isomers of this compound in which the phenyl groups are *cis* or *trans* relative to each other. The relatively sharp melting point and the single methyl doublet observed in the $^1H$ nmr spectrum indicate this material is probably not a mixture of isomers.

The doublet assigned to the methyl protons observed in the $^1H$ nmr spectrum of $(C_6H_5)P[(CH_3)NN(CH_3)]_2P(C_6H_5)$ is in contrast to the distorted triplets assigned to the methyl groups of $P[(CH_3)NN(CH_3)]_3P$[5] and $(C_6H_5)_2P[(CH_3)NN(CH_3)]P(C_6H_5)_2$. The observed "triplets" may be explained by virtual coupling if the phosphorus nuclei are strongly coupled. Molecular models of $P[(CH_3)NN(CH_3)]_3P$ and $(C_6H_5)_2P[(CH_3)NN(CH_3)]P(C_6H_5)_2$ indicate the $^{31}P$ nuclei are or could be in close proximity. Therefore, strong phosphorus–phosphorus coupling could occur through a mechanism not involving the bonding system as well as through the bonds. The fact that only a doublet is observed for the methyl protons of $(C_6H_5)P[(CH_3)NN(CH_3)]_2P(C_6H_5)$ can be explained by the fact that the bond angles may not be such as to allow coupling of the protons with both $^{31}P$ nuclei. The effect that bond angles may have on the phenomenon of virtual coupling has been observed in the $^1H$ nmr spectra of some transition metal complexes having phosphine ligands. Virtual coupling was observed in *trans*-square-planar, octahedral, and trigonal-bipyramidal complexes, but not in *cis* isomers of these complexes.[6,7] Alternatively, direct coupling could explain the observed triplets if the coupling constants of the two $^{31}P$ nuclei are nearly the same relative to the given methyl group. In this case, an overlap of peaks would result in the formation of a triplet.

When the hydrazinophosphorus compounds were allowed to react with triethylaluminum in 1:1, 2:1, and 3:1 mole ratios, only adducts having a 2:1 mole ratio of $Al(C_2H_5)_3$ to the hydrazinophosphorus compound were isolated. The stoichiometry of these adducts and the fact that these adducts exhibit single peaks for methyl groups on the nitrogen atoms in the $^1H$ nmr spectrum and single peaks for phosphorus in the $^{31}P$ nmr spectrum suggest that aluminum is bonded to phosphorus and is tetracoordinate. It should be noted that in the case of benzene solutions of $(C_6H_5)_2P[(CH_3)NN(CH_3)]P(C_6H_5)_2$ and $(C_6H_5)_2P[(CH_3)NN(CH_3)]P(C_6H_5)_2 \cdot [Al(C_2H_5)_3]_2$ single peaks at $-62.5$ and $-61.2$ ppm are observed in the $^{31}P$ nmr spectrum. The fact that these peaks have nearly the same shift suggests that there is a large degree of dissociation of this adduct in benzene solution. Also, the fact that the peaks observed in the $^1H$ nmr spectra were nearly independent of the concentration of triethylaluminum supports this supposition. In this case, therefore, the nmr data probably do not indicate the bonding of the solid adduct.

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## The Reactions of Some Tri-*n*-alkylphosphines with Some Chlorophosphines

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Relatively little attention has been paid until very recently to the reaction of trialkylphosphines with chlorophosphines. Recent work in this laboratory[1,2] and in others[3–6] has indicated that reactions of tertiary alkylphosphines with halophosphines or haloarsines result in either (1) adduct formation or (2) halogen abstraction with the concurrent formation of P–P or As–As bonds and dihalophosphoranes. The objective of the present study was systematically to investigate a number of reactions of the above type in order to determine which reaction, if either, is the generation reaction, to investigate the possibility of extending the synthetic method of chlorine abstraction by tertiary phosphines to new systems, and to investigate the possible relationship of the chlorine-abstraction behavior of tertiary phosphines to adduct or phosphonium halide formation.

