

AN ABSTRACT OF THE THESIS OF

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Title: REACTIONS OF TRIETHYLPHOSPHINE AND RELATED
PHOSPHONIUM CHLORIDES WITH COPPER(I) AND
COPPER(II) CHLORIDE

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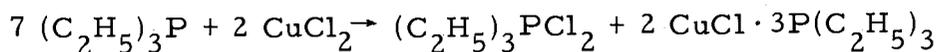
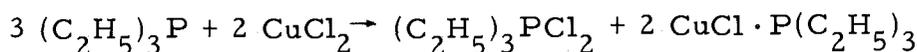
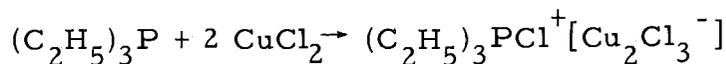
John T. Yoke III

Copper(II) chloride is reduced by triethylphosphine even at -45° , precluding the isolation of a copper(II) chloride-triethylphosphine coordination compound. Various products result, according to the stoichiometric combining ratios 0.5, 1.5, and 3.5 moles of triethylphosphine per mole of copper(II) chloride reduced. These products are identified by comparison with reaction products in copper(I) chloride-triethylphosphine-triethylchlorophosphonium chloride systems. Phase studies, vibrational spectra, and proton and phosphorus nmr spectra are used in the comparison.

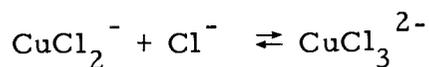
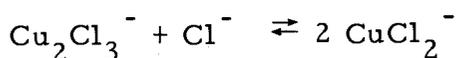
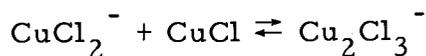
Copper(I) chloride forms two coordination complexes with triethylphosphine, $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ and $\text{CuCl} \cdot 3\text{P}(\text{C}_2\text{H}_5)_3$, which are in equilibrium at 58° at a triethylphosphine pressure of ca. 2 mm.

Copper(I) chloride reacts with one or two molar equivalents of

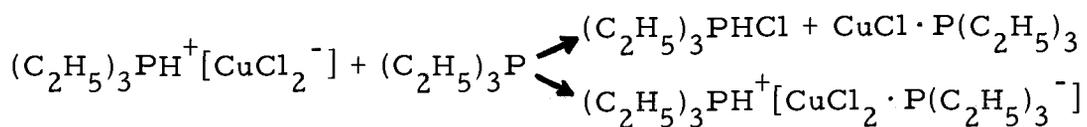
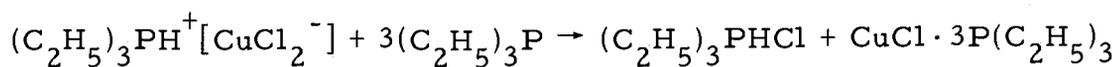
triethylchlorophosphonium chloride at room temperature in the absence of a solvent to give oils of composition $(C_2H_5)_3PCl^+[CuCl_2^-]$ and $(C_2H_5)_3PCl^+[Cu_2Cl_3^-]$. The latter reacts with triethylphosphine to give triethylchlorophosphonium chloride and the complexes $CuCl \cdot P(C_2H_5)_3$ or $CuCl \cdot 3P(C_2H_5)_3$. The characterization of these copper(I) complexes permits the following equations to be written for the copper(II) chloride-triethylphosphine oxidation-reduction reaction:



The compounds $(C_2H_5)_3PCl^+[Cu_2Cl_3^-]$ and $(C_2H_5)_3PCl^+[CuCl_2^-]$ are examples of the remarkable chlorocuprate(I) salts which are liquids at room temperature. Other examples, trialkylammonium chlorocuprates(I), have been prepared by other workers. Still more examples, $[(C_2H_5)_3PH^+]_2[CuCl_3^{2-}]$, $(C_2H_5)_3PH^+[CuCl_2^-]$, and $(C_2H_5)_3PH^+[Cu_2Cl_3^-]$ have been obtained in the present work. Evidence of anion equilibria



has been obtained by study of low-frequency infrared and laser Raman spectra of the liquid salts. The liquid state is stabilized by the melting point depression of mixed species. The chlorocuprate(I) salts react with nucleophiles either by addition to the coordination sphere of copper(I) or by displacement of chloride ion. Although triethylamine and triethylammonium dichlorocuprate(I) react by the displacement pathway, triethylphosphine and triethylphosphonium chloride react by both pathways, according to the equations



Reactions of Triethylphosphine and Related Phosponium
Chlorides with Copper(I) and Copper(II) Chloride

by

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REACTIONS OF TRIETHYLPHOSPHINE AND RELATED PHOSPHONIUM CHLORIDES WITH COPPER(I) AND COPPER(II) CHLORIDE

I. INTRODUCTION

The general area of this research falls within that branch of coordination chemistry commonly referred to as "the reactions of coordinated ligands." One purpose of research in this field is to determine what effect coordination to a metal center has on the reactivity of a Lewis base. The present work is part of a larger program involving studies of the oxidation of ligands possessing Group V donor atoms (nitrogen and phosphorus) by oxygen and by the metals to which they coordinate.

It has long been known that tertiary organic phosphines are oxidized by copper(II) salts such as copper(II) chloride. The reduced copper(I) species thus formed have usually been isolated as their tertiary phosphine complexes, since an excess of the phosphine reducing agent has generally been used. Surprisingly, no study has been made of the nature of the reaction, nor have the oxidation products been characterized.

The main purpose of this work was to study the oxidation-reduction reaction between triethylphosphine and copper(II) chloride, and in particular to characterize in detail all the reaction products. A variety of complexes of the copper(I) produced may be anticipated,

involving coordination with chloride ion, the initial phosphine reagent, or with various possible phosphine oxidation products. Therefore, this research also involves a detailed investigation of the coordination chemistry of copper(I) chloride with triethylphosphine and some of its derivatives.

The results of this study may be compared to related work on the oxidation of triethylamine by copper(II) chloride, and on the autoxidation of triethylphosphine in its cobalt(II) chloride complex.

II. HISTORICAL

A. Copper(I) Halide Complexes of Phosphines

Examples of such complexes have long been known (1). The compounds may be prepared by direct interaction of the components. Thus Holtje and Schlegel (2) observed $\text{CuX} \cdot 2\text{PH}_3$ and $\text{CuX} \cdot \text{PH}_3$ (X=Cl, Br, I) in a solid-vapor equilibrium system. More commonly, an organic solvent has been used, and $\text{CuI} \cdot 2\text{PH}_3$ and $\text{CuX} \cdot \text{PH}_3$ have been isolated from solution (3,4). The only example of a copper(I) halide complex involving a primary aliphatic phosphine is $\text{CuBr} \cdot \text{C}_6\text{H}_{11}\text{PH}_2$, reported by Issleib and Roloff (5), while no such definite complex of a secondary aliphatic phosphine is known (6).

The tertiary phosphine systems have been much more thoroughly investigated. In 1906, Arbuzov (7) reported the preparation of $\text{CuX} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ (X=Cl, Br, I) and $\text{CuI} \cdot 2\text{P}(\text{C}_2\text{H}_5)_3$ from the components. Only the latter was analyzed. Many other copper(I) halide-tertiary phosphine complexes of similar types have been described (1). Recently, Schmidbauer and co-workers (8) have prepared the trimethylphosphine complexes $\text{CuCl} \cdot n\text{P}(\text{CH}_3)_3$ (n=1-4).

Arbuzov's complex $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ is of particular relevance to the present research. He reported that the colorless crystals melt in an open capillary tube at 103-104°, although the substance turns black. More recently (9), the melting point has been reported as 116° with

decomposition. Arbuzov reported that the compound is soluble in chloroform, ethyl bromide, and carbon tetrachloride, slightly soluble in petroleum ether, and very slightly soluble in ether.

The most common coordination numbers of copper(I) are two (linear) and four (tetrahedral) (10). It is usually assumed that copper(I) achieves four-coordination in the complexes $\text{CuX} \cdot \text{PR}_3$ by the formation of tetramers. It was shown that $\text{CuI} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ was isomorphous with $\text{CuI} \cdot \text{As}(\text{C}_2\text{H}_5)_3$, which was found to be tetrameric by a complete X-ray structure determination (11). Similarly, $\text{CuI} \cdot \text{P}(\text{n-C}_4\text{H}_9)_3$ was shown to be tetrameric by diffraction methods (12). Cryoscopic molecular weight determinations (8, 11, 12) in benzene indicate that the tetrameric structure is maintained in solution. In fact, a large number of complexes $\text{CuX} \cdot \text{L}$, where L is a neutral polar molecule, are known to have four-fold molecular weights in solution.

The structure of $[\text{CuI} \cdot \text{As}(\text{C}_2\text{H}_5)_3]_4$, which is taken as a model for this whole group of complexes, consists of a tetrahedron of copper(I) ions, each with an external triethylarsine ligand, and with four iodide ions occupying the face-centers of the tetrahedron. Each iodide bridges three coppers, and each copper has three iodides and one arsine as nearest neighbors.

An interesting exception has been found in the structure of $\text{CuH} \cdot \text{P}(\text{C}_6\text{H}_5)_3$, which is hexameric with the coppers in the corners of

an octahedron, and the phosphines external to the octahedral corners. The hydrides are presumed to be in the face centers (13). Another exception to the tetrameric $[\text{CuX} \cdot \text{L}]_4$ structure is found for $\text{CuBr} \cdot \text{C}_6\text{H}_{11}\text{PH}_2$, which has been reported (5) to be dimeric. A structure involving two bridging bromides and three-coordinate copper was postulated. Similar structures have been postulated for $\text{CuX} \cdot \text{P}(\text{C}_6\text{H}_{11})_3$ ($\text{X} = \text{Cl}, \text{Br}$) on the basis of mass spectral data (14).

Complexes with formulas $\text{CuX} \cdot 2\text{PR}_3$ are assumed to be dimers with four-coordinate copper(I). Thus Mann and co-workers (11) postulated that Arbuzov's complex $\text{CuI} \cdot 2\text{P}(\text{C}_2\text{H}_5)_3$ was related structurally to the known dipy $\text{Cu} \begin{array}{c} \text{I} \\ \diagup \quad \diagdown \\ \text{Cu} \end{array} \text{dipy}$. The compound $\text{CuCl} \cdot 2\text{P}(\text{CH}_3)_3$ (8) as well as complexes $\text{CuX} \cdot 2\text{amine}$ with primary amine ligands (15) were found to have dimeric molecular weights in benzene, and Clifton (16) found $\text{CuCl} \cdot 2\text{NH}(\text{C}_2\text{H}_5)_2$ to be dimeric in nitrobenzene.

A number of complexes $\text{CuX} \cdot 3\text{PR}_3$ are known, of trimethylphosphine and of triphenylphosphine and its derivatives. These are monomeric, with four-coordinate copper(I). The cryoscopic molecular weight of $\text{CuCl} \cdot 3\text{P}(\text{CH}_3)_3$ in benzene (8) and the structure of $\text{CuCl} \cdot 3\text{PCH}_3(\text{C}_6\text{H}_5)_2$ (17) have been determined.

The very unstable $\text{CuCl} \cdot 4\text{P}(\text{CH}_3)_3$ was assumed (8) to have an ionic structure $[\text{Cu}(\text{P}(\text{CH}_3)_3)_4]\text{Cl}$.

B. Coordination and Reduction of Copper(II) by Tertiary Phosphines

Stable coordination compounds of copper(II) with tertiary phosphines were unknown until recently. Zelonka and Baird (18) have prepared a triethylphosphine complex of copper(II) hexafluoroacetylacetonate. The reaction commonly observed is reduction of the copper(II) to copper(I). This reduction affords a second synthetic route to copper(I) phosphine complexes, since an excess of the phosphine is normally used. The mechanisms of such reactions are unknown, but presumably involve as a preliminary step the formation of a copper(II)-phosphine complex which then undergoes an oxidation-reduction reaction, yielding the copper(I) final product. Indications of a transient copper(II) chloride-triethylphosphine complex were given by Jensen (19), who observed intermediate colors during the reaction in an ethanolic solution. The final product of this reaction was the already known complex of Arbuzov, $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$. The preparation of this complex by the oxidation-reduction synthetic route was repeated by Jardine et al. (9).

Many other cases of the reduction of copper(II) by tertiary phosphines may be found in the literature. For example, bis(triphenylphosphine)copper(I) nitrate was prepared (20) from the reaction of copper(II) nitrate with triphenylphosphine, and bromo- and chlorobis(tricyclohexylphosphine)copper(I) were prepared (14) from

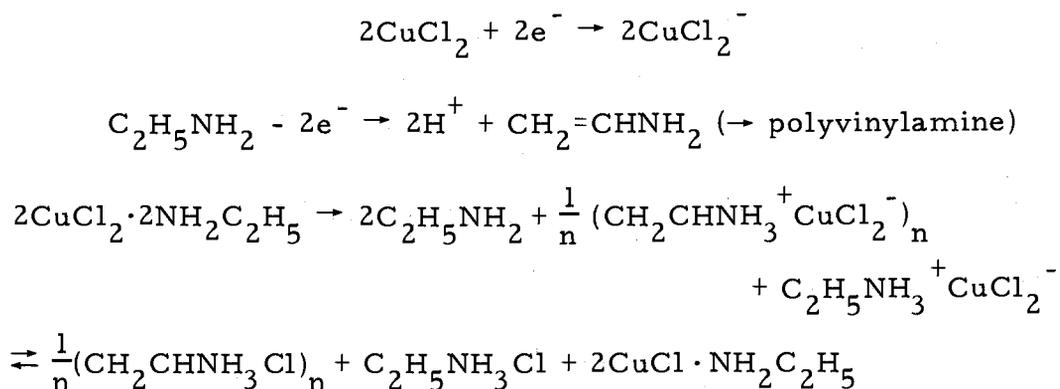
the copper(II) halide and an excess of the phosphine in ethanol.

C. Oxidation of Aliphatic Amines and Phosphines by Copper(II)

1. Oxidation of Amines

In the oxidation of aliphatic amines, the formation of amine N-oxides is unusual, and is brought about only by peroxy compounds. Enamines (or compounds derived from them by further reaction) are the more common products of oxidation of aliphatic amines, for example by halogens, various transition metal halides, or by oxygen under the action of the copper-containing enzyme monamine oxidase.

Complexes of triethylamine are known with copper in both its +1 and +2 oxidation states, with formulas $\text{CuCl}_2 \cdot 2\text{N}(\text{C}_2\text{H}_5)_3$ (21) and $\text{CuCl} \cdot \text{N}(\text{C}_2\text{H}_5)_3$ (22). Similar complexes are formed by ethylamine (23) and diethylamine (16). The systems are related through an oxidation-reduction process, which is induced thermally in the copper(II) complexes. Pertinent equations for the simplest case, with ethylamine, are



Thus the products of reaction of the ethylamines with copper(II) chloride are, firstly, isolable coordination complexes, and secondly, by internal oxidation-reduction of these, neutral and anionic complexes of copper(I) chloride. The oxidation products are themselves polymeric amines, capable of coordination and of salt formation. The reduction products are copper(I) species, alkylammonium dichlorocuprate(I) salts, and $\text{CuX} \cdot \text{amine}$ complexes.

2. Oxidation of Phosphines

In contrast to amines, a variety of oxidizing agents oxidize phosphines to oxides and other products containing the $\text{P}=\text{O}$ phosphoryl group. The autoxidation of free trialkyl phosphines has been investigated (24, 25), and shown to involve a free radical process giving a mixture of phosphoryl products. Autoxidation of coordinated triethylphosphine, in the complex dichlorobis(triethylphosphine)cobalt(II), was shown by Schmidt and Yoke (26) to be a non-radical process involving a $\text{Co}-\text{O}_2$ intermediate or transition state and giving triethylphosphine oxide as the sole oxidation product.

In the case of the oxidation of organophosphines by copper(II), the initial oxidation products have never been characterized. In wet systems, the isolation of tertiary phosphine oxides as eventual reaction products has been reported by Issleib and Zimmerman (27), and by Caughman and Taylor (28).

One possible mode for the oxidation of trialkylphosphines by copper(II) might be by dehydrogenation of the alkyl groups, in a manner similar to the amine oxidation. Vinyl phosphines, which would be formed in such a process, are known compounds (29). The hydrogen ions liberated in such a process would lead to the formation of trialkylphosphonium halides, R_3PHX . Such compounds are known, stable materials, and several have been recently well-characterized by van den Akker and Jellinek (30).

An alternative mode of oxidation of a phosphine by copper(II) might involve oxidation of the phosphorus center, in a manner not possible for amine nitrogen. This type of oxidation was observed by Cohn and Parry (31), who found that copper(II) chloride oxidized dimethylaminodifluorophosphine $(CH_3)_2NPF_2$ to the phosphorane $(CH_3)_2NPF_2Cl_2$. If triethylphosphine were to undergo oxidation by such a process, the expected product would be triethyldichlorophosphorane, $(C_2H_5)_3PCl_2$. This is an extremely moisture-sensitive material which was reported in 1915 by Collie and Reynolds (32). It has been investigated more recently by Spangenberg and Sisler (33, 34) who characterized it by its melting point, infrared and 1H and ^{31}P nmr spectra.

Tertiary phosphine dihalides such as triethyldichlorophosphorane might have either of two structures. The molecular structure would be a trigonal bipyramid such as is found for pentaphenylphosphorane or

for gaseous phosphorus pentachloride. The ionized form which might be expected would be $(C_2H_5)_3PCl^+Cl^-$. In view of the steric requirements of the ethyl groups, an ionized form like that of solid phosphorus pentachloride, $PCl_4^+PCl_6^-$, would not be expected. Gobeau and Baumgartner (35) have reported that $(CH_3)_3PCl_2$ actually occurs as $(CH_3)_3PCl^+Cl^-$, and Issleib and Seidel (36) have reported that other tertiary phosphine dihalides have similar structures. Therefore, the species commonly referred to as trialkyldichlorophosphanes are more correctly named as trialkylchlorophosponium chlorides.

