suggested therefore that the material is best represented as triphenylchlorophosphonium chloride (**3**) in acetonitrile. In nitrobenzene one absorption was found at −8 ppm. Addition of 1 equiv of aluminum chloride shifted the absorption to −65 ppm. It was suggested therefore that the phosphorane **2** prevails in nitro-

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(1) This research has been supported by the National Science Foundation under NSF GP 4997X and by the National Institutes of Health under GM 12625.

(2) For an excellent review see D. S. Payne in "Topics in Phosphorus Chemistry," Vol. 4, Interscience Publishers, New York, N. Y., 1967, p 85.

(3) (a) R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, **74**, 60 (1962); (b) J. E. Griffiths, *J. Chem. Phys.*, **41**, 3510 (1964); (c) H. J. Emeleus and G. S. Harris, *J. Chem. Soc.*, 1494 (1959); (d) H. J. Emeleus and J. M. Miller, *J. Inorg. Nucl. Chem.*, **28**, 662 (1966); (e) J. F. Nixon, *ibid.*, **27**, 1281 (1965); (f) G. S. Harris and D. S. Payne, *J. Chem. Soc.*, 4617 (1956).

(4) G. A. Wiley and W. R. Stine, *Tetrahedron Letters*, 2321 (1967).

benzene and that aluminum chloride converts it into triphenylchlorophosphonium tetrachloroaluminate.

The results of Wiley and Stine are of particular importance to our understanding of the structures of these compounds. The apparently important role of the solvent is also of considerable interest. Unfortunately their data do not establish that the material which absorbs at −8 ppm is **2** or a rapidly equilibrating mixture of **2** and **3**. It is the purpose of this report to present data which extend their study and which modify their conclusion concerning the species showing the −8-ppm absorption.

Experimental Section

Materials. Nitrobenzene and acetonitrile were dried over calcium chloride, distilled, and stored over molecular sieves. Triphenylphosphine was recrystallized from ethanol, mp 79–80°. Phenyldichlorophosphine and diphenylchlorophosphine were commercial samples. Their ^{31}P nmr spectra agreed well with those reported in the literature. Standard solutions of chlorine in nitrobenzene and acetonitrile were prepared by adding gaseous chlorine to the solvent and standardizing iodometrically. Alternatively chlorine was added to a known volume of nitrobenzene. The exact amount was determined by weighing. The molarity was determined from the measured density of a standard nitrobenzene–chlorine solution. The solutions of reaction products were prepared by adding the appropriate amounts of chlorine–solvent mixture to the phosphine which was under nitrogen and cooled in an ice bath. After the addition more nitrobenzene was often added to dissolve all of the solid precipitate. The solutions were allowed to warm to room temperature, and the ^{31}P nmr spectra were recorded as soon as possible. It was found that, on standing, reactions occurred which caused the production of new phosphorus-containing materials.

Spectral Measurements. All ^{31}P nmr spectra were recorded with a Varian Associates HA-100 operating at 40.5 MHz. Chemical shifts are reported relative to 85% phosphoric acid as an external standard. All spectra were recorded both in the presence of and in the absence of the external standard.

Results and Discussion

In an initial experiment excess chlorine was added to a solution of triphenylphosphine in nitrobenzene. The ^{31}P nmr spectrum showed only one absorption at −66 ppm. This result was completely different from that of Wiley and Stine. They prepared their triphenylphosphine–chlorine adducts by adding chlorine to a solution of triphenylphosphine in carbon tetrachloride. The precipitate was dissolved in the appropriate solvent and then investigated by nmr.[5] Repetition of the experiment by Stine gave a material with an absorption at −5 ppm, and in this laboratory a value of −2.5 ppm was obtained on a material prepared by their procedure. These results show that excess chlorine has a powerful effect on the nature of the substances present in solution. As a consequence, a detailed investigation was undertaken of the structures of the materials formed from triphenylphosphine, diphenylchlorophosphine, and phenyldichlorophosphine with varying amounts of chlorine. The results are collected in Table I.