### Experimental Section

**Reagents.**—Triethylphosphine and diethylchlorophosphine were obtained from K & K Laboratories. Methyldichlorophosphine was obtained from the FMC Co. and was distilled at 79–83°. Tri-*n*-butylphosphine was obtained from the Carlisle Chemical Works, Inc., and the fraction boiling at 40° (0.05 mm) was retained for use. Tri-*n*-octylphosphine was obtained from the Matheson Coleman and Bell Co. Bis(dimethylamino)-chlorophosphine was prepared by the method of Evleth, *et al.*[7] Tri-*n*-propylphosphine was prepared in a manner similar to that reported by Davies, *et al.*[8,9] Dimethylchlorophosphine was prepared by the method of Parshall.[10]

**Procedures.**—A Vacuum Atmospheres Model HE-43 inert-atmosphere box equipped with a Model HE-93B Dri-Train was used for manipulation and storage of all reagents. All solvents were dried and stored over calcium hydride except acetonitrile. Acetonitrile was distilled from phosphorus(V) oxide. Infrared spectra were obtained using a Beckman IR-10 spectrophotom-

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TABLE I

REACTIONS OF EXCESS TRIALKYLPHOSPHINES WITH PHOSPHORUS TRICHLORIDE IN BENZENE

| | | | Analysis, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | | P | | H | | Cl | |
| Trialkylphosphine | Product | Mp, °C | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found |
| $P(C_2H_5)_3$ | $P(C_2H_5)_3Cl_2$ | 242–247 | 38.12 | 37.92 | 16.38 | 16.13 | 8.00 | 8.25 | 37.50 | 38.17 |
| $P(n\text{-}C_3H_7)_3$ | $P(C_3H_7)_3Cl_2$ | 141–148 | 46.77 | 46.66 | 13.40 | 13.63 | 9.15 | 9.09 | 30.68 | 30.61 |
| $P(n\text{-}C_8H_{17})_3$ | $P(C_8H_{17})_3Cl_2$ | 88–90 | 65.29 | 63.36 | 7.01 | 6.69 | 11.64 | 11.37 | 16.06 | 15.62 |

eter. The infrared spectra of solids were obtained as Nujol and Kel-F mulls of the solid supported between KBr plates. The infrared spectra of liquids were obtained without solvent using KBr cells having Teflon spacers. The proton magnetic resonance spectra were obtained using a Varian Model A-60A nmr spectrometer equipped with a variable-temperature probe and using tetramethylsilane as an internal reference. The phosphorus nuclear magnetic resonance spectra were obtained using a Varian Model V-4300-2 instrument equipped with a field-homogeneity control, magnetic insulation, and field stabilizer and using 85% phosphoric acid as an external reference. The mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer run at an ionizing voltage of 70 eV. Melting points were determined using a Thomas-Hoover melting point apparatus in sealed tubes and are uncorrected. The elemental analyses were done by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Schwarzkopf Analytical Laboratories, Woodside, N. Y.

**Reactions of Trialkylphosphines with Phosphorus Trichloride in Benzene.**—Trialkylphosphines in small excess were mixed with phosphorus trichloride in benzene solution. An orange-red amorphous solid which appeared to be elemental phosphorus and was inflamed by concentrated nitric acid precipitated in each case. White, crystalline trialkyldichlorophosphorane was obtained by evaporation of the benzene filtrate. Data concerning these phosphoranes are listed in Table I. The nmr spectra, both $^1H$ and $^{31}P$, were in accordance with the formulation of the white products as dihalophosphoranes.

**The Reactions of Triethylphosphine, Tri-*n*-propylphosphine, and Tri-*n*-octylphosphine with Phenyldichlorophosphine.**—In each case the stoichiometric amount of the tertiary phosphine was added to the phenyldichlorophosphine. An exothermic reaction followed within a few seconds, resulting in the formation of a solid mixture. The solid was washed with cold (−5°) acetonitrile, and the insoluble material was shown to be tetraphenylcyclotetraphosphine by observation of melting point,[11] infrared spectrum,[12] and $^{31}P$ nmr spectrum.[13] The yields of tetraphenylcyclotetraphosphine were above 80% in all cases.