D. Chlorocuprate(I) Complexes

In addition to reacting with amines to form neutral complexes, copper(I) chloride can react with ammonium chlorides $AmHCl$ to give anionic complexes of copper(I). Copper(I) chloride is insoluble in water and most organic solvents, but dissolves in a concentrated chloride ion solution to give a variety of chlorocuprate(I) complex anions. Ahrland and Rawsthorne (37) determined the stability constants of the $CuCl_2^-$ and $CuCl_3^{2-}$ ions in water, and Sukhova et al. (38) studied the composition and stabilities of $Cu_mCl_n^{(n-m)-}$ species, where $m=1-5$ and $n=1-9$.

Many examples of solid chlorocuprate(I) salts with a variety of cations have been obtained from such solutions in water, alcohol, etc. (39). Remy and Laves (40) prepared solid chlorocuprate(I) salts

with mono-, di-, tri- and tetra-methylammonium cations. The compositions corresponded to various anion formulas, such as CuCl_2^- , CuCl_3^{2-} , and $\text{Cu}_2\text{Cl}_3^{3-}$. Clifton (16, 23, 41) prepared solid ethylammonium and diethylammonium dichlorocuprates(I), and Porterfield (42) prepared solid tetraethylammonium dichlorocuprate(I). The surprising thing about triethylammonium dichlorocuprate(I), which was prepared by Weiss (22, 43) simply by direct combination of equimolar amounts of powdered copper(I) chloride and triethylammonium chloride under nitrogen at room temperature, is that it is a liquid, despite its salt-like formation $(\text{C}_2\text{H}_5)_3\text{NH}^+[\text{CuCl}_2^-]$. No solvent is necessary in this case, in contrast to the solid chlorocuprates(I), where a solvent is required to bring the copper(I) chloride and ammonium chloride into reaction.

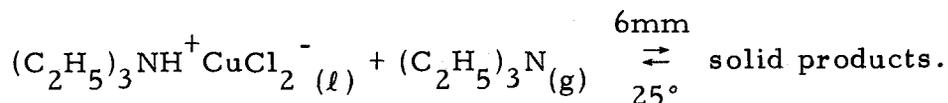
X-ray diffraction studies have been conducted on a number of the solid complexes and have so far shown four structural types: (1) discrete linear CuCl_2^- ions, as in $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_2\text{CH}_2(\text{C}_2\text{H}_5)_2\text{NH}_2(\text{CuCl}_2^-)$ (44), (2) infinite chains of CuCl_4 tetrahedra sharing edges, as in $(\text{Cu}(\text{NH}_3)_4)(\text{CuCl}_2)_2$ (45), (3) infinite chains of CuCl_4 tetrahedra sharing corners, as in K_2CuCl_3 (46), (4) infinite double chains of CuCl_4 tetrahedra sharing corners, as in CsCu_2Cl_3 (47).

Vibrational spectroscopic studies of chlorocuprate(I) anions have been conducted. Assignments for a $\text{D}_{\infty h}$ CuCl_2^- ion were made as follows: Rodley, Goodgame, and Cotton (48) compared the

far-infrared spectrum of solid $[(C_6H_5)_2CH_3AsO)_4Cu][CuCl_2]_2$ with that of the corresponding perchlorate, and assigned a band at 410 cm^{-1} to the dichlorocuprate(I) anion asymmetric stretch, ν_3 . Creighton and Lippincott (49) found a single partly polarized Raman line at 296 cm^{-1} for an ether extract of an aqueous hydrochloric acid-copper(I) chloride solution, and assigned it to the symmetric stretch ν_1 . Waters and Basak (50) studied a tri-n-butyl phosphate solution of lithium and copper(I) chlorides, and placed the above frequencies at 405 cm^{-1} and 300 cm^{-1} , respectively. They also observed the bending frequency, ν_2 , at 109 cm^{-1} . Similar low frequency infrared and Raman spectral studies of various alkylammonium chlorocuprates(I) have been made in conjunction with the present work by Porterfield (42) and by Porterfield and Good (51), and will be discussed subsequently.

The anionic complexes reported by Weiss (21, 22, 42) and Clifton (16, 23, 41) were found to undergo further reactions with the parent amines. Phase studies indicated that ethylammonium dichlorocuprate(I) would bind two or three moles of ethylamine, giving liquid products $C_2H_5NH_3^+[CuCl_2 \cdot nC_2H_5NH_2^-]$ ($n=1, 2$), or would react with an equimolar amount of ethylamine to give a solid mixture of triethylammonium chloride and $CuCl \cdot NH_2C_2H_5$. The identification of the latter products was based on X-ray powder diffraction patterns. Phase studies indicated that diethylammonium dichlorocuprate(I) will

take up one mole of diethylamine to give a liquid product, formulated as $[(C_2H_5)_2NH_2^+][CuCl_2 \cdot NH(C_2H_5)_2^-]$, or that it will take up two moles of diethylamine to give a solid product. The latter was formulated as a discrete complex, $[(C_2H_5)_2NH_2^+][CuCl_2 \cdot 2NH(C_2H_5)_2^-]$, rather than as a mixture of diethylammonium chloride and $CuCl \cdot 2NH(C_2H_5)_2$, again on the basis of X-ray powder patterns. Weiss observed the equilibrium



The solid products were postulated to be a mixture of triethylammonium chloride and chloro(triethylamine)copper(I). In a re-investigation of this system, Clifton obtained the X-ray powder diffraction pattern of the solid reaction products. This information has not been previously reported and is given in Table V for comparison with the analogous phosphine systems described in the present work.

III. EXPERIMENTAL

A. Materials

1. Copper Chlorides

a. Copper(II) Chloride. Finely ground blue copper(II) chloride dihydrate (Baker and Adamson Reagent Grade or Mallinckrodt Analytical Reagent) was converted to the anhydrous salt by being heated at 115° until completely brown in color. The anhydrous salt was used immediately after drying.

b. Copper(I) Chloride. Copper(I) chloride was prepared from Reagent Grade copper(II) chloride by the sulfite reduction technique (52). The white product was washed with glacial acetic acid, absolute ethanol, and diethyl ether, dried in vacuo at room temperature, and stored in a vacuum desiccator over phosphorus(V) oxide. Material showing any sign of discoloration was discarded.

2. Phosphorus Reagents

a. Phosphorus Trichloride. Phosphorus trichloride (Baker and Adamson Reagent Grade) was distilled under nitrogen. The fraction boiling at 74.5° (uncorr.) at 764 torr was collected.

b. Phosphorus Pentachloride. Phosphorus pentachloride (Baker and Adamson Reagent Grade) was sublimed at 165° in a tube furnace

under a stream of chlorine gas. The white product was stored under nitrogen until use.

c. Triethylphosphine. Triethylphosphine was prepared by the Grignard reaction of ethyl magnesium bromide with phosphorus trichloride in ether, according to the method of Hibbert (53) as modified by Schmidt (54). The triethylphosphine was distilled under nitrogen into aqueous potassium diiodoargentate(I), to form a white precipitate of the tetrameric (10) 1:1 triethylphosphine-silver iodide adduct. The precipitate was filtered, recrystallized from acetone, then dried and stored in vacuo over KOH.

Triethylphosphine was easily liberated from the silver iodide complex thermally in the vacuum line. It was purified by repeated fractional condensation, and a middle fraction was taken for use. Tensiometric homogeneity was the criterion of purity. Experimental vapor pressures for various samples were 13.0 torr at 23°, 14.0 torr at 25°, and 16.0 torr at 27°, all of which match well the values from the Clausius-Clapeyron plot ($\log P$ vs. $1/T$) constructed from the data of Thompson and Linnett (55), Hooge and Christen (56), Kaesz and Stone (57), CRC Handbook of Chemistry and Physics (58), Hatfield and Yoke (59), and Schmidt (54).

d. Triethylphosphine Oxide. Triethylphosphine oxide was prepared by the oxidation of triethylphosphine with mercury(II) oxide (60). It was purified by distillation in vacuo with mild application of heat

and used immediately. ^{31}P nmr (CCl_4) -46.8, (C_6H_6) -46.6 (Lit. (61) -48.3).

e. Triethylphosphonium Chloride. Triethylphosphine (3.01 g, 2.55 millimole) was distilled from a tared vacuum line storage vessel into 150 ml of benzene contained in a round bottomed flask fitted with gas inlet and outlet tubes bearing stopcocks and attached to the vacuum line. The benzene had been degassed by three freezing-pumping-thawing cycles. Nitrogen was admitted to the apparatus, which was then removed from the vacuum line. Hydrogen chloride was bubbled through concentrated sulfuric acid and into the triethylphosphine solution, which was stirred magnetically at room temperature. The flocculent white solid initially formed was subsequently converted into an immiscible liquid. By analogy to the triphenylphosphine system (30), it is suggested that the second step corresponds to the formation of $[(\text{C}_2\text{H}_5)_3\text{PH}^+][\text{HCl}_2^-]$. The hydrogen chloride addition was then terminated, and the apparatus was flushed with nitrogen. All volatile materials were removed in vacuo, leaving 3.84 g (2.48 millimole) of white solid triethylphosphonium chloride; yield 97%.

The crude product was purified by sublimation in vacuo at 130° , m. p. $217-221^\circ$; lit. (30) $205-210^\circ$; Anal. Calcd. for $(\text{C}_2\text{H}_5)_3\text{PHCl}$: C, 46.61; H, 10.43; Cl, 22.92. Found: C, 46.70; H, 10.37; Cl, 22.42. The compound was soluble in methanol, chloroform, acetonitrile, and dimethylformamide, slightly soluble in acetone,

insoluble in carbon tetrachloride, hexane, chlorobenzene, benzene, ethyl acetate, and trichloroethylene, and was decomposed by water or by exposure to the room atmosphere. The ir (Nujol) showed P-H at 2275, 888, and 855 (sh) cm^{-1} ; lit. (30) 2300, 895, and 860 cm^{-1} . ^1H nmr (CHCl_3) δ 1.40(m), 2.63(m), 6.97 (d, $J_{\text{P-H}}$ 489 Hz); ^{31}P nmr -20.5 ppm vs. external H_3PO_4 (d, $J_{\text{P-H}}$ 489 Hz). The d-spacings are given in Table IV.

f. Triethylchlorophosphonium Chloride (Triethyldichlorophosphorane). This was prepared from triethylphosphine and phosphorus trichloride (mole ratio 3:2) in benzene, according to the procedure of Spangenberg and Sisler (33, 34), and was recrystallized from toluene. Anal. Calcd. for $(\text{C}_2\text{H}_5)_3\text{PCl}_2$: C, 38.11; H, 7.99; P, 16.38. Found: C, 38.33; H, 8.07; P, 16.49. m.p. 238-243° (d); ^1H nmr (CDCl_3) δ 3.35(m), 1.45(m); ^{31}P nmr -110. Lit. (34) m.p. 242-247° (d); ^1H nmr, δ 3.36(m), 1.44(m); ^{31}P nmr -114.

g. Triethylchlorohydroxyphosphorane. A solution of triethylphosphine oxide in benzene was saturated with hydrogen chloride and evaporated to dryness in vacuo, leaving a white solid, m.p. 129-134°, ir (Nujol) 2380-2300w, 1555m, 1270m, 1238m, 1145m, 1068w, 1047s, 1010s, 970m, 815m, 777s, 756s, 666vw; ^1H nmr (concentration-dependent)(CH_3CN) δ 14.10(s), 1.96(m), 1.20(m); (CDCl_3) δ 12.49(s), 2.15(m), 1.28(m); ^{31}P nmr (CDCl_3) -82.6(s). An identical material was obtained during attempted preparations of

triethylchlorophosphonium chloride (32, 33) when protection from moisture was inadequate. Anal. Calcd. for $(C_2H_5)_3PClOH$: C, 42.24; H, 9.45; P, 18.15; Cl, 20.87. Found: C, 42.00; H, 9.80; P, 18.32; Cl, 20.95.

3. Solvents

a. Ethanol. A 60 ml quantity of Reagent Grade ethanol, 5 g of magnesium turnings, and several drops of ethyl bromide were maintained at reflux in a one liter flask until nearly all of the magnesium was converted to the ethoxide. A large amount of ethanol was then added and distilled from the magnesium ethoxide. A 50 ml forerun was discarded, and a fraction with a boiling point of 78.0° at 770 torr was collected and stored over Linde #3-A Molecular Sieves.

b. Acetonitrile. Acetonitrile (Matheson, Coleman, and Bell) was purified using the procedure of Weiss (43). Acidic impurities were removed by washing three times with ice-cold 50% aqueous sodium hydroxide, shaking with anhydrous sodium sulfate, and filtering. Basic impurities and residual water were removed by shaking with phosphorus(V) oxide until a fine suspension was obtained. The suspension was decanted into a nitrogen-flushed distillation apparatus and distilled under nitrogen. A middle fraction with a boiling point of 81.5° at 760 torr was collected over calcium hydride. This fraction was transferred into a storage bulb on the vacuum line. The vapor

pressure of the purified acetonitrile was 6 torr at -23° , and 94 torr at 25° . These values match well the values from the Clausius-Clapeyron plot ($\log P$ vs. $1/T$) constructed from data taken from the CRC Handbook of Chemistry and Physics (58).

c. Benzene. Reagent Grade benzene (Matheson, Coleman, and Bell) was washed with portions of concentrated sulfuric acid until the acid layer remained clear. The benzene layer was shaken with anhydrous sodium sulfate, decanted into a nitrogen-flushed distillation apparatus, and distilled under nitrogen onto Linde #3-A Molecular Sieves. A middle fraction with a boiling point of 79.5° at 762 torr was collected and stored under nitrogen.

d. Toluene. Reagent Grade toluene (Matheson, Coleman, and Bell) was washed with concentrated sulfuric acid until the acid layer remained clear. The toluene layer was then shaken with anhydrous sodium sulfate, decanted into a nitrogen-flushed distillation apparatus, and distilled under nitrogen onto Linde #3-A Molecular Sieves. A middle fraction with a boiling point of 109.5° at 763 torr was collected and stored under nitrogen.

e. Deuteriochloroform. Chloroform-d containing 1% tetramethylsilane (Diaprep, Inc., Atlanta, Georgia, Lot #680701, isotopic purity 99.8%) was used as received as a solvent for some nmr studies.

4. Other Materials

a. Hydrogen Chloride. Hydrogen chloride (Matheson Gas Products) was bubbled through a gas-washing bottle containing concentrated sulfuric acid, and then passed through a glass wool filter to remove any acid spray.

b. Chlorine. Chlorine (Hooker Chemical Corporation, Tacoma, Washington) was passed through a washing tower of concentrated sulfuric acid, and then through a glass wool filter.

c. Nitrogen. Pre-purified Grade nitrogen (Air Reduction Company) was used from the cylinder as received. The maximum amount of oxygen is guaranteed by the supplier to be less than 8 ppm.

Unless otherwise stated, all other chemicals used in this study were of Reagent Grade, or of the highest quality commercially available.

B. Analytical Methods

1. Carbon and Hydrogen

Carbon and hydrogen microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee, and by C. F. Geiger, Ontario, California.

2. Phosphorus

Phosphorus microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Attempts were made to employ a Karl Fischer titration as an analytical method for the determination of trivalent phosphorus, as described by Hayton and Smith (62). The method gave insufficiently reproducible results to be used.

3. Chloride

The chloride content was determined gravimetrically.

4. Copper

The copper content was determined by a compleximetric titration employing ethylenediaminetetraacetate ion and copper(II) sulfate. Accurately weighed samples were converted to copper(II) sulfate by treatment with nitric acid to oxidize the copper(I) present, and then subsequent evaporation to fumes with sulfuric acid. The samples were then dissolved in distilled water and made up to 100 ml in volumetric flasks. Ten ml aliquots were pipetted into Erlenmeyer flasks containing 50 ml of distilled water. A 50.00 ml quantity of standardized $\text{Na}_2\text{H}_2\text{EDTA}$ (approximately 0.01M) was then pipetted into the flask. The pH of the resulting solution was adjusted to the

range 5-6 (Universal pH Indicator Paper) by adding approximately two grams of ammonium acetate. The solution was heated to boiling and 0.5 ml of a 0.1% solution in methanol of [1-(2-pyridylazo)-2-naphthol] PAN indicator (63) was added. The excess EDTA was then back-titrated using standardized copper(II) sulfate solution (approximately 0.01M). The color change of the indicator is green to purple. The known EDTA and copper(II) sulfate solutions were standardized by the same method, using pure copper foil as a primary standard.

C. Instrumental Methods

All samples of oxygen- or moisture-sensitive compounds were loaded in spectral cells, melting point tubes, etc., under dry nitrogen in a glove box.

1. Infrared Spectra

Infrared spectra, in the range 4000 to 625 cm^{-1} , were recorded on Beckman Model IR-5, Beckman Model IR-8, or Perkin-Elmer Model 621 double-beam recording spectrophotometers. Infrared spectra in the range 625 to 180 cm^{-1} were recorded on either Perkin-Elmer Model 621 or Perkin-Elmer Model 180 double-beam recording grating spectrophotometers. Sodium chloride cells were used in the range 4000 to 625 cm^{-1} ; polyethylene cells were used in the range 625 to 180 cm^{-1} . Samples were studied as Nujol or

Fluorolube (Kel-F-10) mulls, or as thin films. The wavelength scale was calibrated using the spectrum of polystyrene film.

2. Raman Spectra

Raman spectra in the range 4000 to 100 cm^{-1} were obtained with a Cary Model 82 instrument with a Coherent Radiation Laboratories Argon Ion Laser Model 52B operated at 514.5 nm . Samples were contained in sealed glass capillaries having flattened bottoms to reduce scattering of the laser beam.