Treatment of triphenylphosphine with varying amounts of chlorine (series A) showed that the chemical shift of the new absorption varied as a function of the relative amounts of chlorine added. When 1 mole or less of chlorine was added, an absorption was found between +9 and +11 ppm.[6] When less than 1 mole of chlorine was added, an absorption was also found at +5.7 ppm. The absorption is due to triphenylphosphine. When 1 or more moles of chlorine was added, the absorption for triphenylphosphine disappeared, and the major absorption shifted to increasingly negative values until, as mentioned before, it reached −65 ppm when a large excess of chlorine was added.

Table I

Series	Compound	Chlorine: phosphine	^{31}P absorptions, ppm
A	$(C_6H_5)_3P$	0.43	+5.7, +9
A		0.96	+11
A		1.44	−16
A		1.77	−35
A		2.03	−48
B	$(C_6H_5)_2PCl$	0.43	−82, +26
B		0.94	+25
B		2.04	−67
B	$(C_6H_5)_2PCl \cdot AlCl_3$	1.0	−92
C	$C_6H_5PCl_2$	0.5	−162, +43
C		0.98	−162, +41
C		1.81	+32
C		3.37	+25
C	$C_6H_5PCl_2 \cdot AlCl_3$	1.0	−100.5
D[a]	$C_6H_5PCl_2$	0.7	−161, +36

[a] This reaction was carried out in acetonitrile.

Treatment of a triphenylphosphine (1 mole)–chlorine (0.5 mole) reaction mixture with increasing amounts of a solution of anhydrous hydrogen chloride in nitrobenzene also caused a change in chemical shift of one of the two absorptions to more negative values. The triphenylphosphine absorption did not change. The shifts ranged from −5 ppm, when a trace of hydrogen chloride was added, to −58 ppm, when an excess was present.

Diphenylchlorophosphine was allowed to react with less than equivalent amounts of chlorine (series B). The major absorptions were those of the starting material and a material with an absorption at +26 ppm. In the presence of an equivalent amount of chlorine, the material absorbing at +25 ppm was by far the major species present. When 2 moles of chlorine was added, the major absorption was found at −67 ppm. Diphenylchlorophosphine, chlorine, and aluminum chloride, equivalent amounts, gave a solution which showed an absorption at −92 ppm which is assigned to diphenyldichlorophosphonium tetrachloroaluminate. It should be noted though that the absorption could also be due to a rapidly equilibrating mixture of the phosphonium salt with diphenyltrichlorophosphorane and aluminum chloride. In view of the very large negative chemical shift, the equilibrium undoubtedly must lie very far toward the phosphonium salt.

Phenyldichlorophosphine and 1 mole or less of chlorine gave a positive absorption at +43 ppm. Excess chlorine caused a downfield movement of this peak; however, the change was relatively small. Aluminum chloride was much more effective and led to a shift to −101 ppm. The absorption is assigned to phenyltrichlorophosphonium tetrachloroaluminate or an equilibrium mixture of it with phenyltetrachlorophosphorane and aluminum chloride. Once again though the equilibrium must lie very far toward the ions.

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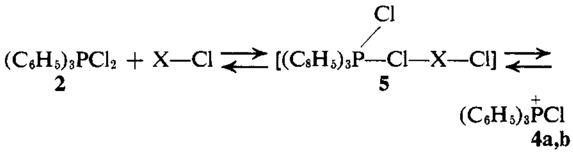
(5) W. R. Stine, private communication.

(6) The exact value of the absorption varied slightly from experiment to experiment. In one case it was observed at +14 ppm. The variation may be due to the formation of traces of hydrogen chloride which promotes some ionization.

Phenyldichlorophosphine with 0.7 mole of chlorine in acetonitrile showed an absorption for starting material, −161 ppm, and a new one at +36 ppm; on standing the absorption shifted to −27 ppm, and a new absorption appeared at −77 ppm.