Evaporation of the acetonitrile filtrate resulted in each case in the isolation of a white solid. The solids were shown to be the corresponding dichlorophosphoranes $R_3PCl_2$ ($R = C_2H_5$, $C_3H_7$, $C_8H_{17}$) by comparison of melting point, infrared, $^1H$ nmr, and $^{31}P$ nmr data with the corresponding data for independently prepared samples of $(C_2H_5)_3PCl_2$, $(C_3H_7)_3PCl_2$, and $(C_8H_{17})_3PCl_2$, respectively.

**The Reactions of Tri-*n*-propylphosphine and Tri-*n*-octylphosphine with Diphenylchlorophosphine.**—The stoichiometric amount of the tertiary phosphine was added to the diphenylchlorophosphine. A viscous oil that slowly crystallized over a period of 12 hr formed in each case. The solids were washed with cold (−5°) acetonitrile and filtered. The insoluble materials were recrystallized from acetonitrile and shown in each case to be tetraphenyldiphosphine by comparison of melting points,[14] infrared specta,[14] and $^{31}P$ nmr spectra.[14]

The acetonitrile filtrates were evaporated leaving white solid residues which in each case were shown to be the corresponding trialkyldichlorophosphoranes by comparison of melting points, infrared, $^1H$ nmr, and $^{31}P$ nmr data with the corresponding data of known samples.

**The Reactions of Triethylphosphine, Tri-*n*-propylphosphine, and Tri-*n*-butylphosphine with Methyldichlorophosphine.**—In each reaction the stoichiometric amount of tertiary phosphine was added to methyldichlorophosphine. The reaction of triethylphosphine with methyldichlorophosphine was exothermic and resulted in the formation of a solid–liquid mixture within a period of 2–3 min. The reaction of tri-*n*-propylphosphine required warming to 100° for 10 min to complete the reaction. The reaction of tri-*n*-butylphosphine with methyldichlorophosphine required a temperature of 150° over a period of 10 min for completion. The $^{31}P$ nmr spectrum of this reaction mixture contains two principal peaks at +14.7 and −16.5 ppm before heating, as well as three smaller peaks at −1.7, −33.7, and +77.9 ppm. In each case the reaction mixture was washed with cold (−5°) hexane. The solid residue in each case was shown so be the corresponding trialkyldichlorophosphorane.

When, in each case, the hexane was removed from the liquid under vacuum, a liquid residue remained. These liquids obtained, in each case, were shown to be pentamethylcyclopentaphosphine by comparison of $^1H$ nmr spectra,[15] boiling points,[16] $^{31}P$ nmr spectra,[17] and mass spectral data[18] with corresponding data in the literature. The yields of pentamethylcyclopentaphosphine were above 80% except for the reaction of tri-*n*-butylphosphine with methyldichlorophosphine, in which case complete separation of $(C_4H_9)_3PCl_2$ and pentamethylcyclopentaphosphine was not achieved and the yield was, therefore, not determined.

It should be noted that the reaction of tri-*n*-octylphosphine with methyldichlorophosphine resulted in formation of unidentified oil.

**The Reaction of Triethylphosphine with Dimethylchlorophosphine.**—Triethylphosphine was added to dimethylchlorophosphine resulting in a vigorous exothermic reaction and formation of a white solid. This solid, after recrystallization from hexane, melted at 87–90°. The $^1H$ nmr spectrum obtained using $CDCl_3$ as a solvent consists of a broad peak at $\tau$ 7.37 (average) and a multiplet at $\tau$ 8.60 (average). These peaks are in the ratio of 1.00:1.75. The peaks observed in the $^{31}P$ nmr spectrum are listed in Table II. *Anal.* Calcd for $[(C_2H_5)_3PP(CH_3)_2]Cl$: C, 44.76; H, 9.86; P, 28.86; Cl, 16.52. Found: C, 39.85; H, 9.99; P, 29.35; Cl, 16.66. Though the C analysis is low, the other analyses agree with the above formula. Carbon analyses in phosphorus-containing compounds are commonly low.

**The Reaction of Tri-*n*-propylphosphine with Dimethylchlorophosphine.**—Tri-*n*-propylphosphine (0.83 g, 5.2 mmol) in 5 ml of diethyl ether was added to dimethylchlorophosphine (0.50 g, 5.2 mmol) in 5 ml of diethyl ether resulting in the formation of a liquid, two-phase mixture. The ether layer was discarded and the remaining ether was removed under vacuum. The $^1H$ nmr spectrum of the residue consisted of a very broad peak at $\tau$ 7.48 (average), a broad singlet at $\tau$ 8.31, and a multiplet at $\tau$ 8.82.