3. Nuclear Magnetic Resonance Spectra

NMR spectra were obtained with a Varian HA-100 instrument. Tetramethylsilane was used as either an internal or an external standard for proton spectra. Chemical shifts are reported in ppm (δ) vs. TMS. Phosphorus-31 spectra were obtained at 40.488 MHz . Phosphoric acid (85%) was used as the reference by the tube-interchange method for the majority of the phosphorus spectra. The resonance of the sample was located by sweeping in the HR mode. Phosphoric acid was inserted in the probe and sweeping continued until a phosphoric acid resonance was located. The direction of sweep was reversed and the phosphoric acid signal modulated with an external oscillator to give a series of sidebands separated by a known frequency. The reference and sample tubes were interchanged and

the sweep was continued through the sample resonance. The resonance frequency was thus located relative to the first upper sideband of phosphoric acid (2500 Hz) using the frequency separation of the reference sidebands for scale calibration. This frequency shift relative to phosphoric acid was then converted into ppm vs. H_3PO_4 by dividing the measured frequency shift by 40.488 MHz. Phosphorus(III) oxide (Van Ness Associates, Glendale, California) contained in a capillary tube was used as an external reference for some ^{31}P spectra. The chemical shift of P_4O_6 was found by the tube-interchange method to be -112.5 ppm vs. phosphoric acid; lit (61, 64) -112.5 ppm. Spectra using P_4O_6 as a reference were calibrated in ppm relative to P_4O_6 , and then converted to ppm vs. phosphoric acid by subtracting 112.5 ppm. All phosphorus chemical shifts are thus reported as ppm vs. phosphoric acid.

4. X-Ray Powder Diffraction Patterns

X-ray powder diffraction patterns were obtained using a General Electric X-Ray Diffraction Unit. Sealed Lindemann capillaries were used in a 114.6 mm diameter powder camera with nickel-filtered $\text{Cu-K}\frac{\alpha}{1}$ radiation. Values of d-spacings corresponding to angles of 2θ were taken from standard tables (65) constructed from the Bragg equation. Intensities of lines were visually estimated.

5. Conductivity Measurements

Conductivities were measured using an Industrial Instruments Model RC16B2 Conductivity Bridge and a modified Industrial Instruments cell. The cell constant, 0.102 cm^{-1} was determined concurrently by Dr. W. W. Porterfield in this laboratory.

6. Melting Point Determination

Melting points were determined on a Mel-Temp Laboratory Devices Capillary Melting Point Apparatus. Samples were contained in sealed capillaries.

D. General Preparation of Complexes

Coordination compounds were synthesized using a glass high-vacuum system or a nitrogen-filled dry box similar to those described by Shriver (66). All stopcocks and glass joints were lubricated with Dow Corning High Vacuum Grease Silicone Lubricant. With a combination of a mechanical oil forepump, a mercury diffusion pump, and liquid nitrogen traps, residual pressures in the vacuum system were routinely reduced to 10^{-6} torr, adequate for this work. Complexes were synthesized in a reaction assembly consisting of a reaction tube or bulb containing a teflon-coated magnetic stirring bar, and a connecting tube fitted with a high-vacuum stopcock and standard taper

joints for attachment to the vacuum system.

The method of preparation of the complexes depended upon the nature of the reactants. These can be divided into three groups: (1) a solid plus a volatile liquid, (2) a solid plus a solid, and (3) two solids plus a volatile liquid. Preparations of the first type were accomplished as follows. The solid reactant was weighed into the reaction tube or flask in the dry box. The reaction assembly was closed, removed from the dry box, attached to the vacuum system and evacuated. The tare weight was recorded and the assembly was reattached to the vacuum system. An excess of the volatile liquid was condensed in the reaction assembly by cooling it to -196° . The stopcock was closed, the assembly was detached, and the components were allowed to interact while being stirred by the magnetic spin bar. If desired, the reaction assembly was maintained at a specific temperature by an appropriate slush bath.

Equilibrium pressure-temperature data were obtained by opening the reaction assembly, maintained at the desired temperature by slush baths or by water circulating from a constant temperature bath, to a manometer on the vacuum system. The molar composition of the reaction mixture was determined by weighing the reaction assembly. Volatile liquid could be either distilled from or condensed into the reaction assembly. By these methods, the equilibrium pressures for a series of known molar compositions were determined. The

stoichiometries and the stabilities of complexes formed in each system were determined by inspection of the isothermal pressure-composition phase diagrams obtained by plotting these experimental data. If a mixture of specific composition was desired, volatile liquid was condensed in a tared reaction assembly and weighed. The mass of solid reactant required was determined and weighed into a second reaction assembly in the dry box. This assembly was then evacuated on the vacuum system and the volatile liquid was condensed quantitatively into it.

In the case of two solid reactants, both materials were weighed out in the dry box and combined in a reaction assembly. If desired, a volatile solvent could be condensed onto or distilled from the reaction mixture on the vacuum system. Systems involving two solids and a liquid were handled in a similar manner. If a mixture of exact composition was desired, a weighed quantity of volatile liquid was transferred quantitatively to the reaction assembly as described above.

E. System Copper(I) Chloride - Triethylphosphine

1. Phase Studies

Copper(I) chloride dissolved in triethylphosphine, and at 26° and above a triethylphosphine:copper(I) chloride mole ratio of 3.5, the system consisted of a liquid solution in equilibrium with

triethylphosphine vapor. Triethylphosphine was removed in portions in the course of isothermal pressure-composition measurements. The data are given in Table I and Figure 1. At 26° the pressure fell to less than 1 torr as the triethylphosphine:copper(I) chloride mole ratio decreased to 3.0, leaving a white solid. The temperature was then raised to 58°, causing the solid to melt and the equilibrium pressure to rise to about 2.5 torr. Removal of triethylphosphine was continued at 58° to a mole ratio of 1.0, leaving another white solid with a negligible dissociation pressure. These phase studies indicated the existence of the two solid compounds, $\text{CuCl} \cdot 3\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$.

2. Chloro(triethylphosphine)copper(I)

This was prepared more readily by interaction of exactly equimolar quantities of the components in acetonitrile in a vacuum line reaction bulb, followed by removal of the solvent in vacuo. The reaction assembly was opened in a dry box and a sample of the material was taken for analysis. Anal. Calcd. for $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$: mole ratio 1.00; Cu, 29.26; Cl, 16.32; C, 33.18; H, 6.96. Found: mole ratio 0.99; Cu, 29.09; Cl, 16.14; C, 32.89; H, 6.77.

3. Chlorotris(triethylphosphine)copper(I)

A 1.2233 g quantity of triethylphosphine (10.35 millimole) was

condensed onto 0.3458 g of copper(I) chloride (3.493 millimole; mole ratio 2.964) in a vacuum line reaction assembly, and the mixture was allowed to stand for two weeks.

F. System Copper(I) Chloride - Triethylphosphonium Chloride

1. Triethylphosphonium Dichlorocuprate(I)

Triethylphosphonium dichlorocuprate(I) was synthesized by adding 1.896 g (19.1 millimole) of copper(I) chloride to 2.958 g (19.1 millimole) of triethylphosphonium chloride in a reaction assembly in a dry box. The two white powders reacted on contact at room temperature to give a pale yellow-green liquid of composition $(C_2H_5)_3PH^+[CuCl_2^-]$.

2. Triethylphosphonium Trichlorocuprate(I)

Upon mixing 2.60 millimole of triethylphosphonium chloride and 1.30 millimole of copper(I) chloride, a yellow-green oil of composition $[(C_2H_5)_3PH^+]_2[CuCl_3^{-2}]$ was obtained. A yellow-green oil of the same composition was prepared by dissolving 0.631 g (4.08 millimole) of triethylphosphonium chloride in 1.034 g (4.08 millimole) of triethylphosphonium dichlorocuprate(I). Upon gentle heating (about 50°) and stirring, all of the triethylphosphonium chloride dissolved, producing a faintly yellow-green liquid.

3. Triethylphosphonium Trichlorodicuprate(I)

When 0.398 g (2.58 millimole) of triethylphosphonium chloride was added to 0.510 g (5.16 millimole) of copper(I) chloride under nitrogen, the two white powders reacted on contact to give a pale yellow-green liquid of composition $[(C_2H_5)_3PH^+][Cu_2Cl_3^-]$. A yellow-green oil of the same composition was prepared by dissolving 0.401 g (4.05 millimole) of copper(I) chloride in 1.033 g (4.07 millimole) of triethylphosphonium dichlorocuprate(I).

G. System Triethylphosphonium Dichlorocuprate(I) - Triethylphosphine

1. One to One Molar Proportions

A 1.0059 g (8.51 millimole) sample of triethylphosphine was condensed at -196° onto 2.1621 g (8.52 millimole) of triethylphosphonium dichlorocuprate(I) in a vacuum line reaction bulb. An exothermic reaction occurred as the mixture was allowed to warm to room temperature, giving a white solid product, m.p. $85-95^\circ$. A sample of the same composition, m.p. $92-96^\circ$, was obtained by removal of solvent in vacuo from a solution of 0.2734 g (1.768 millimole) of triethylphosphonium chloride and 0.3862 g (1.762 millimole) of chloro(triethylphosphine)copper(I) in 5 ml of acetonitrile.

2. One to Three Molar Proportions

A large excess of triethylphosphine was condensed onto triethylphosphonium dichlorocuprate(I). A vigorous reaction took place as the contents of the reaction bulb were allowed to thaw. The excess of triethylphosphine was pumped away at room temperature; as the pressure dropped to a negligible value, a white solid remained in which 3.0 moles of triethylphosphine were retained per mole of triethylphosphonium dichlorocuprate(I). Upon heating the sample to 58°, it melted and the pressure rose, permitting the removal of additional triethylphosphine.

The white solid was prepared more conveniently by the reaction of 1.4169 g (11.99 millimole) of triethylphosphine and 1.0140 g (4.00 millimole) of triethylphosphonium dichlorocuprate(I) in 10 ml of acetonitrile. The solution was stirred at room temperature for 4 hours, and the solvent was then removed in vacuo.

H. System Copper(I) Chloride - Triethylchlorophosphonium Chloride

1. Triethylchlorophosphonium Dichlorocuprate(I)

Upon mixing 0.186 g (0.98 millimole) of triethylchlorophosphonium chloride with 0.097 g (0.98 millimole) of copper(I) chloride at room temperature under nitrogen, the two white powders reacted on contact to yield a light green oil of composition $[(C_2H_5)_3PCl^+][CuCl_2^-]$.

2. Triethylchlorophosphonium Trichlorodicuprate(I)

A mixture of 0.523 g (2.77 millimole) of triethylchlorophosphonium chloride and 0.548 g (5.53 millimole) of copper(I) chloride at room temperature under nitrogen spontaneously formed a dark green-black oil of composition $[(C_2H_5)_3PCl^+][Cu_2Cl_3^-]$.

I. System Triethylchlorophosphonium Trichlorodicuprate(I) - Triethylphosphine

1. Phase Studies

An excess of triethylphosphine was condensed onto 1.16 millimole of dark triethylchlorophosphonium trichlorodicuprate(I) in a tared vacuum line reaction tube, giving a white solid and colorless liquid. The excess of triethylphosphine was then removed at 30.5° during a pressure-composition phase study. These data are given in Table VI and in Figure 13. As triethylphosphine was removed, only a white solid with a negligible dissociation pressure remained. The gain in weight of the system corresponded to retention of 6.88 millimole of triethylphosphine (mole ratio $(C_2H_5)_3P: Cu=2.97$). This solid melted on heating to 58°, and the equilibrium pressure rose to about 2 torr, allowing further removal of triethylphosphine until the pressure again fell to a negligible value. At this point, the product was a white solid in which 2.36 millimole of triethylphosphine had been

retained (mole ratio $(C_2H_5)_3P: Cu=1.02$), corresponding to a composition of $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 2(C_2H_5)_3P$. To a portion of this, exactly enough triethylphosphine was added to regenerate the first solid, of composition $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 6(C_2H_5)_3P$. These phase studies indicate that there are two equations for the reaction of triethylphosphine with triethylchlorophosphonium trichlorodicuprate(I), corresponding to the uptake of three and one moles of triethylphosphine respectively per mole of copper(I) present in the system. The products of these two stoichiometric preparations were more conveniently prepared as described below.

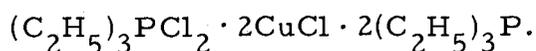
2. Triethylchlorophosphonium Chloride - Chlorotris(triethylphosphine)copper(I)

Triethylchlorophosphonium chloride (0.166 g, 0.88 millimole) and chlorotris(triethylphosphine)copper(I) (0.787 g, 1.75 millimole) were dissolved in the minimum amount of acetonitrile, and the solvent removed in vacuo, leaving a white solid of composition $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 6(C_2H_5)_3P$.

3. Triethylchlorophosphonium Chloride - Chloro(triethylphosphine)copper(I)

Triethylchlorophosphonium chloride (0.283 g, 1.49 millimole) and chloro(triethylphosphine)copper(I) (0.655 g, 3.01 millimole) were dissolved in the minimum amount of acetonitrile, and the solvent

removed in vacuo, leaving a white solid of composition



J. The Oxidation - Reduction Reaction of Copper(II) Chloride with Triethylphosphine

1. Preliminary Investigations

The oxidation-reduction reaction between copper(II) chloride and triethylphosphine was observed in benzene, acetonitrile, and ethanol. Transient purple and brown colors were observed as frozen layers of triethylphosphine and of a solution of copper(II) chloride in ethanol were allowed to thaw; the final products were colorless.

However, the reaction was usually carried out by allowing neat triethylphosphine-anhydrous copper(II) chloride mixtures to warm from -196° to room temperature with magnetic agitation. No reaction was observed at -78° in six months. The reaction was slow at -45° , but proceeded rapidly above -23° . At sufficiently low triethylphosphine:copper(II) chloride reactant mole ratios (e.g. 0.50), the reaction product was a dark green-black oil. Addition of more triethylphosphine to this oil, or the use of an excess initially, gave colorless products: a white solid, plus a colorless liquid if the mole ratio were greater than 3.5. The excess triethylphosphine could be readily pumped off in the vacuum line to a mole ratio of 3.5 at room temperature, giving a white solid product.

2. Phase Studies

Triethylphosphine (4.0293 g, 34.10 millimole) was condensed onto 0.3808 g (2.83 millimole) of copper(II) chloride at -196° in a vacuum line reaction assembly and the mixture was allowed to warm to room temperature. A vigorous exothermic reaction occurred, which yielded a white solid material and a clear, colorless liquid. Triethylphosphine was removed in portions by distillation at 25° in the vacuum line in the course of a pressure-composition phase study. These data are given in Table VIII and Figure 16. As the composition approached a triethylphosphine:copper mole ratio of 3.5, the pressure fell to a negligible value and only a white solid remained. Upon heating to 58° , the pressure rose to two torr. Removal of triethylphosphine was then continued to a mole ratio of 1.5, at which point the pressure again fell to a negligible value, and only a white solid remained in the reaction assembly. These phase studies demonstrate two stoichiometries for the reaction of triethylphosphine with copper(II) chloride, corresponding to the proportions 3.5 and 1.5 moles of triethylphosphine respectively per mole of copper(II).

3. Preparation of Reaction Products from Specific Molar Proportions of the Reagents

a. From Triethylphosphine and Copper(II) Chloride in 0.5:1

Molar Proportions. Anhydrous copper(II) chloride (2.4490 g,

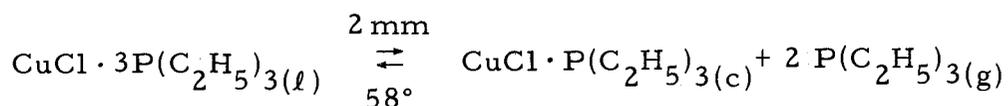
18.22 millimole) was placed in a reaction flask containing 25 ml of benzene. Triethylphosphine (1.0765 g, 9.11 millimole) was added under nitrogen to the copper(II) chloride-benzene mixture, and the resulting mixture was stirred magnetically. An immediate reaction took place which yielded a benzene-insoluble dark green-black oil. Stirring at room temperature for 60 hours brought about no further changes in the system. The reaction assembly was attached to the vacuum line and the solvent removed in vacuo, yielding a viscous green-black oil with a negligible vapor pressure.

b. From Triethylphosphine and Copper(II) Chloride in 3.5:1 Molar Proportions. Triethylphosphine (2.0350 g, 17.22 millimole) was condensed at -196° onto copper(II) chloride (0.6605 g, 4.91 millimole) in a vacuum line reaction assembly. As the assembly slowly warmed to room temperature, a vigorous exothermic reaction occurred, yielding a white solid product with a negligible dissociation pressure at 25° .

IV. RESULTS

A. Copper(I) Chloride - Triethylphosphine Complexes

The results of isothermal phase studies of the system copper(I) chloride-triethylphosphine are shown in Table I and Figure 1. They demonstrate the existence of two complexes with phosphine:copper mole ratios of 3:1 and 1:1 respectively. Both complexes are white crystalline solids at room temperature; chlorotris(triethylphosphine)-copper(I) melts below 58°, while chloro(triethylphosphine)copper(I) melts at 222-224°. They are related by the equilibrium



They are prepared more readily by direct interaction of stoichiometric amounts of the reagents, using no solvent for the 3:1 complex and acetonitrile for the 1:1 complex.

The infrared spectra of the compounds and of free triethylphosphine are similar, with some simplification for the coordinated phosphine in 900-1200 cm^{-1} region, attributed to the presence of only one rotomer of the ligand (67). The infrared spectra of triethylphosphine and of the 1:1 complex are presented in Figure 2, while that of the 3:1 complex is given in Figure 17.