The data from series A show that the initial reaction product of triphenylphosphine with chlorine in nitrobenzene has a considerably more positive ^{31}P nmr chemical shift than that observed by Wiley and Stine.[4] It is believed that the absorption is that of triphenyldichlorophosphorane (**2**); however, one cannot completely exclude the possibility of there being some triphenylchlorophosphonium ion in equilibrium with it. It is interesting to note that **2** is not in rapid equilibrium on the nmr time scale with starting material. Addition of 1 mole of strong Lewis acid such as aluminum chloride causes dissociation into the phosphonium salt. Chlorine and hydrogen chloride apparently act in a similar fashion. There is good precedent for reaction of hydrogen chloride with chloride ion to give the bichloride ion in nitrobenzene.



$$(C_6H_5)_3PCl_2 + X{-}Cl \rightleftarrows [(C_6H_5)_3P{-}Cl{-}X{-}Cl] \rightleftarrows (C_6H_5)_3\overset{+}{P}Cl\ ClXCl^-$$

2 **5** **4a,b**

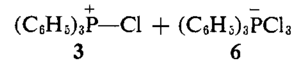
X = H, Cl

Herbrandson and coworkers[7] have shown that the association constant for chloride ion and hydrogen chloride is at least 500 in nitrobenzene. They have also observed that tetraethylammonium chloride is virtually insoluble in nitrobenzene but is quite soluble, 0.659 *M*, in 0.633 *M* hydrogen chloride in nitrobenzene. Dissociation of **2** by hydrogen chloride is therefore not an unreasonable way of explaining the change in chemical shift as it is added. The exact mechanism for the dissociation is not known. It may proceed through a transition state or intermediate, **5**, or perhaps **2** dissociates to a small degree and the equilibrium is shifted by formation of the bichloride ion. In any event the equilibrium must be rapid on the nmr time scale; otherwise one would expect to find two absorptions at *ca.* +14 and −65 ppm.

Attack by chlorine on **2** can yield triphenylchlorophosphonium trichloride (**4b**, X = Cl). Very little is known about the trichloride anion. It is quite unstable in water.[8] There is good evidence for its formation when tetraethylammonium chloride is allowed to react with chlorine[9] and some evidence for its formation when trimethylsulfonium chloride is allowed to react with chlorine.[10] In the present work it has been observed that the products of the reactions of 1 mole of triphenylphosphine and diphenylchlorophosphine with 1 mole of chlorine are much less soluble in nitrobenzene than those obtained when an excess of chlorine is added. Similarly, it was found that triphenylbenzylphosphonium chloride was quite insoluble in nitrobenzene but considerably more soluble in chloride–nitrobenzene. These findings all support the trichloride anion hypothesis.

Evidence that nitrobenzene is a relatively good solvent for cations but relatively poor for anions has been provided by Sadek and Fuoss.[11] They studied ion-pair dissociation of tetrabutylammonium bromide in nitrobenzene–methanol mixtures. They concluded that nitrobenzene was particularly effective in solvating the tetrabutylammonium ion, and methanol had a similar role in solvating the bromide ion. In the examples under study here, chlorine and hydrogen chloride can function in a manner similar to methanol.

Wiley and Stine[4] considered the possibility that the −8 ppm absorption was due to a rapidly equilibrating mixture of the triphenylchlorophosphonium cation with the triphenyltrichlorophosphate anion (**6**). On



$$(C_6H_5)_3\overset{+}{P}{-}Cl + (C_6H_5)_3\overset{-}{P}Cl_3$$

3 **6**

the other hand, Beveridge and coworkers[12] originally concluded on the basis of conductivity data that these ions are present in acetonitrile.

More recently Harris and Ali[13] have reinvestigated the conductance of the triphenylphosphine–chlorine reaction product in acetonitrile in the presence of added chloride ion. Their results are in accord with the exclusive formation of triphenylchlorophosphonium chloride.

Harris and Ali also studied the conductance of the triphenylphosphine–chlorine reaction product in nitrobenzene. They concluded that partial ionization occurs. It is not clear just how the solution was prepared, and it may be that some triphenylchlorophosphonium trichloride was present.