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The approximate area ratios of these overlapping peaks are 1.00:2.00:1.95. Table II lists the observed $^{31}$P shifts. *Anal.* Calcd for $[(C_3H_7)_3PP(CH_3)_2]Cl$: C, 51.46; H, 10.60; P, 24.13; Cl, 13.81. Found: C, 51.16; H, 10.53; P, 24.23; Cl, 13.99. The yield was 1.01 g (78% of theory).

**The Reaction of Tri-*n*-butylphosphine with Dimethylchlorophosphine.**—Using the same procedure as described in the reaction of tri-*n*-propylphosphine with dimethylchlorophosphine, ether solutions of tri-*n*-butylphosphine and dimethylchlorophosphine were allowed to react. The $^1$H nmr spectrum of the product contained a broad peak at $\tau$ 7.45 and broad multiplets at $\tau$ 8.31 and 9.01. Table II lists the $^{31}$P nmr data. *Anal.* Calcd for $[(C_4H_9)_3PP(CH_3)_2]Cl$: C, 56.27; H, 11.14; P, 20.73; Cl, 11.86. Found: C, 55.99; H, 11.11; P, 21.03; Cl, 11.83. The yield was 80% of theory.

**The Reaction of Tri-*n*-octylphosphine with Dimethylchlorophosphine.**—The reaction of tri-*n*-octylphosphine with dimethylchlorophosphine resulted in formation of a viscous oil. This oil was soluble in diethyl ether, hexane, benzene, chloroform, and acetonitrile. The $^1$H nmr spectrum consists of a complex series of overlapping peaks from $\tau$ 8.40 to 9.21. The $^{31}$P nmr data are listed in Table II.

**The Reaction of Triethylphosphine with Phosphorus Trichloride in Diethyl Ether.**—Triethylphosphine (0.50 g, 4.2 mmol) in 5 ml of diethyl ether and phosphorus trichloride (0.29 g, 2.1 mmol) in 5 ml of diethyl ether were added simultaneously and slowly to 20 ml of diethyl ether at −20°. A white precipitate immediately formed and was isolated by filtration. This solid was kept at −20°, since at room temperature it became yellow-orange and tacky. This solid did not melt up to 330°, but changed to a brown color. The $^1$H nmr spectrum obtained using $CDCl_3$ as a solvent at −20° contained broad overlapping peaks in the region from $\tau$ 6.42 to 9.06. At room temperature, peaks attributable to $(C_2H_5)_3PCl_2$ at $\tau$ 6.64 and 8.56 were observed. *Anal.* Calcd for $[(C_2H_5)_3P]_2Cl_3$: C, 38.57; H, 8.09; P, 24.87; Cl, 28.47. Found: C, 38.40; H, 8.29; P, 24.70; Cl, 28.42. The yield of this solid was 0.36 g (57% of theory). The product described above was also obtained if the reactants were combined in a 1:1 mole ratio.

Phosphorus trichloride (0.29 g, 2.1 mmol) in 5 ml of diethyl ether was slowly added to a solution of triethylphosphine (0.75 g, 6.3 mmol) in 20 ml of diethyl ether at room temperature. The white precipitate that resulted was filtered and dried under vacuum. It was stable at room temperature and melted at 138–141°. The $^1$H nmr spectrum consists of a group of peaks at $\tau$ 6.62 (average), a broad peak at $\tau$ 7.61 (average), and a series of peaks at $\tau$ 8.63 (average). *Anal.* Calcd for $[(C_2H_5)_3P]_3PCl_3$: C, 43.96; H, 9.22; P, 25.19; Cl, 21.63; Found: C, 43.73; H, 9.52; P, 24.90; Cl, 21.55. The yield was 0.86 g (83% of theory).