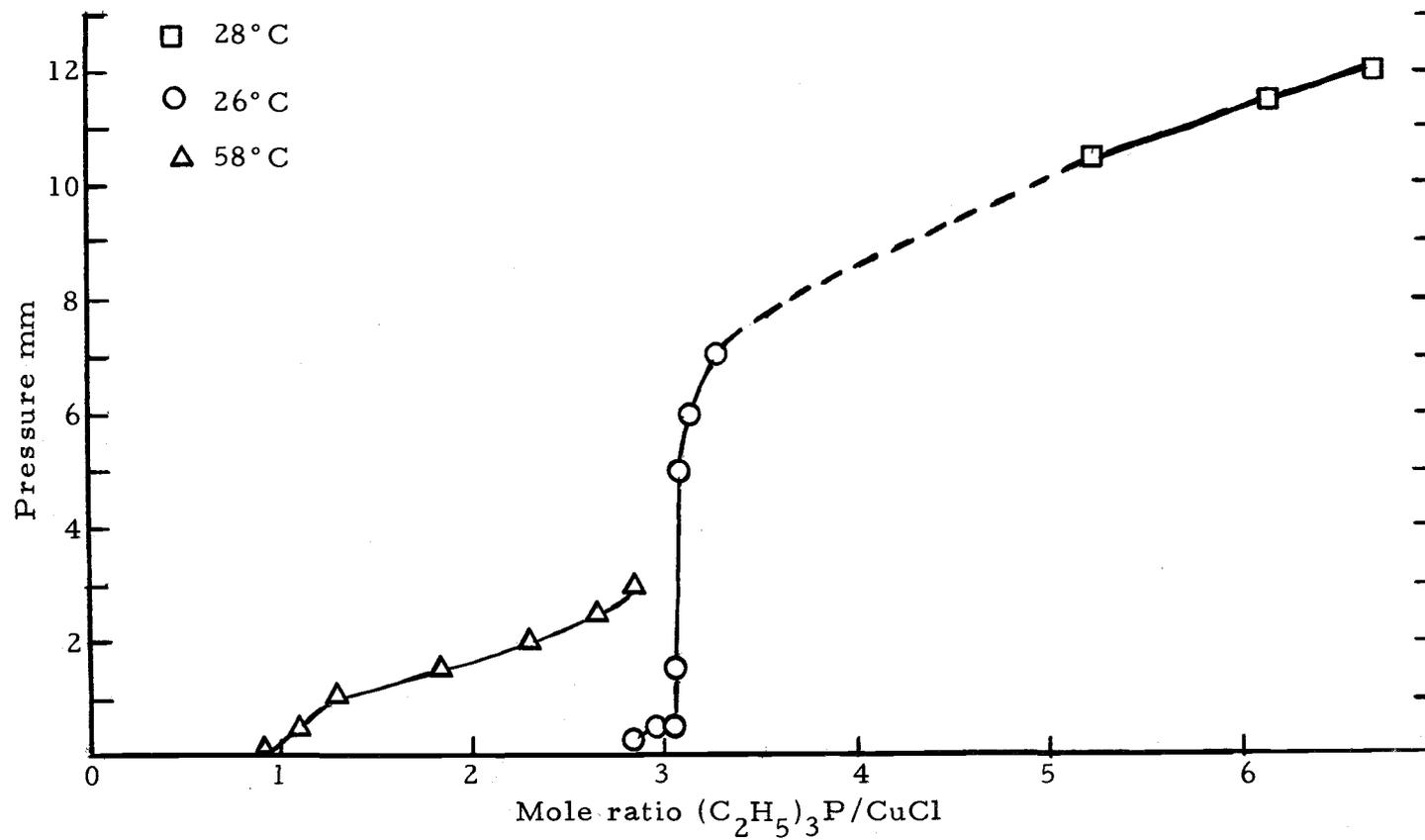


Figure 1. Isotherms for the system $CuCl + (C_2H_5)_3P$.

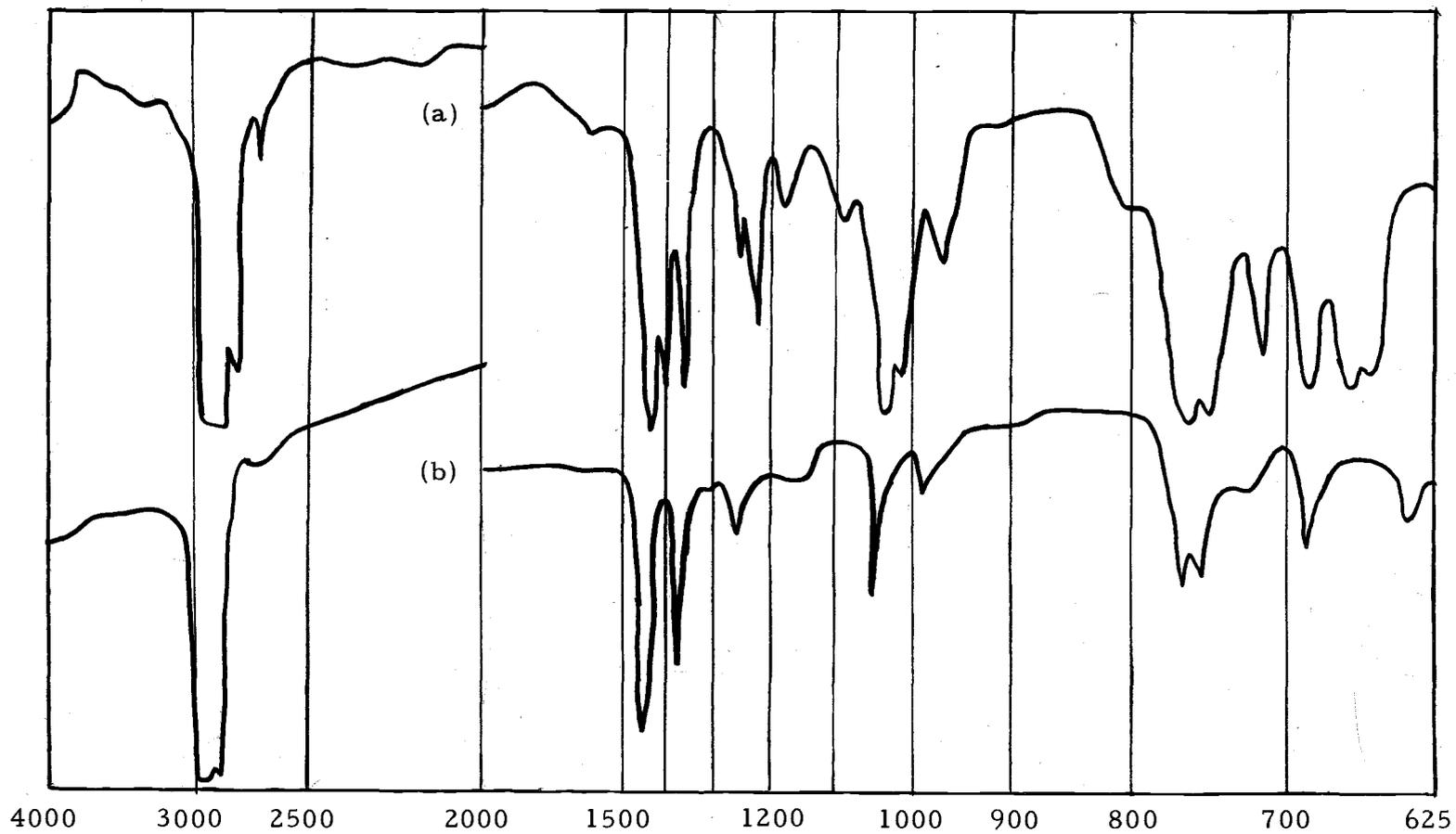


Figure 2. Infrared spectra (cm^{-1}) of (a) $(\text{C}_2\text{H}_5)_3\text{P}$ (neat film) and (b) $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ (Nujol mull).

Table I. Pressure-composition data for the system, copper(I) chloride - triethylphosphine.

	Mole Ratio Et ₃ P/CuCl	Pressure mm
<u>28°</u>	6.68	12.0
	6.13	11.5
	5.21	10.5
<u>26°</u>	3.27	7.0
	3.13	6.0
	3.08	5.0
	3.06	1.5
	3.04	0.5
	2.96	0.5
	2.82	< 0.5
<u>58°</u>	2.82	3.0
	2.66	2.5
	2.29	2.0
	1.83	1.5
	1.30	1.0
	1.10	0.5
	0.91	< 0.5

The proton and ³¹P nuclear magnetic resonance spectra were obtained for the complexes, except that chloro(triethylphosphine)copper(I) was insufficiently soluble to permit observation of its phosphorus resonance in a single scan. Repetitive scans using a computer of average transients permitted qualitative observations of a broad signal, but quantitative data were not obtained. The chemical shifts are given in Table II for the complexes, for triethylphosphine (which is known (33, 68, 69) to have a second order proton spectrum, appearing as an octet), and for the solution of copper(I) chloride in

triethylphosphine as solvent (mole ratio copper:phosphine ca. 1:20).

Table II. Nmr chemical shifts for the system $\text{CuCl}-(\text{C}_2\text{H}_5)_3\text{P}$.

	$(\text{C}_2\text{H}_5)_3\text{P}^{\text{a}}$	$\text{CuCl}\cdot\text{P}(\text{C}_2\text{H}_5)_3^{\text{b}}$	$\text{CuCl}\cdot 3\text{P}(\text{C}_2\text{H}_5)_3^{\text{c}}$	CuCl in $(\text{C}_2\text{H}_5)_3\text{P}^{\text{a,d}}$
^1H (δ)	1.13	1.15, 1.61	1.09, 1.60	0.87, 1.17
^{31}P (ppm)	+19.5	---	+14.7	+18.3

^a Neat.

^b In CH_2Cl_2 .

^c In CDCl_3 .

^d Mole ratio ca. 1:20.

The phosphorus nmr spectrum of the solution of copper(I) chloride in triethylphosphine underwent changes in shape and intensity in the temperature range -10 to $+50^\circ$, as shown in Figure 3. (No change was observed in the proton spectrum in the range -10 to $+35^\circ$.) The $+50^\circ$ phosphorus resonance resembles that of triethylphosphine itself, and is due to a complex combination of PCH_2CH_3 and PCH_2CH_3 couplings. This resolution is progressively lost on cooling. Moreover, only a single average resonance for coordinated and free triethylphosphine is observed in the temperature range studied, in keeping with the expected lability of the copper(I) species. The loss of structure of the phosphorus resonance at lower temperatures may be due (8) to a decrease in the rate of exchange to a point permitting further splitting by the ^{63}Cu and ^{65}Cu nuclei, both of which have $I = 3/2$.

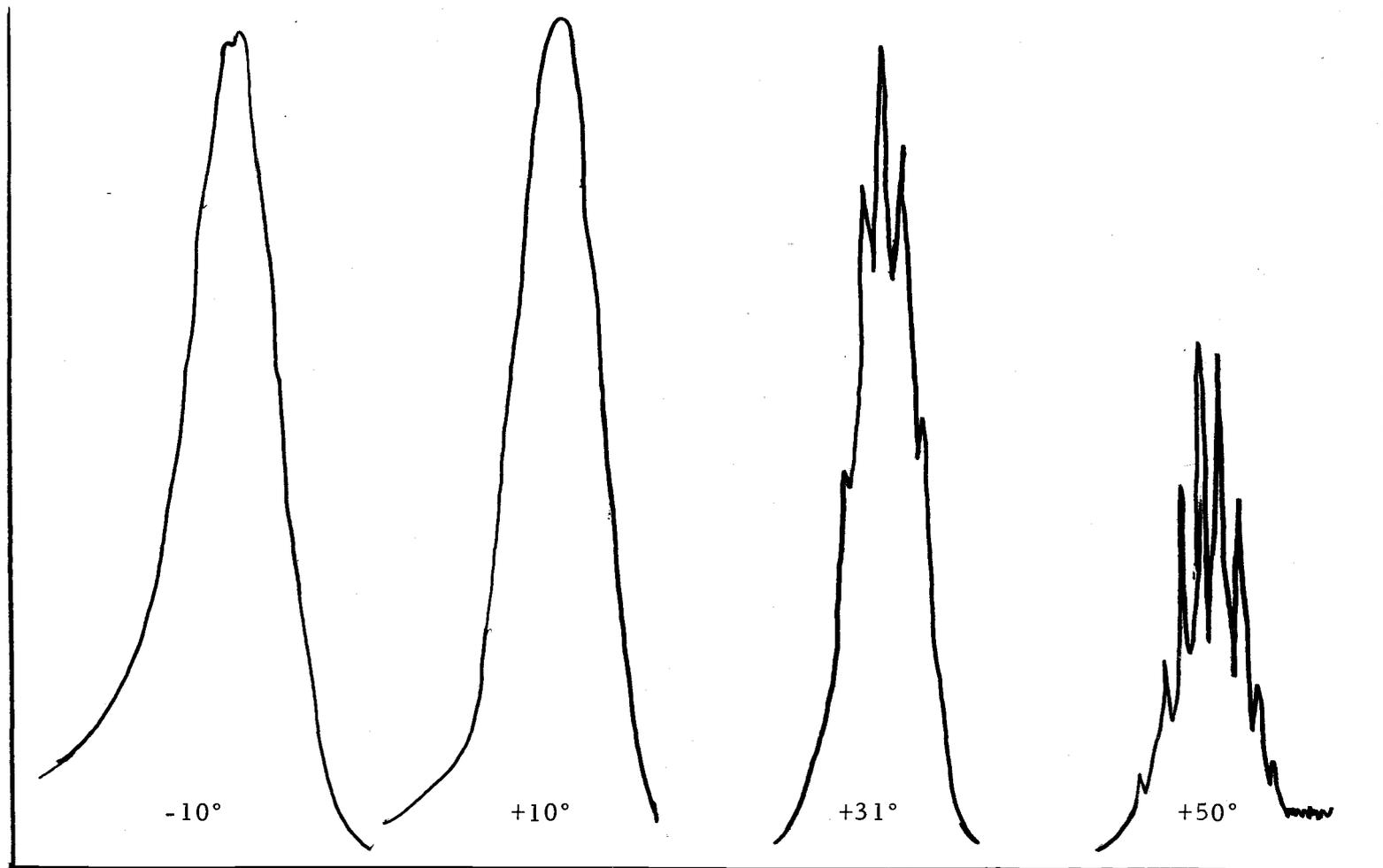


Figure 3. Temperature dependence of the ^{31}P nmr of a solution of CuCl in $(\text{C}_2\text{H}_5)_3\text{P}$ (mole ratio ca. 1:20).

B. System Copper(I) Chloride—Triethylphosphonium Chloride

Triethylphosphonium chloride and copper(I) chloride react, merely upon contact of the two white powders at room temperature under nitrogen, to produce yellow-green oils. The formal compositions of the oils vary with the mole ratios of the reactants. Three oils were prepared having mole ratios and formal compositions of 2:1, $[(C_2H_5)_3PH^+]_2[CuCl_3^{2-}]$, 1:1, $[(C_2H_5)_3PH^+][CuCl_2^-]$, and 1:2, $[(C_2H_5)_3PH^+][Cu_2Cl_3^-]$. The parent triethylphosphonium chloride and the three oils contain the same triethylphosphonium cation, $(C_2H_5)_3PH^+$, but the anions present are the chloride ion and the various chlorocuprate(I) species. This series of materials allows one to study the effect of the nature of the anion upon the cation.

The proton and ^{31}P nmr spectra were obtained for the four materials. The chemical shifts and values of the coupling constants J_{P-H} are given in Table III. The ^{31}P nmr chemical shift and the J_{P-H} coupling constant are relatively independent of the anion, and the values of J_{P-H} obtained from the ^{31}P nmr agree satisfactorily with those obtained from the proton spectra. The proton chemical shifts are more variable with changes in the anion. For the neat oils, the shift of \underline{CH}_3 varies from 2.04 to 2.24 δ , and of \underline{CH}_2 varies from 3.11 to 3.40 δ ; these are complex multiplets due to couplings with phosphorus and with the other protons. The corresponding shifts of

triethylphosphonium chloride are not comparable, as this solid salt was studied in chloroform solution. The shift of the widely split doublet P-H of triethylphosphonium chloride in chloroform (6.97δ) may be compared with that of triethylphosphonium dichlorocuprate(I) in chloroform (6.60δ). This comparison suggests that there is more hydrogen bonding to chloride ion than to the complex anion (70).

Table III. Nmr chemical shifts and coupling constants J_{P-H} for the system $CuCl-(C_2H_5)_3PHCl$.

	1H		^{31}P	
	δ	J_{P-H} (Hz)	ppm	J_{P-H}
$(C_2H_5)_3PHCl^a$	1.40, 2.64, 7.14	487	-20.5	489
$[(C_2H_5)_3PH^+]_2[CuCl_3^{-2}]^b$	2.06, 3.29, 7.56	487	-20.9	477
$[(C_2H_5)_3PH^+][CuCl_2^-]^b$	2.24, 3.40, 7.60	480	-21.5	480
$[(C_2H_5)_3PH^+][Cu_2Cl_3^-]^b$	2.04, 3.11, 7.31	482	-20.7	477

^aIn $CDCl_3$.

^bNeat.