The results of reaction series B and C are similar to those obtained with A. As expected the chemical shifts of the species formed in the presence of 1 mole or less of chlorine become more positive as the number of phenyl groups is decreased. Pentachlorophosphorane absorbs at +80 ppm. It is also evident that the action of chlorine in promoting dissociation diminishes as the number of phenyl groups decreases. This is not unreasonable: the greater inductive effect of the chlorine atoms over that of the phenyl groups will tend to destabilize the cations. Further support for this conclusion is obtained by the observation that phenyltetrachlorophosphorane is not very highly dissociated in acetonitrile.

The difference between the results reported here and those of Wiley and Stine are undoubtedly due to the different methods of preparing the triphenylphosphine–chlorine reaction product. When the material is isolated as the solid, it may contain some trichloride anion, or bichloride may be formed by hydrolysis. A rapidly equilibrating mixture of **2** and **3** will have a ^{31}P nmr absorption between those of **2** and **3**.

When 1 mole of chlorine was added to triphenylphosphine in acetonitrile, the major absorption was found at −47 ppm rather than at −62 ppm as reported by Wiley and Stine. It was also noted that excess (2 moles) chlorine led to an absorption at −65.5 ppm.

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(7) (a) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **76**, 4049 (1954); (b) H. F. Herbrandson and R. T. Dickerson, *ibid.*, **81**, 4102 (1959).

(8) M. S. Sherril and E. F. Izard, *ibid.*, **53**, 1667 (1931).

(9) (a) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923); (b) J. C. Evans and G. Y. S. Lo, *J. Chem. Phys.*, **44**, 3638 (1966).

(10) L. Dobbin and O. Masson, *J. Chem. Soc.*, **47**, 67 (1885).

(11) H. Sadek and R. M. Fuoss, *J. Am. Chem. Soc.*, **72**, 301 (1950).

(12) A. D. Beveridge, G. S. Harris, and F. Inglis, *J. Chem. Soc.*, *A*, 520 (1966).

(13) G. S. Harris and M. F. Ali, *Tetrahedron Letters*, 37 (1968).

When the reaction product was prepared as a solid and then dissolved in acetonitrile, the major absorption was found at −54 ppm. These results indicate that 2 and 3 are in equilibrium in acetonitrile, but the equilibrium lies far toward 3 which is of course in agreement with the conductivity data.[12]

Stereochemically Nonrigid Organometallic Molecules. XVII.[1] The Crystal and Molecular Structure of Bis(cyclooctatetraene)triruthenium Tetracarbonyl[2]

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Received June 27, 1968

Abstract: The crystal and molecular structures of the fluxional molecule bis(cyclooctatetraene)triruthenium tetracarbonyl, $(C_8H_8)_2Ru_3(CO)_4$, have been determined from 1056 independent, nonzero reflections collected with a counter diffractometer. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions $a = 9.737$ Å, $b = 12.591$ Å, and $c = 15.268$ Å ($\rho_{obsd} = 2.18$ g cm^{-3}; $\rho_{calcd} = 2.21$ g cm^{-3}). The structure, excluding hydrogen atoms, was solved from Patterson and electron density maps and refined by least-squares methods to a conventional unweighted R factor of 4.07%. The molecules are dissymmetric; by taking into account anomalous dispersion by the ruthenium atoms, the correct enantiomorph has been selected for the crystal studied. Each molecule contains a triangle of Ru atoms (metal–metal distances of 2.782 (2), 2.928 (2), and 2.947 (2) Å), similar to that in $Ru_3(CO)_{12}$, and two cyclooctatetraene rings, each bound to a pair of ruthenium atoms. The structure is in accord with the mass spectral evidence for the existence of a metal atom cluster and accounts for the observed characteristic infrared spectrum in the CO stretching region. The bonding of the rings to pairs of metal atoms is extraordinary and cannot be related to any single type of olefin–metal interaction known. Instead it may be described as about halfway between two known and more-or-less symmetrical orientations for a $(C_8H_8)M_2$ system. Thus the exceptional deformability which might be expected for a fluxional molecule along the reaction coordinate of its rearrangement pathway is strikingly illustrated.