**The Thermal Reaction of $[(C_2H_5)_3P]_3PCl_3$ with $PCl_3$.**—Phosphorus trichloride (0.08 g, 0.6 mmol) was added to $[(C_2H_5)_3P]_3PCl_3$ (0.29 g, 0.59 mmol) in 10 ml of toluene. The resulting solution was warmed to the boiling point for 1.5 hr resulting in the formation of a red-orange precipitate. This solid was filtered, washed with boiling acetonitrile, filtered again, and dried under vacuum. The red-orange solid did not melt up to 330°; it reacted violently with concentrated nitric acid. *Anal.* Found: P, 92.40; C, 4.32; H, 1.27; Cl, 1.49. The yield was 75% of theory based on the equation $[(C_2H_5)_3P]_3PCl_3 + PCl_3 \rightarrow 3(C_2H_5)_3PCl_2 + 2P$. Toluene and acetonitrile filtrates were combined and evaporated to dryness leaving a white solid residue. This solid melted at 240–246° after drying under vacuum (lit.[19] mp for $(C_2H_5)_3PCl_2$, 240–250°). The infrared and $^1$H nmr spectra were identical with the corresponding spectra of $(C_2H_5)_3PCl_2$. The yield of $(C_2H_5)_3PCl_2$ was 0.31 g (91% of theory).

**The Reaction of Triethylphosphine with Phenyldichlorophosphine in Diethyl Ether.**—Triethylphosphine (0.25 g, 2.1 mmol) in 5 ml of diethyl ether cooled to −20° was added to phenyldichlorophosphine (0.38 g, 2.1 mmol) in 10 ml of diethyl ether also maintained at −20°. A white solid immediately formed. The mixture was then evaporated to dryness. The resulting dry, white crystals were dissolved in cold (−20°) $CDCl_3$. The $^1$H nmr spectrum of this solution consisted of two overlapping peaks at $\tau$ 2.06 (average) assigned to phenyl protons as well as a broad peak at $\tau$ 7.38 and a broad peak at $\tau$ 8.73 assigned to ethyl protons. These peaks are in the approximate ratio of 1.0:1.5. The $CDCl_3$ solution was allowed to warm to +25° and the $^1$H nmr spectrum was obtained immediately. This spectrum exhibits the growth of peaks attributable to a mixture of $(C_6H_5P)_4$ and $(C_2H_5)_3PCl_2$. *Anal.* Calcd for $[(C_6H_5)(Cl)PP(C_2H_5)_3]Cl$: Cl, 23.86. Found: Cl, 24.28.

**The Thermal Decomposition of $[(C_6H_5)(Cl)PP(C_2H_5)_3]Cl$.**—The crystalline solid $(C_6H_5)(Cl)PP(C_2H_5)_3Cl$ (0.45 g, 1.5 mmol) was added to 20 ml of hexane and the resulting mixture was maintained at the boiling point for 1.5 hr. The mixture was evaporated to dryness, washed with 10 ml of cold (−5°) acetonitrile, and filtered. The solid material was dried under vacuum; mp 150–156° (lit.[11] mp for $(C_6H_5P)_4$, 154.5–156°). The infrared spectrum of the solid is identical with that published for $(C_6H_5P)_4$.[12] The acetonitrile filtrate was evaporated to dryness, leaving a white solid residue. This solid was shown to be $(C_2H_5)_3PCl_2$ by comparison of melting point, infrared spectrum, and $^1$H nmr spectrum with the corresponding data for a known sample of $(C_2H_5)_3PCl_2$.

**The Reaction of Triethylphosphine with Methyldichlorophosphine in Diethyl Ether.**—Methyldichlorophosphine (0.50 g, 2.3 mmol) in 3 ml of diethyl ether was added to triethylphosphine (0.51 g, 2.3 mmol) in 5 ml of diethyl ether at 0°. The resulting white precipitate was filtered and dried under vacuum; mp 76–78°. The $^1$H nmr spectrum consisted of broad peaks at $\tau$ 7.56 and 8.62 (average). *Anal.* Calcd for $[(CH_3)(Cl)PP(C_2H_5)_3Cl$: C, 35.77; H, 7.72; P, 26.35; Cl, 30.16. Found: C, 35.54; H, 7.98; P, 26.06; Cl, 29.85. The yield of this solid was 0.82 g (81% of theory).