The specific conductance of triethylphosphonium dichlorocuprate(I) as a neat oil at 25° was found to be $1.35 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Infrared and Raman spectra in the region $4000-625 \text{ cm}^{-1}$ of triethylphosphonium chloride and of the three oils are presented in Figure 4 and Figure 5 respectively. The spectra of the three oils are similar to those of triethylphosphonium chloride, with the exception of the region $2000-2500 \text{ cm}^{-1}$. This region corresponds to the P-H

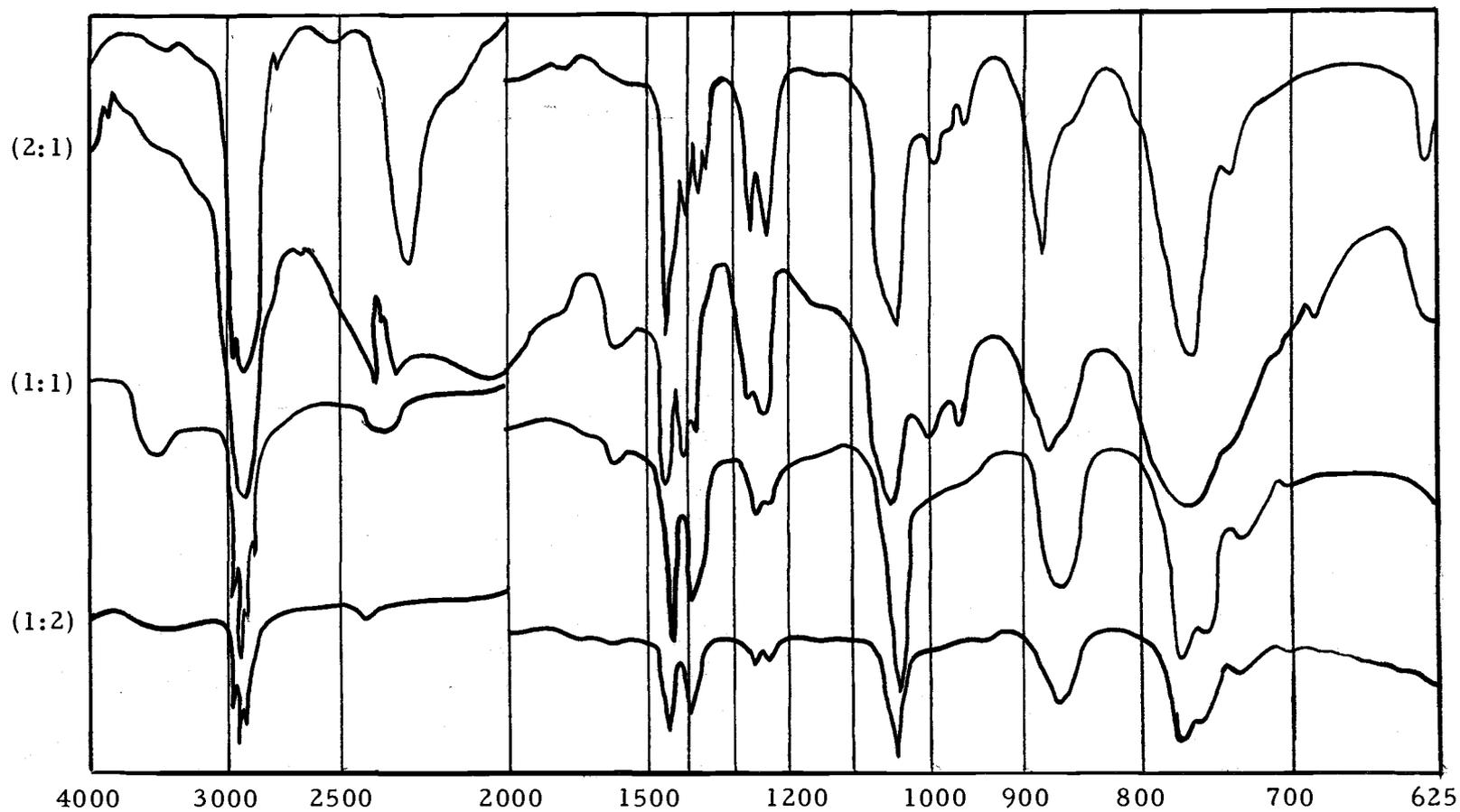


Figure 4. Infrared spectra (cm^{-1}) of $(C_2H_5)_3PHCl$ (top, Nujol mull) and of $(C_2H_5)_3PHCl-CuCl$ reaction products (neat oils, mole ratios as indicated).

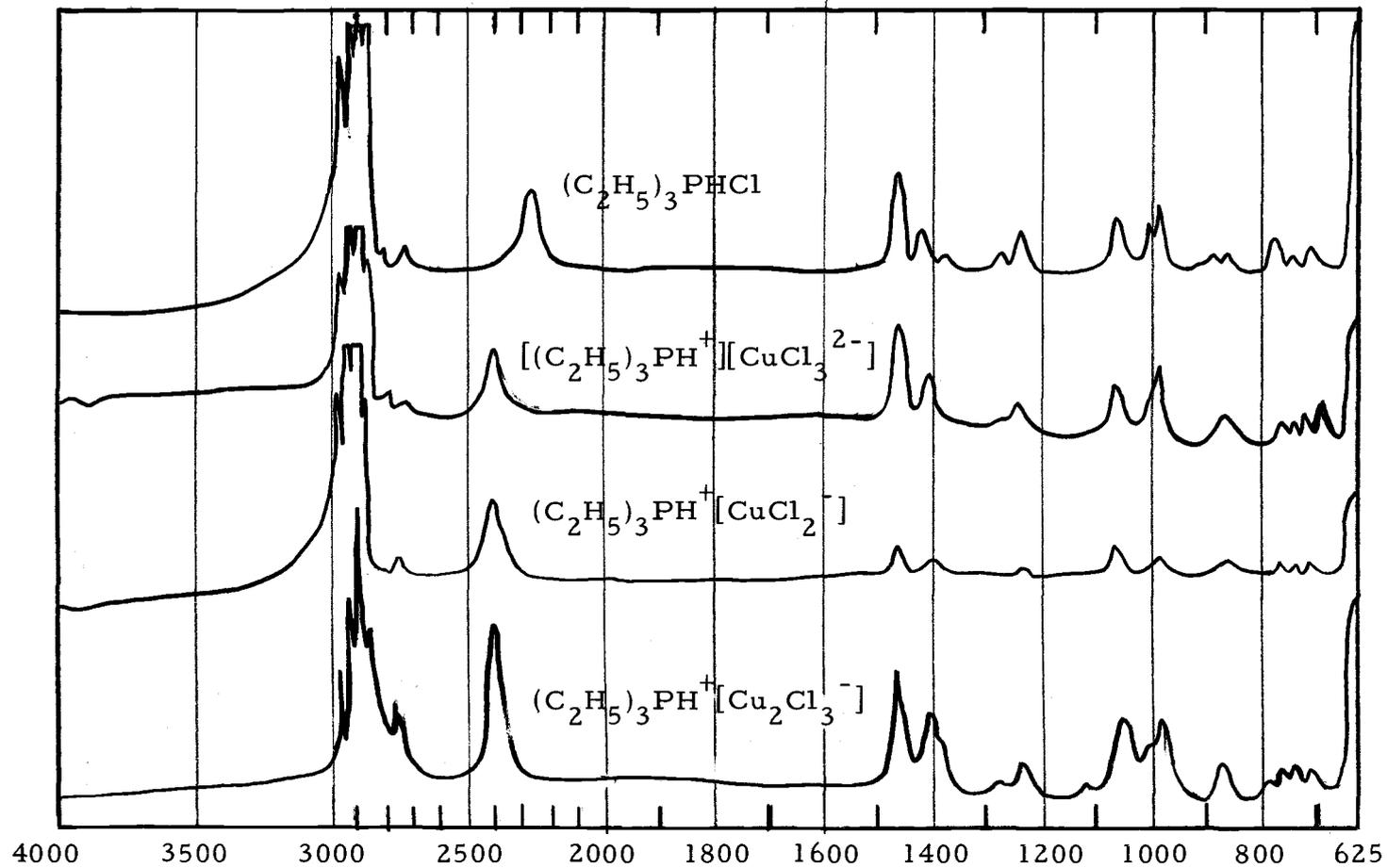


Figure 5. Raman spectra (Δcm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PHCl}$ (Nujol mull) and of triethylphosphonium chlorocuprate(I) oils.

frequency of the cation. Triethylphosphonium chloride has $\nu_{\text{P-H}}$ at 2275 cm^{-1} (ir) and 2287 cm^{-1} (Raman); (lit. (30), 2300 cm^{-1} (ir)). The frequency $\nu_{\text{P-H}}$ shifts to 2400 cm^{-1} for the oil of composition $[(\text{C}_2\text{H}_5)_3\text{PH}^+]_2[\text{CuCl}_3^{-2}]$, to 2370 cm^{-1} for the oil of composition $[(\text{C}_2\text{H}_5)_3\text{PH}^+][\text{CuCl}_2^-]$, and to 2430 cm^{-1} for the oil of composition $[(\text{C}_2\text{H}_5)_3\text{PH}^+][\text{Cu}_2\text{Cl}_3^-]$. This shift to higher frequencies indicates that there is much less hydrogen bonding of the triethylphosphonium cation to the complex anions than to the simple chloride anion. Similar results were obtained in the comparison of $[(\text{C}_6\text{H}_5)_3\text{PH}^+][\text{HCl}_2^-]$ with $(\text{C}_6\text{H}_5)_3\text{PHCl}$ made by van den Akker and Jellinek (30).

The $625\text{-}100 \text{ cm}^{-1}$ region of the far-infrared and the Raman spectra of the four materials are presented in Figure 6 and Figure 7 respectively. Frequencies attributable to the organic cation are common to all the spectra. Those additional absorptions seen in the chlorocuprate(I) spectra but not in the spectrum of the simple chloride may be attributed to the complex anion species. Thus, all four spectra show a strong carbon-phosphorus absorption about 630 cm^{-1} . Triethylphosphonium dichlorocuprate(I) has a strong Raman absorption at 302 cm^{-1} corresponding to the previously reported (49, 50) symmetric stretch ν_1 of a linear CuCl_2^- ion, and an infrared absorption at 410 cm^{-1} corresponding to the previously reported (48) asymmetric stretch ν_3 . The addition of chloride ion (giving the formal

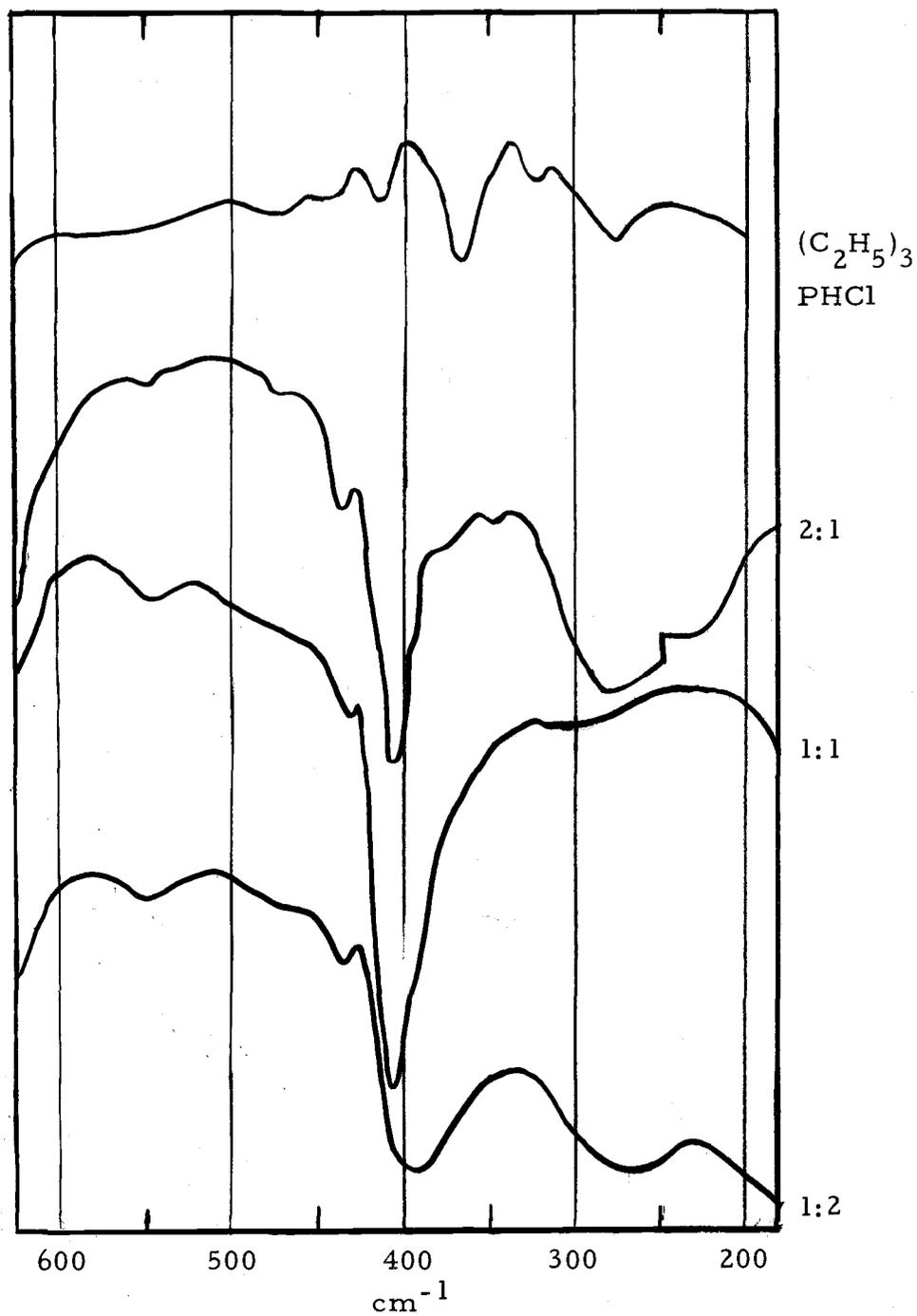


Figure 6. Far infrared spectra (cm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PHCl}$ (top, Nujol mull) and of $(\text{C}_2\text{H}_5)_3\text{PHCl-CuCl}$ reaction products (neat oils, mole ratios as indicated).

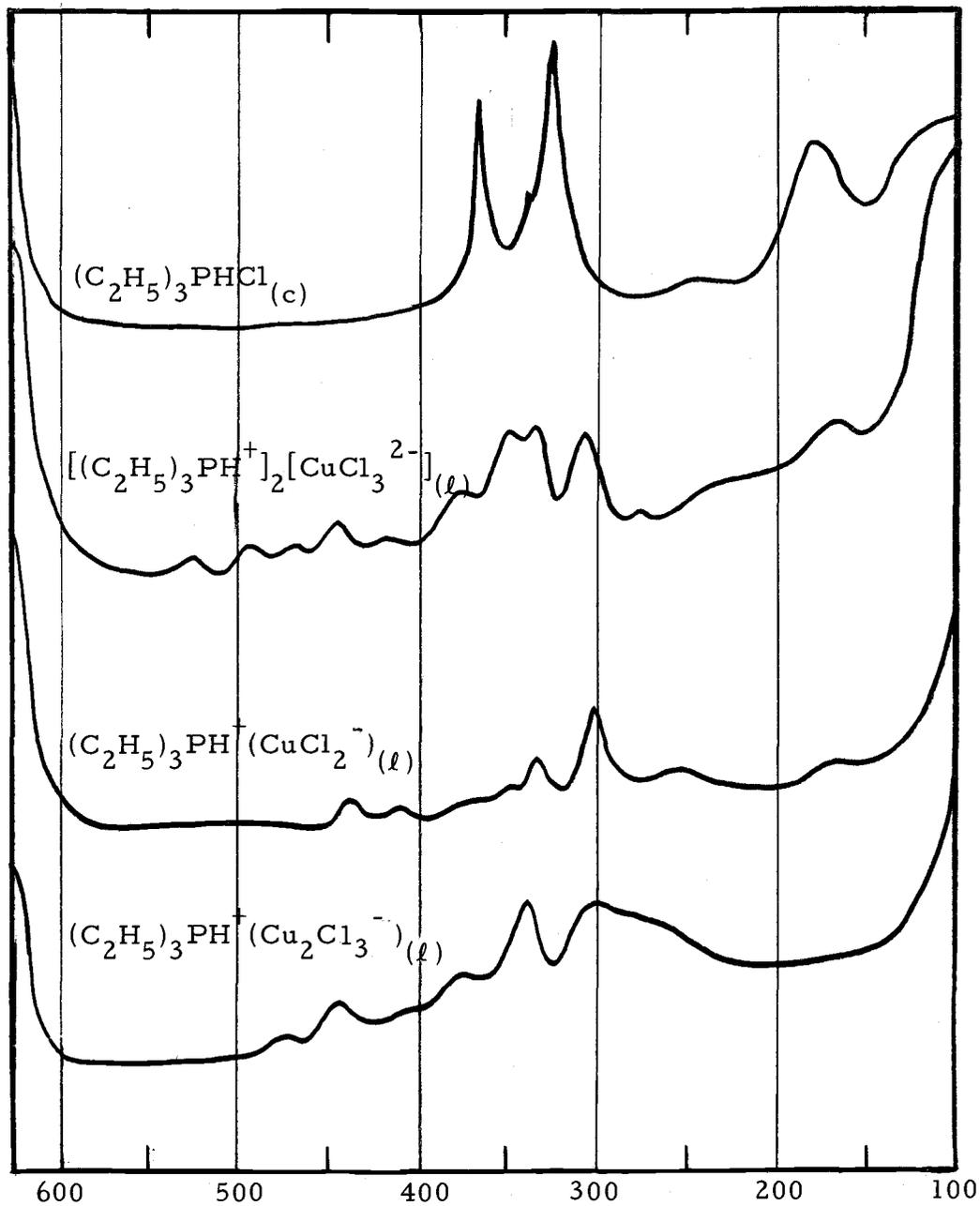


Figure 7. Raman spectra (Δcm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PHCl}$ and of triethylphosphonium chlorocuprate(I) oils.

composition $[(C_2H_5)_3PH^+]_2[CuCl_3^{2-}]$) or of copper(I) chloride (giving the formal composition $[(C_2H_5)_3PH^+][Cu_2Cl_3^-]$) does not lead to marked changes in the infrared ν_3 absorption at about 410 cm^{-1} , although there is considerable broadening in the latter case. The Raman spectra, especially in the ν_1 region of about 302 cm^{-1} show the greatest changes. For the oil of formal composition $[(C_2H_5)_3PH^+]_2[CuCl_3^{2-}]$, ν_1 is maintained as a sharp absorption. In addition, increased intensity is seen in the region $325\text{-}345\text{ cm}^{-1}$. For the oil formally containing the $Cu_2Cl_3^-$ anion, the 302 cm^{-1} absorption is greatly decreased, broadened, and shifted to lower frequencies.