Among the various products that have been isolated and characterized from the reaction of $Ru_3(CO)_{12}$ with cyclooctatetraene(COT),[4-7] there is one which is produced exclusively when the process is carried out in refluxing octane. The crystalline substance so obtained is shown by elemental analysis and mass spectrum to be $C_{16}H_{16}Ru_3(CO)_4$, and its proton nmr spectrum at room temperature consists of one sharp peak. Consequently, the compound was expected to contain a metal atom cluster and is also a fluxional organometallic molecule, with the fluxional behavior implying retention of C_8H_8 monocycles. It was obviously of interest to elucidate the structure of $(COT)_2Ru_3(CO)_4$ in the solid state, and a single-crystal X-ray study was undertaken. The results of this study, which have previously been briefly communicated,[8] are reported here in full.

Experimental Procedure

Crystalline $C_{16}H_{16}Ru_3(CO)_4$ was prepared by the reaction of $Ru_3(CO)_{12}$ with cyclooctatetraene in refluxing octane as described previously.[6] Optical examination showed the lustrous, red, air-stable crystals to be orthorhombic prisms, and preliminary Weissenberg (0*kl* and 1*kl* levels) and precession (*h*0*l*, *h*1*l*, *hk*0, and *hk*1 levels) photographs indicated Laue symmetry *mmm*, with slight deviations from this symmetry attributable to anomalous dispersion effects and suggesting crystal point group 222. The observed systematic absences ($h00$ for $h \neq 2n$, $0k0$ for $k \neq 2n$, and $00l$ for $l \neq 2n$) indicated the unique choice of the orthorhombic space group $P2_12_12_1$. The unit cell dimensions, determined with copper radiation (λ Kα_1 1.5405 Å, λ Kα_2 1.5443 Å) by a method described elsewhere,[9] are $a = 9.737 \pm 0.005$ Å, $b = 12.591 \pm 0.007$ Å, and $c = 15.268 \pm 0.008$ Å. The observed density of 2.18 g cm^{-3}, determined by flotation, agrees with the calculated density of 2.21 g cm^{-3} for a formula weight of 623.6, $Z = 4$, and a unit cell volume of 1871.8 Å^3.

Intensity data were collected on a General Electric quarter-circle automated XRD-6 diffractometer equipped with a Datex control unit. A crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was so aligned that its a axis coincided with the φ axis of the instrument. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 5.73 and 7.05 in., respectively. Mo Kα radiation, filtered by zirconium foil, was used to measure 1165 independent reflections lying within one octant of a sphere in reciprocal space corresponding to d spacings $\geqslant 1$ Å. The intensities were measured with a scintillation counter with the pulse height discriminator set to receive 95% of the Mo Kα radiation with the window centered on the Mo Kα peak. The data were collected using a coupled $\omega/2\theta$ scan technique at a 2θ scan rate of 2°/min. The peak counts, P, were obtained from a 2θ scan of 1.33°

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[1] Part XVI: F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 5418 (1968).

[2] This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society and by the National Science Foundation under Grant No. GP-7034X.

[3] J. F. Norris Predoctoral Fellow, 1967–1968.

[4] M. I. Bruce, M. Cooke, M. Green, and F. G. A. Stone, *Chem. Commun.*, 523 (1967).

[5] W. K. Bratton, F. A. Cotton, A. Davison, J. W. Faller, and A. Musco, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

[6] F. A. Cotton, A. Davison, and A. Musco, *J. Am. Chem. Soc.*, **89**, 6796 (1967).

[7] F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968).

[8] M. J. Bennett, F. A. Cotton, and P. Legzdins, *ibid.*, **89**, 6797 (1967).

[9] M. J. Bennett, F. A. Cotton, and J. Takats, *ibid.*, **90**, 903 (1968).