**The Thermal Decomposition of $[(CH_3)(Cl)PP(C_2H_5)_3]Cl$.**—The crystalline solid $[(C_2H_5)_3PP(Cl)(CH_3)]Cl$ (1.07 g, 4.55 mmol) was added to 20 ml of hexane and maintained at the boiling point of hexane for 1 hr. After cooling to −5°, the mixture was filtered and the solid was recrystallized from toluene; mp 239–248° (lit.[19] mp for $(C_2H_5)_3PCl_2$, 240–250°). The infrared and $^1$H nmr spectra of this solid were identical with the corresponding spectra of $(C_2H_5)_3PCl_2$. The hexane was evaporated from the above filtrate yielding a solid–liquid residue. The liquid was isolated by extraction with cold hexane. The infrared and $^1$H nmr spectra of the liquid are identical with the corresponding spectra of $(CH_3P)_5$.

## Discussion

These experiments have demonstrated that at room temperature in the absence of solvent or, in some instances, in benzene solution, tri-*n*-alkylphosphines generally abstract chlorine exothermally from phosphorus trichloride, phenyldichlorophosphine, and diphenylchlorophosphine to yield the corresponding tri-*n*-alkyldichlorophosphorane and a phosphorus polymer, tetraphenylcyclotetraphosphine or tetraphenyldiphosphine, respectively. On the other hand, reactions of tri-*n*-alkylphosphines with dimethylchlorophosphine were shown to yield only adducts of the general formula $[R_3PP(CH_3)_2]Cl$ under these conditions.

The reaction of methyldichlorophosphine with triethylphosphine is exothermic and immediately results in the formation of triethyldichlorophosphorane and pentamethylcyclopentaphosphine. The reactions of

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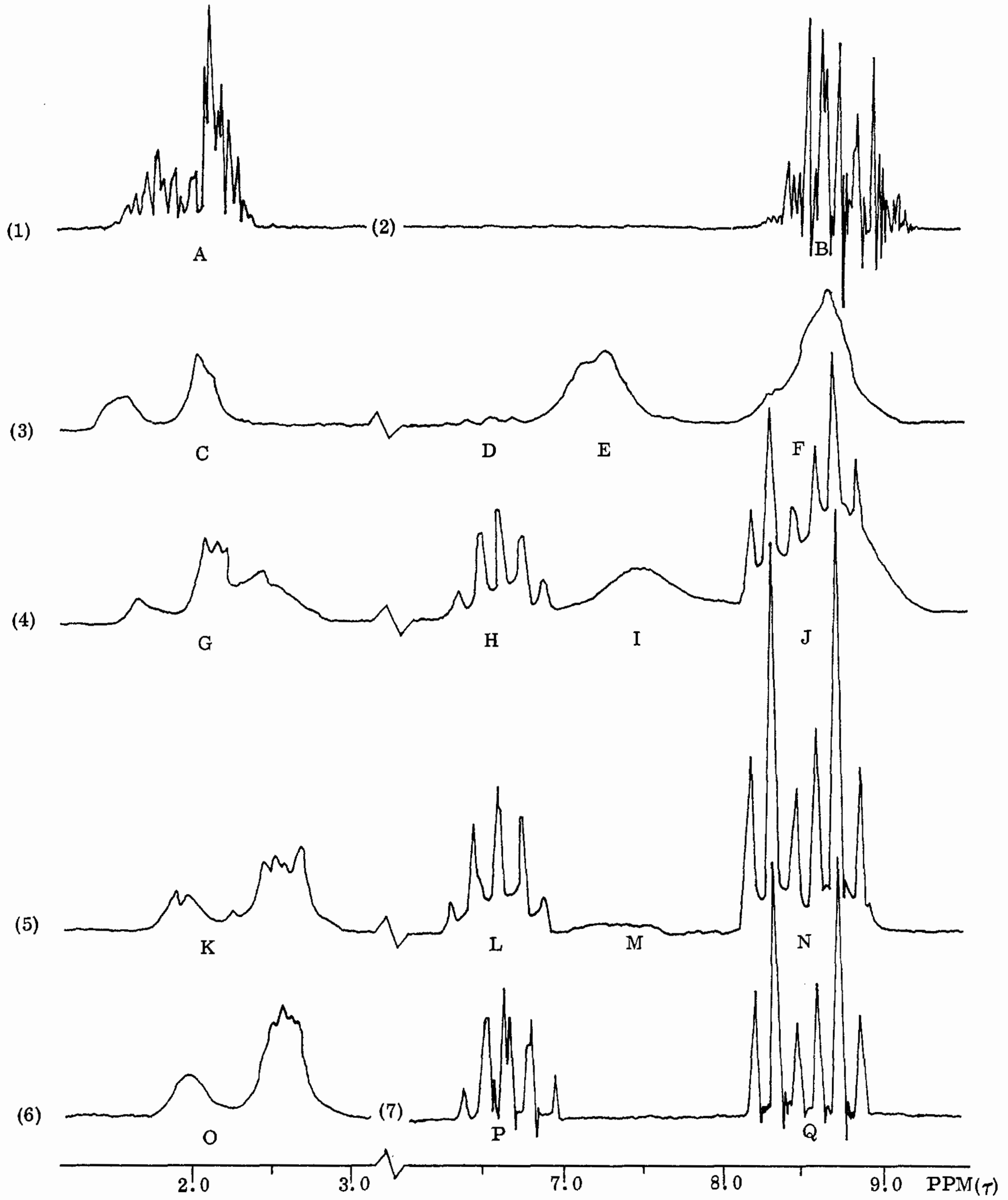
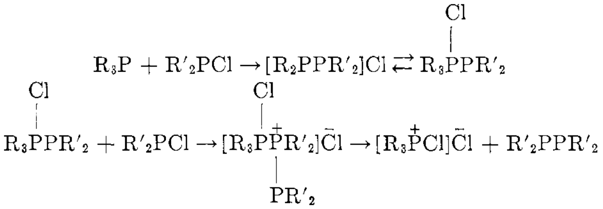