C. System Triethylphosphonium Dichlorocuprate(I) — Triethylphosphine

The oil, triethylphosphonium dichlorocuprate(I), combines with an exactly equimolar amount of triethylphosphine to give white solid products. A material of identical composition, $(C_2H_5)_3PHCl \cdot CuCl \cdot P(C_2H_5)_3$, can be obtained by the removal of solvent in vacuo from an equimolar solution of triethylphosphonium chloride and chloro(triethylphosphine)copper(I) in acetonitrile. Solutions of the two samples in methylene chloride have nearly identical nmr spectra. Proton spectra are (δ) 1.30(m), 2.55(m), and 7.13(d, J_{P-H} 489 Hz) for the first, and (δ) 1.33(m), 2.55(m), and

7.14(d, $J_{\text{P-H}}$ 497 Hz) for the second. Phosphorus nmr spectra are +10.9(s), -19.6(d, $J_{\text{P-H}}$ 488 Hz) for the first, and +10.8(s), -20.1(d, $J_{\text{P-H}}$ 491 Hz) for the second.

The X-ray powder diffraction pattern of the first sample is given in Table IV, in comparison with the powder patterns of triethylphosphonium chloride and of chloro(triethylphosphine)copper(I). The corresponding powder patterns of the analogous amine system (triethylammonium chloride, chloro(triethylamine)copper(I), and the product of reaction of equimolar amounts of triethylammonium dichlorocuprate(I) and triethylamine) are given for comparison in Table V. The infrared spectrum of the white solid product from the reaction of triethylphosphonium dichlorocuprate(I) with an equimolar amount of triethylphosphine is given in Figure 8. When an excess of triethylphosphine is used in the reaction, and the excess amount is subsequently pumped off in the vacuum line, a different white solid product is obtained whose composition corresponds to the binding of three moles of triethylphosphine per mole of triethylphosphonium dichlorocuprate(I). The composition, therefore, is $(\text{C}_2\text{H}_5)_3\text{PHCl} \cdot \text{CuCl} \cdot 3\text{P}(\text{C}_2\text{H}_5)_3$. The infrared spectrum of this product is also given in Figure 8.

Table IV. X-ray powder diffraction data for triethylphosphonium chloride—copper(I) chloride—triethylphosphine systems.

d	Intensity ^a	d	Intensity ^a	d	Intensity ^a
$(C_2H_5)_3PHCl$					
8.23	vw	3.78	vs	2.47	w
7.44	s	3.37	s	2.26	w
5.34	s	2.86	m	2.14	m
4.74	vw	2.67	m	2.07	m
4.29	s				
$CuCl \cdot P(C_2H_5)_3$					
9.94	m	3.64	m	2.30	m
8.93	vs	3.49	vw	2.23	m
6.32	vw	3.14	s	2.16	w
5.71	w	2.96	s	2.10	m
5.13	vs	2.82	m	2.04	m
4.46	s	2.69	m	1.99	m
3.99	m	2.57	vs	1.94	m
3.84	vw	2.47	s	1.90	w
$[(C_2H_5)_3PH^+][CuCl_2^-] + (C_2H_5)_3P$					
9.87	w	3.14	s	2.21	vw
8.89	vs	2.96	s	2.10	w
5.15	s	2.82	vw	2.04	m
4.45	m	2.68	w	1.99	w
3.97	vw	2.46	m	1.94	w
3.63	m	2.29	w		

^a v = very, s = strong, m = medium, w = weak.

Table V. X-ray powder diffraction data for triethylammonium chloride—copper(I) chloride—triethylamine systems.

d	Intensity ^a	d	Intensity ^a	d	Intensity ^a
$(C_2H_5)_3NHCl$					
7.28	s	2.54	m	1.79	m
5.09	m	2.23	vw	1.75	vw
4.17	s	2.16	w	1.72	vw
3.57	s	2.08	m	1.62	w
3.21	s	1.98	w	1.58	vw
2.70	m	1.93	w		
$CuCl \cdot N(C_2H_5)_3$					
8.66	s	2.48	w	1.87	m
4.97	s	2.38	s	1.84	vw
4.32	m	2.22	w	1.75	vw
3.85	w	2.15	w	1.72	m
3.50	w	2.09	w	1.68	w
3.04	s	2.03	m	1.54	w
2.86	s	1.97	m	1.49	w
2.59	m	1.92	vw	1.31	vw
$[(C_2H_5)_3NH^+][CuCl_2^-] + (C_2H_5)_3N$					
8.69	s	3.05	m	2.09	w
7.34	m	2.87	m	2.03	w
4.99	m	2.70	m	1.97	w
4.24	m	2.38	m	1.87	vw
3.55	m	2.23	w	1.79	vw
3.21	m	2.15	w	1.72	vw

^a v = very, s = strong, m = medium, w = weak.

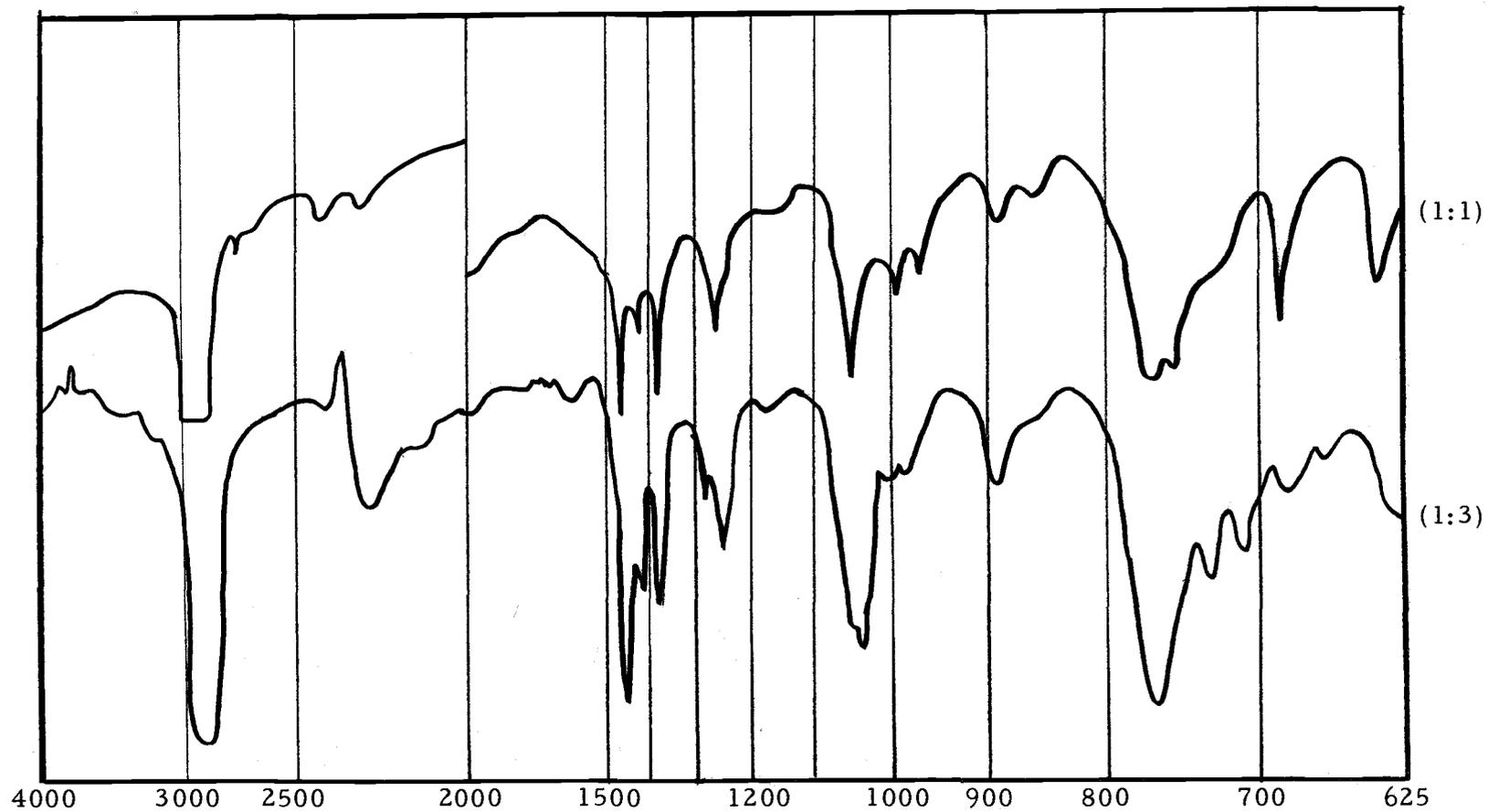


Figure 8. Infrared spectra (cm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PH}^+[\text{CuCl}_2^-]-(\text{C}_2\text{H}_5)_3\text{P}$ reaction products (Nujol mulls, mole ratios as indicated).

D. System Copper(I) Chloride – Triethylchlorophosphonium Chloride

Triethylchlorophosphonium chloride (triethyldichlorophosphorane) was exceedingly difficult to handle, due to its extreme sensitivity to moisture. Preliminary preparative work, in a good wooden drybox, led only to the isolation of the partial hydrolysis product, triethylchlorohydroxyphosphorane, which could also be obtained from triethylphosphine oxide and hydrogen chloride. It was not until a welded steel drybox was obtained, with an evacuable lock and fitted with an oxygen- and moisture-removing circulatory system for the nitrogen atmosphere, that this compound could be prepared, purified, and transferred.

The characterization of triethylchlorophosphonium chloride, by analysis, melting point, infrared, and proton and ^{31}P nmr spectra gave excellent agreement with the previous report of Spangenberg and Sisler (33). The infrared spectrum is shown in Figure 17. The far infrared spectrum is given in Figure 9. The Raman spectrum, which has not been previously reported is given in Figures 10 and 11. The proton nmr showed two multiplets at δ 1.45 and 3.35, and the ^{31}P nmr was a singlet at -110 ppm.

Triethylchlorophosphonium chloride and copper(I) chloride react upon contact of the two white powders under nitrogen to produce green oils of compositions determined by the mole ratios of the

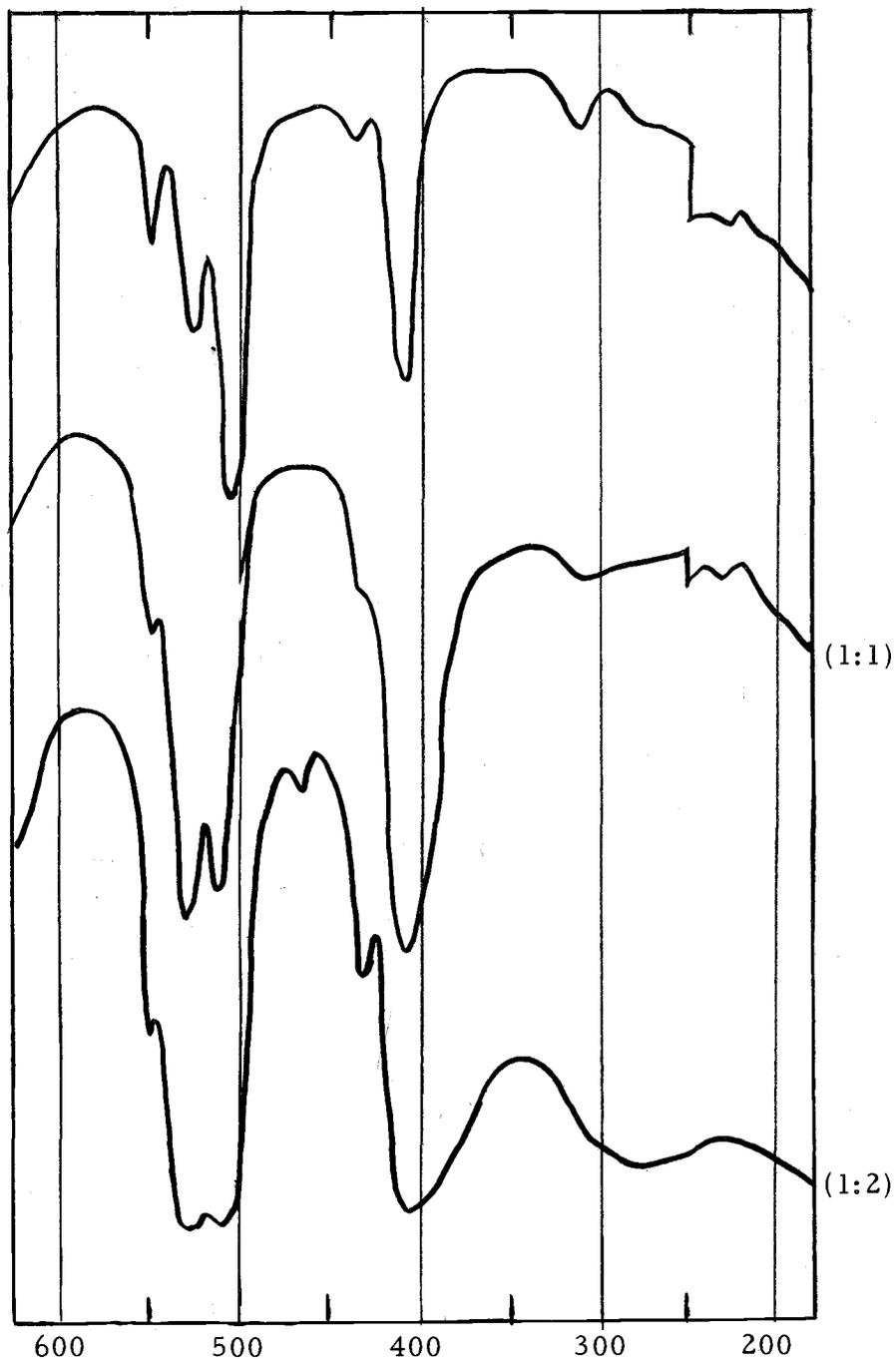


Figure 9. Far infrared spectra (cm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ (top, Nujol mull) and $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ - CuCl reaction products (neat oils, mole ratios as indicated).

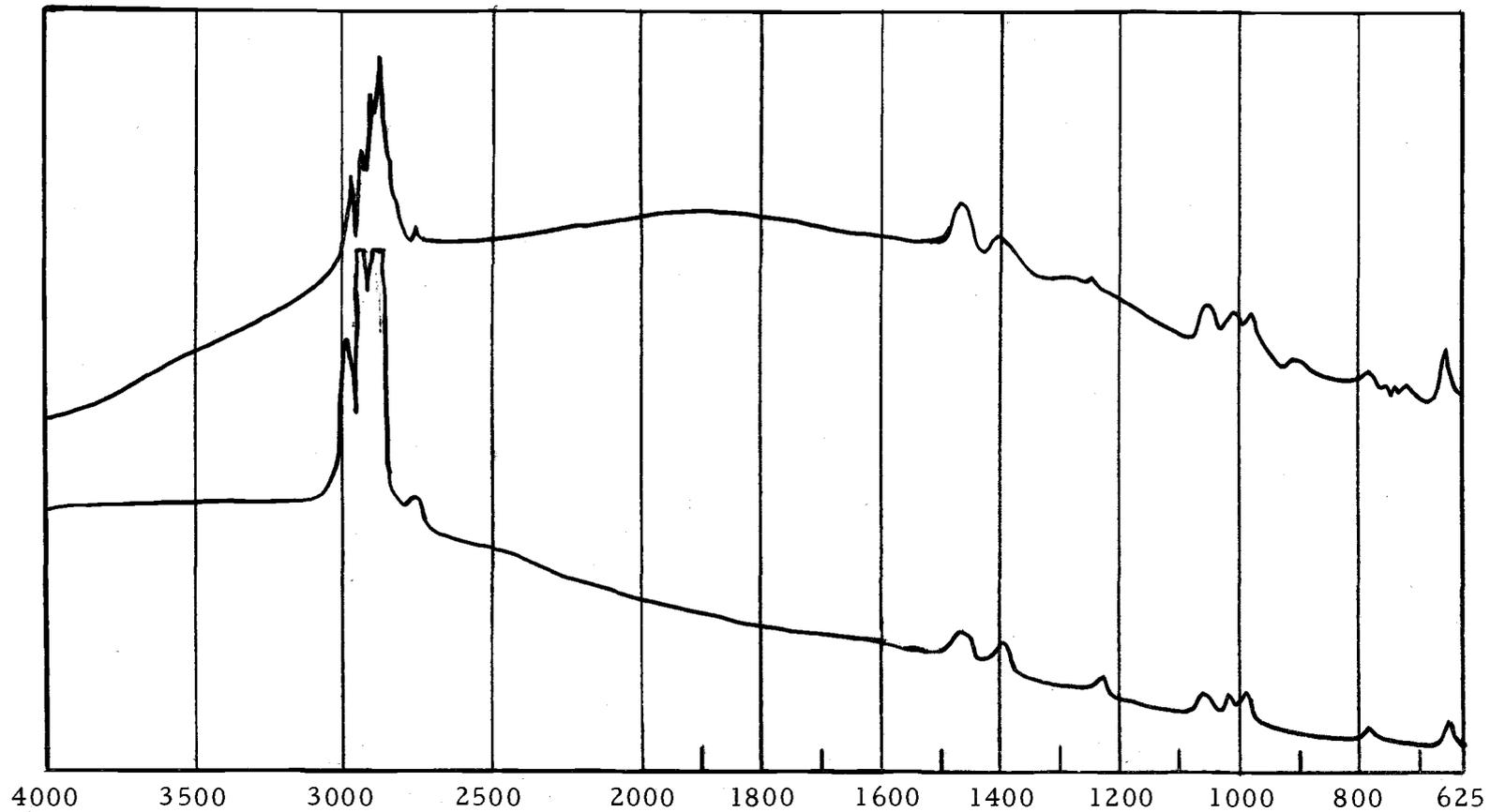


Figure 10. Raman spectra (Δcm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ (top, solid) and $(\text{C}_2\text{H}_5)_3\text{PCl}^+[\text{CuCl}_2^-]$ (neat oil).

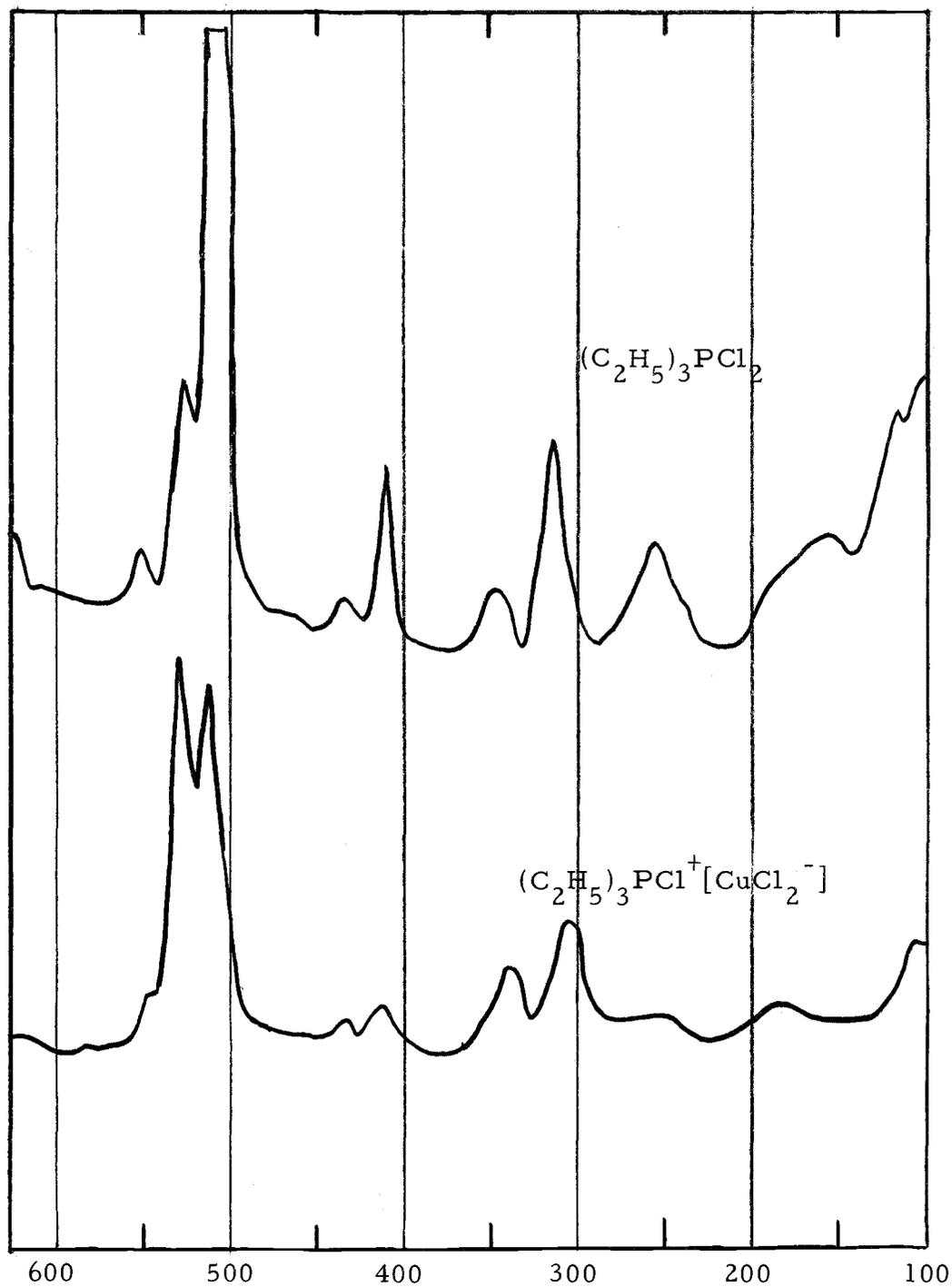


Figure 11. Raman spectra (Δcm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ (top, Nujol mull) and $(\text{C}_2\text{H}_5)_3\text{PCl}^+[\text{CuCl}_2^-]$ (neat oil).

reactants. Two oils were prepared having phosphorus:copper mole ratios and formal compositions of 1:1, $[(C_2H_5)_3PCl^+][CuCl_2^-]$, and 1:2, $[(C_2H_5)_3PCl^+][Cu_2Cl_3^-]$. The proton nmr of the latter as a neat oil consisted of two multiplets at δ 2.44 and 3.99, while the ^{31}P nmr was a singlet at -110 ppm. The infrared spectra (4000-625 cm^{-1}) of the two oils are given in Figure 12. The Raman spectrum of the light yellow-green $[(C_2H_5)_3PCl^+][CuCl_2^-]$ is given in Figures 10 and 11; that of the green-black oil $[(C_2H_5)_3PCl^+][Cu_2Cl_3^-]$ could not be obtained due to its thermal decomposition in the laser beam. The far-infrared spectra (625-180 cm^{-1}) of the triethylchlorophosphonium salts are given in Figure 9.

E. System Triethylchlorophosphonium Trichlorodicuprate(I) — Triethylphosphine

The results of an isothermal phase study of this system are shown in Table VI and Figure 13. They demonstrate the existence of two reaction products, having formal compositions $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 6P(C_2H_5)_3$ and $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 2P(C_2H_5)_3$ respectively. Materials having the compositions $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 2P(C_2H_5)_3$ and $(C_2H_5)PCl_2 \cdot 2CuCl \cdot 6P(C_2H_5)_3$ may also be obtained by the removal of solvent from mixtures of triethylchlorophosphonium chloride and two molar equivalents of either chloro(triethylphosphine)copper(I) or

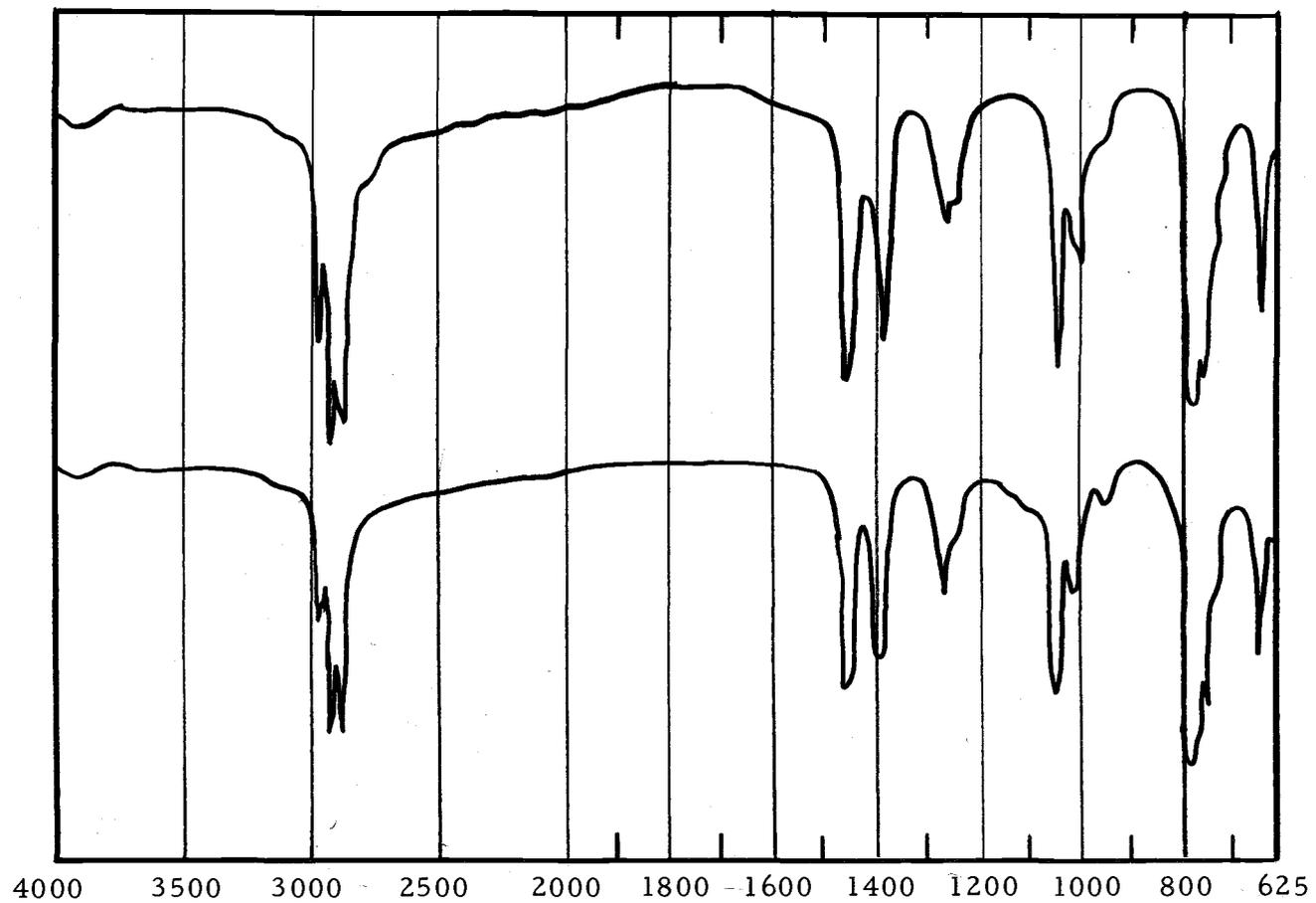


Figure 12. Infrared spectra (cm^{-1}) of $(C_2H_5)_3PCl^+[CuCl_2]^-$ (top) and $(C_2H_5)_3PCl^+[Cu_2Cl_3]^-$ (neat oils).

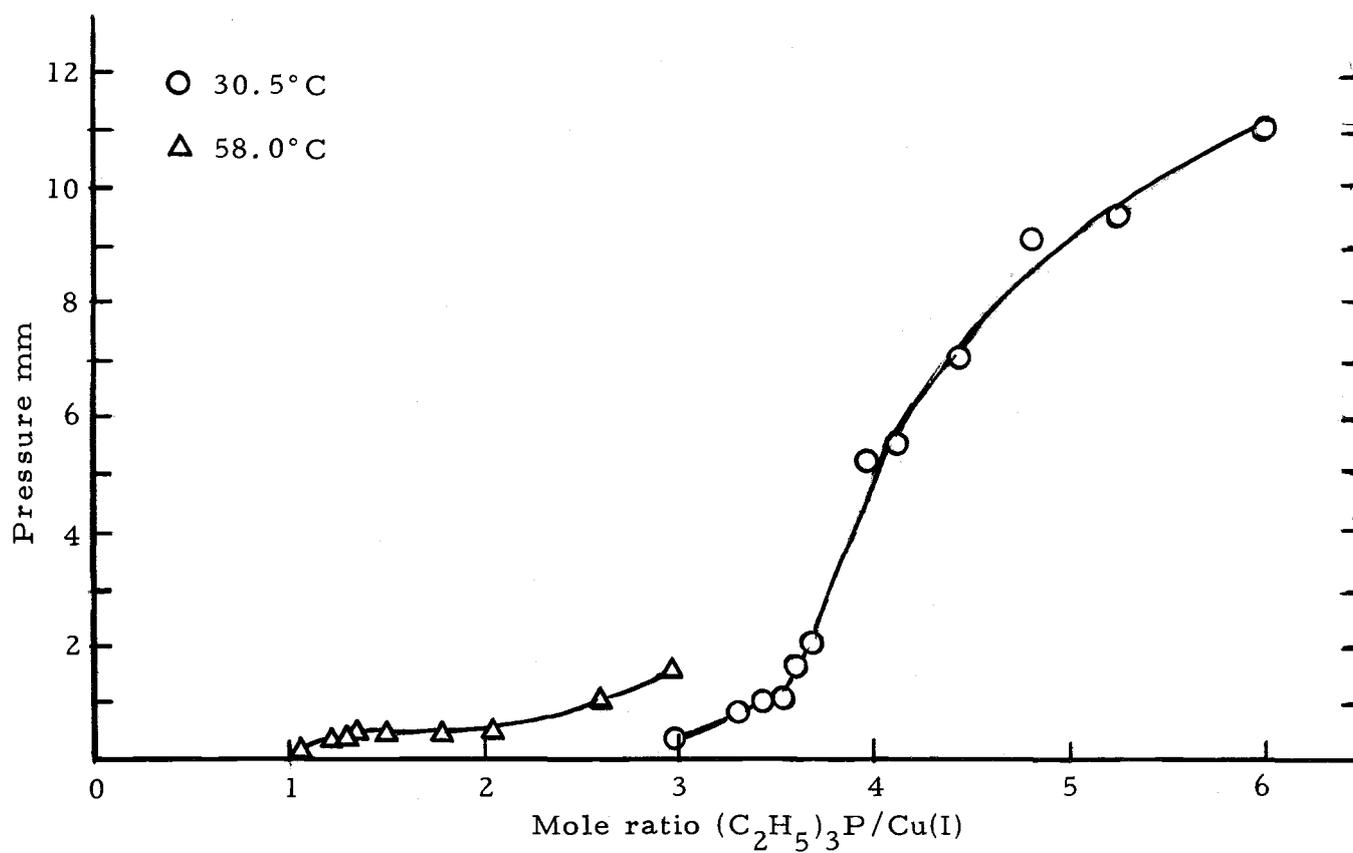


Figure 13. Isotherms for the system $(C_2H_5)_3PCl^+(Cu_2Cl_3^-) + (C_2H_5)_3P$.

chlorotris(triethylphosphine)copper(I) in acetonitrile. The materials obtained in this manner have infrared and far-infrared spectra identical to those of the reaction products obtained in the phase study. These spectra are presented in Figures 14 and 17 (infrared) and in Figure 15 (far-infrared). The Raman spectra are also nearly identical (Table VII). The Raman study was hindered by severe fluorescence.

Table VI. Pressure-composition data for the system, triethylchlorophosphonium trichlorodocuprate(I) —triethylphosphine.

	Mole Ratio (C ₂ H ₅) ₃ P/Cu(I)	Pressure mm
30.5°	6.00	11.0
	5.25	9.5
	4.81	9.0
	4.43	7.0
	4.11	5.5
	3.96	5.3
	3.68	2.0
	3.61	1.7
	3.52	1.0
	3.43	1.0
	3.31	1.0
	2.97	0.5
58.0°	2.97	1.5
	2.59	1.0
	2.04	0.5
	1.79	0.5
	1.50	0.5
	1.36	0.5
	1.28	0.3
	1.22	0.3
	1.03	0.1
	1.02	< 0.1

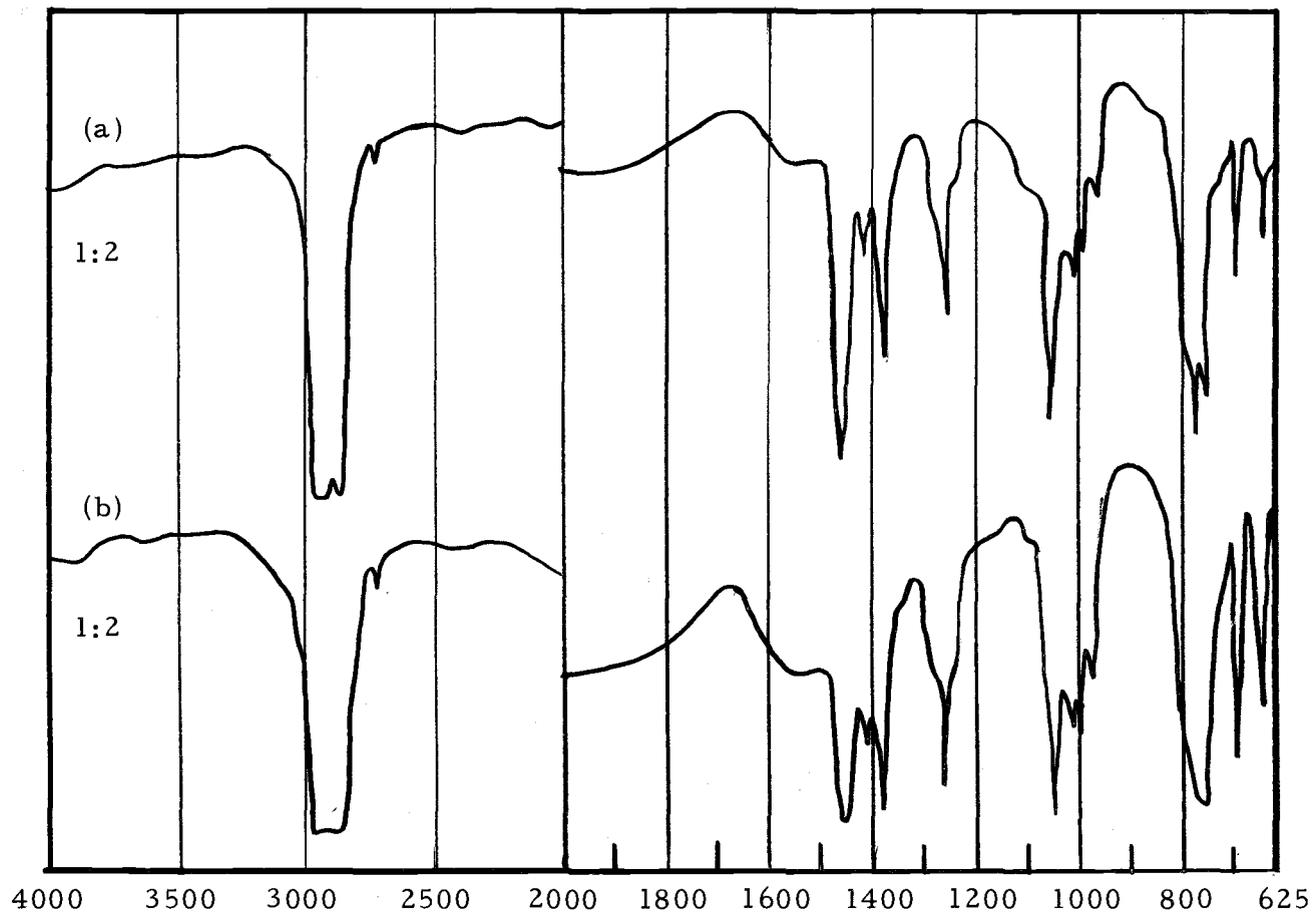


Figure 14. Infrared spectra (cm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PCl}_2\text{-CuCl-(C}_2\text{H}_5)_3\text{P}$ compositions (Nujol mulls, mole ratios as indicated). (a) From $(\text{C}_2\text{H}_5)_3\text{PCl}^+[\text{Cu}_2\text{Cl}_3^-]$ and $(\text{C}_2\text{H}_5)_3\text{P}$. (b) From $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ and $\text{CuCl}\cdot\text{P}(\text{C}_2\text{H}_5)_3$.