Figure 1.—The $^1$H nmr spectra of (1) phenyldichlorophosphine, (2) triethylphosphine, (3) $(C_2H_5)_3PP(C_6H_5)(Cl)$ at −20°, (4) the same solution as (3) at +25°, (5) the same solution as (3) and (4) after 12 hr at +25°, (6) tetraphenylcyclotetraphosphine, and (7) triethyldichlorophosphorane. In all cases the solvent was $CDCl_3$, and $Si(CH_3)_4$ was used as an internal reference.

tri-*n*-propylphosphine and tri-*n*-butylphosphine with methyldichlorophosphine yield liquid products. The two principal peaks in the $^{31}$P nmr spectrum of the reaction mixture of tri-*n*-butylphosphine and methyldichlorophosphine do not correspond to starting materials nor to the expected pentamethylcyclopentaphosphine and they are consistent with the values found for other phosphine adducts discussed below. If these reaction mixtures are heated, however, pentamethylcyclopentaphosphine and the corresponding tri-*n*-alkyldichlorophosphorane are formed. At lower temperatures in ethereal solution, some of the reactions which had resulted in chlorine abstraction gave adducts which subsequently decomposed at higher temperatures to give the expected chlorine-abstraction products.

The course of the decomposition of one of these adducts is shown by the $^1$H nmr spectra illustrated in Figure 1. Peaks A and B in Figure 1(1) and 1(2) illustrate the $^1$H nmr spectra of phenyldichlorophosphine and triethylphosphine, respectively. Peaks C, D, E, and F (Figure 1(3)) are those obtained for a

$CDCl_3$ solution of $[(C_2H_5)_3PP(C_6H_5)Cl]Cl$ at −20°. Peak C is assigned to phenyl protons; peaks E and F are attributable to the methylene and methyl protons, respectively, of the ethyl group. The broadness of peaks E and F is typical of the peaks observed in the $^1H$ nmr spectra of all adducts isolated in this study. The small peak, D, indicates a small concentration of triethyldichlorophosphorane at this temperature. The $^1H$ nmr spectrum observed for the above solution 15 min after it was allowed to warm to room temperature is represented by peaks G, H, I, and J in Figure 1(4). Changes of shape are noted for each of the peaks compared with the corresponding peaks above. The overlapping quartets and the two sets of triplets attributable to the methylene and methyl protons, respectively, of triethyldichlorophosphorane can be clearly seen in peaks H and J, respectively. These changes are more pronounced in the $^1H$ nmr spectrum obtained for the above solution after allowing it to stand at room temperature for 12 hr (Figure 1(5)). Peak M, corresponding to peaks E and I above, has nearly disappeared. Peak K, attributable to phenyl protons, may be compared with the $^1H$ nmr spectrum of tetraphenylcyclotetraphosphine, Figure 1(6), peak O, below. Peaks L and N may be compared with the $^1H$ nmr spectrum of an authentic sample of triethyldichlorophosphorane, peaks P and Q, Figure 1(7). Thus it appears that adduct formation is an intermediate step in the chlorine-abstraction process. A possible mechanism for the chlorine-abstraction reaction is represented by



$$R_3P + R'_2PCl \rightarrow [R_2PPR'_2]Cl \rightleftarrows R_3\overset{Cl}{\overset{|}{P}}PR'_2$$

$$R_3\overset{Cl}{\overset{|}{P}}PR'_2 + R'_2PCl \rightarrow [R_3\overset{Cl}{\overset{|}{P}}\underset{PR'_2}{\underset{|}{\overset{+}{P}}}R'_2]\bar{Cl} \rightarrow [R_3\overset{+}{P}Cl]\bar{Cl} + R'_2PPR'_2$$

where R = $n$-alkyl and R′ = $C_6H_5$.

The peaks observed in the $^{31}P$ nmr spectra of the new adducts are listed in Table II. The upfield signal is in the range from +14.7 to +51.0 ppm. The downfield signal is in the range from −14.5 to −33.7 ppm. The $^{31}P$ nmr spectrum of $[(C_4H_9)_3PAs(CH_3)_2]Cl$ exhibits a single peak at −16.2 ppm relative to 85% phosphoric acid.[20] The $^{31}P$ nmr shifts of a number of aminophosphonium salts are in the range from −29.4 to −54.0 ppm relative to 85% phosphoric acid.[21] These facts suggest that the downfield signals obtained for the adducts reported in this study are attributable to phosphonium phosphorus nuclei. If this is true, these adducts would be phosphinophosphonium chlorides and the upfield signals would be attributable to phosphino phosphorus nuclei.

The orange-red products isolated in the reactions of tri-$n$-alkylphosphines with phosphorus trichloride varied in their percentage of phosphorus from 88.79 to 92.42. The other elements present were carbon, hydrogen, and chlorine. These analytical results suggest that the orange-red materials were phosphorus networks having chlorine or organic end groups.

Table II

| Compound | $^{31}P$ shifts relative to 85% phosphoric acid, ppm | Area ratio |
|---|---|---|
| $[(C_2H_5)_3PP(CH_3)_2]Cl$ | +42.2, −33.7 | 1:1 |
| $[(C_3H_7)_3PP(CH_3)_2]Cl$ | +47.9, −22.5 | 1:1 |
| $[(C_4H_9)_3PP(CH_3)_2]Cl$ | +51.0, −21.2 | 1:1 |
| $[(C_8H_{17})_3PP(CH_3)_2]Cl$ | +25.9, −14.5 | 1:1 |
| $[(C_4H_9)_3PP(CH_3)(Cl)]Cl$ | +14.7, −16.5 | 1:1 |

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## The Preparation and Properties of Strontium Iridium Hydride[1]

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As part of a general study of ternary hydrides, we have examined the systems involving alkaline earth metals and the platinum metals. The systems Sr–Ir–H, Ca–Ir–H, Ca–Rh–H, Sr–Rh–H, Ca–Ru–H, and Sr–Ru–H all gave new ternary phases which appear to be related. This note describes the compound formed in the strontium–iridium–hydrogen system which has been studied most intensively. The compound is formed by heating a mixture of strontium hydride and iridium in a hydrogen atmosphere. No absorption of hydrogen was observed.

Ternary hydrides have been formed with alkali metals in combination with transition metals. The first to be reported were $Li_4RhH_4$ and $Li_4RhH_5$.[2] Graefe has described hydrides of lithium with rhodium, iridium, palladium, and platinum.[3] Magee and others have described lithium rhodium compounds in detail and have extended the lithium systems to include

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