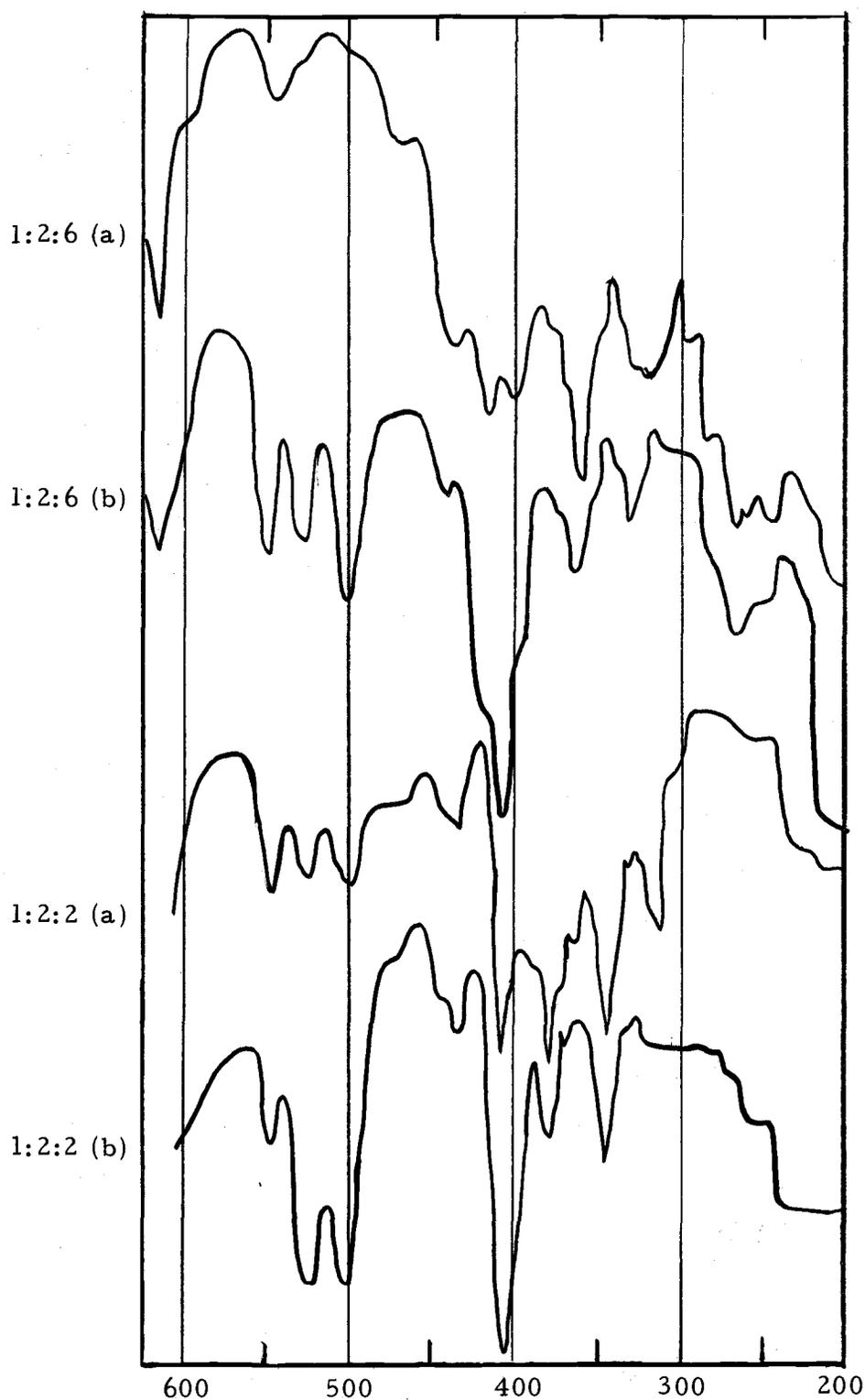


Figure 15. Far infrared spectra (cm^{-1}) of $(\text{C}_2\text{H}_5)_3\text{PCl}_2\text{-CuCl-}(\text{C}_2\text{H}_5)_3\text{P}$ compositions (Nujol mulls, mole ratios as indicated). (a) From $(\text{C}_2\text{H}_5)_3\text{PCl}^+[\text{Cu}_2\text{Cl}_3^-]$ and $(\text{C}_2\text{H}_5)_3\text{P}$. (b) From $(\text{C}_2\text{H}_5)_3\text{PCl}_2$ and $\text{CuCl-P}(\text{C}_2\text{H}_5)_3$ complexes.

Table VII. Raman spectra ($\Delta \text{ cm}^{-1}$) of triethylchlorophosphonium chloride—copper(I) chloride—triethylphosphine compositions.

Peak	Intensity ^a	Peak	Intensity ^a	Peak	Intensity ^a
$[(\text{C}_2\text{H}_5)_3\text{PCl}^+][\text{Cu}_2\text{Cl}_3^-] + 6(\text{C}_2\text{H}_5)_3\text{P}$ (1:2:6 composition)					
2963	m	1287	m	668	m
2929	s	1123	m	624	s
2903	s	1058	m	511	m
2886	s	1011	m	434	vw
1463	s	984	m	365	w
1423	m	974	m	335	m
1383	vw	711	m	317	w
1294	m	688	m		
$[(\text{C}_2\text{H}_5)_3\text{PCl}^+][\text{Cu}_2\text{Cl}_3^-] + 2(\text{C}_2\text{H}_5)_3\text{P}$ (1:2:2 composition)					
2960	m-s	1418	w	508	w-m
2935	s	1260	m	382	w
2900	s	1048	vw	355	m
2875	s	985	w	318	vw
2806	w	688	m	270	vvw
2736	w	638	m	110	w
1456	m	530	vw	60	s
$(\text{C}_2\text{H}_5)_3\text{PCl}_2 + 2 \text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ (1:2:2 composition)					
2965	m-s	1240	w	528	w
2936	s	1125	w-m	508	vs
2900	s	1060	w	442	vw
2877	s	1050	m	413	w
2821	vw	994	m-s	382	w-m
1458	m	980	m-s	357	m-s
1423	m	753	m	316	w
1384	w	690	vs	258	vw
1264	w	640	vs		

^a v = very, s = strong, m = medium, w = weak.

Nmr spectra of the various samples were obtained in deuteriochloroform solution. For the material of composition $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 2P(C_2H_5)_3$ prepared by the first method, 1H nmr (δ) 1.16(m), 1.57(m), 3.23(m); for the material of this composition prepared by the second method, 1H nmr (δ) 1.23(m), 1.60(m), 3.18(m); ^{31}P nmr -112 ppm. For the material of composition $(C_2H_5)_3PCl_2 \cdot 2CuCl \cdot 6(C_2H_5)_3P$ prepared by the first method, 1H nmr (δ) 1.10(m), 1.58(m), 3.31(m); ^{31}P nmr -112, +14.9 ppm; for the material of this composition prepared by the second method, 1H nmr (δ) 1.13(m), 1.60(m), 3.36(m); ^{31}P nmr +14.1 ppm.

F. The Oxidation—Reduction Reaction of Copper(II)
Chloride with Triethylphosphine

The results of an isothermal phase study of the system copper(II) chloride--triethylphosphine after the redox reaction had taken place to give colorless products, are given in Table VIII and Figure 16. The data are presented on a weight basis of the original reactants. The results indicate the existence of two stoichiometries for the reaction of these two compounds. These combining ratios correspond respectively to the reaction of 3.5 and 1.5 moles of triethylphosphine with one mole of copper(II) chloride.

Table VIII. Pressure-composition data for the system, copper(II) chloride—triethylphosphine (after oxidation—reduction).

	Mole Ratio (C ₂ H ₅) ₃ P/CuCl ₂ (original weight basis)	Pressure mm
27° C	12.05	12.5
	8.45	12.0
	6.10	11.0
	5.02	9.5
	4.40	8.0
	3.90	6.0
	3.78	3.0
	3.60	1.5
	3.55	1.0
	3.47	< 0.5
58° C	3.38	2.0
	2.60	1.5
	1.90	0.8
	1.60	0.5
	1.52	0.5
	1.48	0.3
	1.47	< 0.1

When neat triethylphosphine and copper(II) chloride are combined in exactly 3.5:1 molar proportions, an exothermic reaction occurs rapidly above -23°, yielding white solid products. The infrared spectrum (1600-625 cm⁻¹) of the reaction products is presented in Figure 17. The Raman spectrum (3000-625 cm⁻¹) is presented in Figure 18. The far-infrared and the Raman spectra (625-100 cm⁻¹) of the reaction products are given in Figure 19. Proton and ³¹P nmr spectra were obtained for a solution of the reaction products in

deuteriochloroform. The chemical shifts determined are ^1H nmr, (δ) 1.08(m), 1.57(m), 3.35(m); ^{31}P nmr, -112, +14.9 ppm.

The existence of a third combining ratio, not revealed in the phase study, was demonstrated by the reaction of triethylphosphine and copper(II) chloride in 0.5:1 molar proportions in benzene. The product of this reaction, after the removal of benzene in vacuo, was a viscous green-black oil. The infrared spectrum of this oil is given in Figure 20.

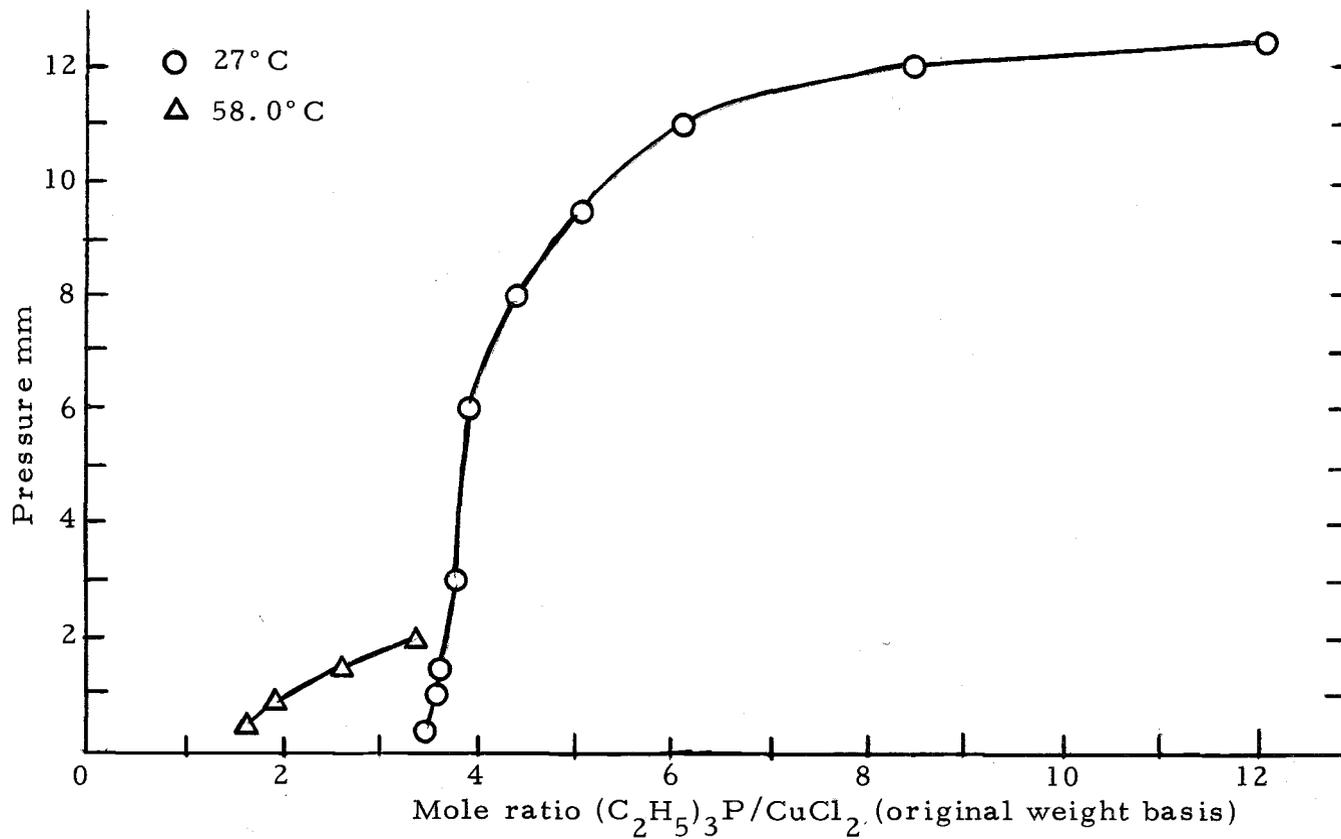


Figure 16. Isotherms for the system $CuCl_2 + (C_2H_5)_3P$ (after oxidation-reduction).

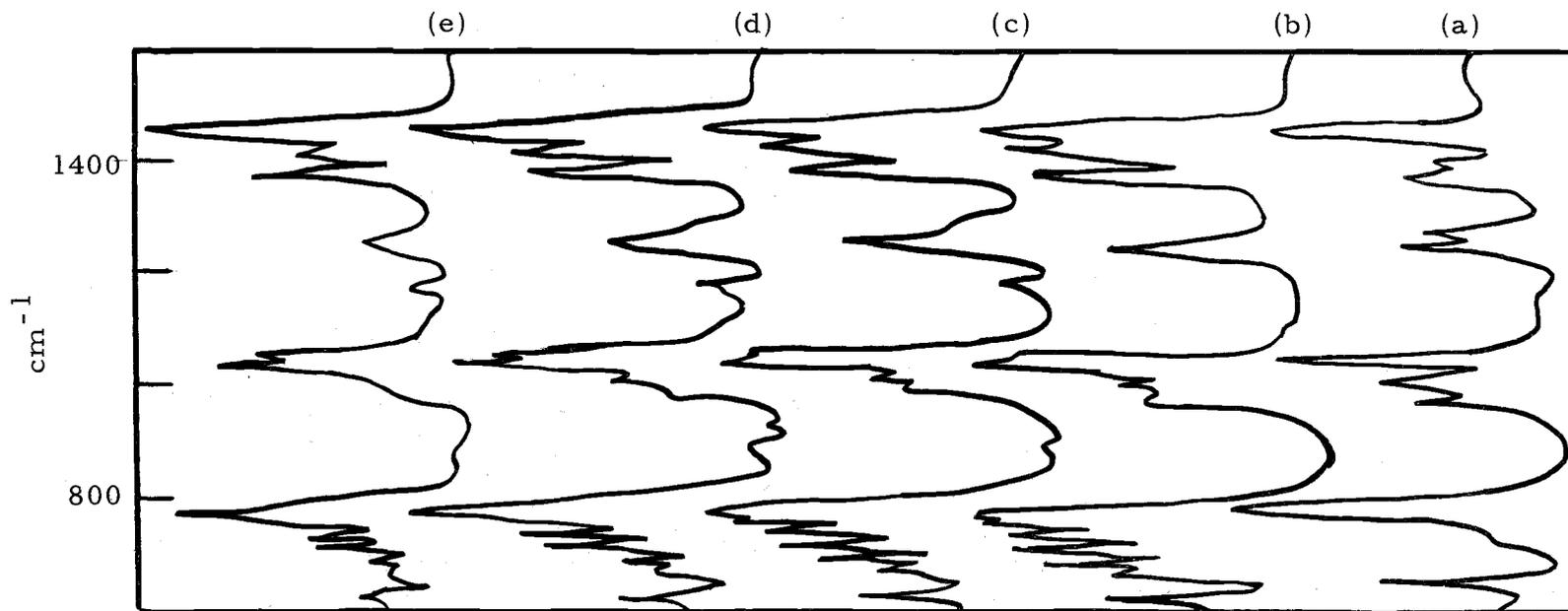


Figure 17. Infrared spectra (cm⁻¹, Nujol mulls) of (a) (C₂H₅)₃PCl₂ (b) CuCl · 3P(C₂H₅)₃ (c) (C₂H₅)₃P-CuCl₂ oxidation-reduction products (mole ratio 3.5:1) (d) (C₂H₅)₃PCl⁺[Cu₂Cl₃⁻]- (C₂H₅)₃P (mole ratio 1:6) and (e) (C₂H₅)₃PCl₂ · CuCl · 3P(C₂H₅)₃ (mole ratio 1:2).

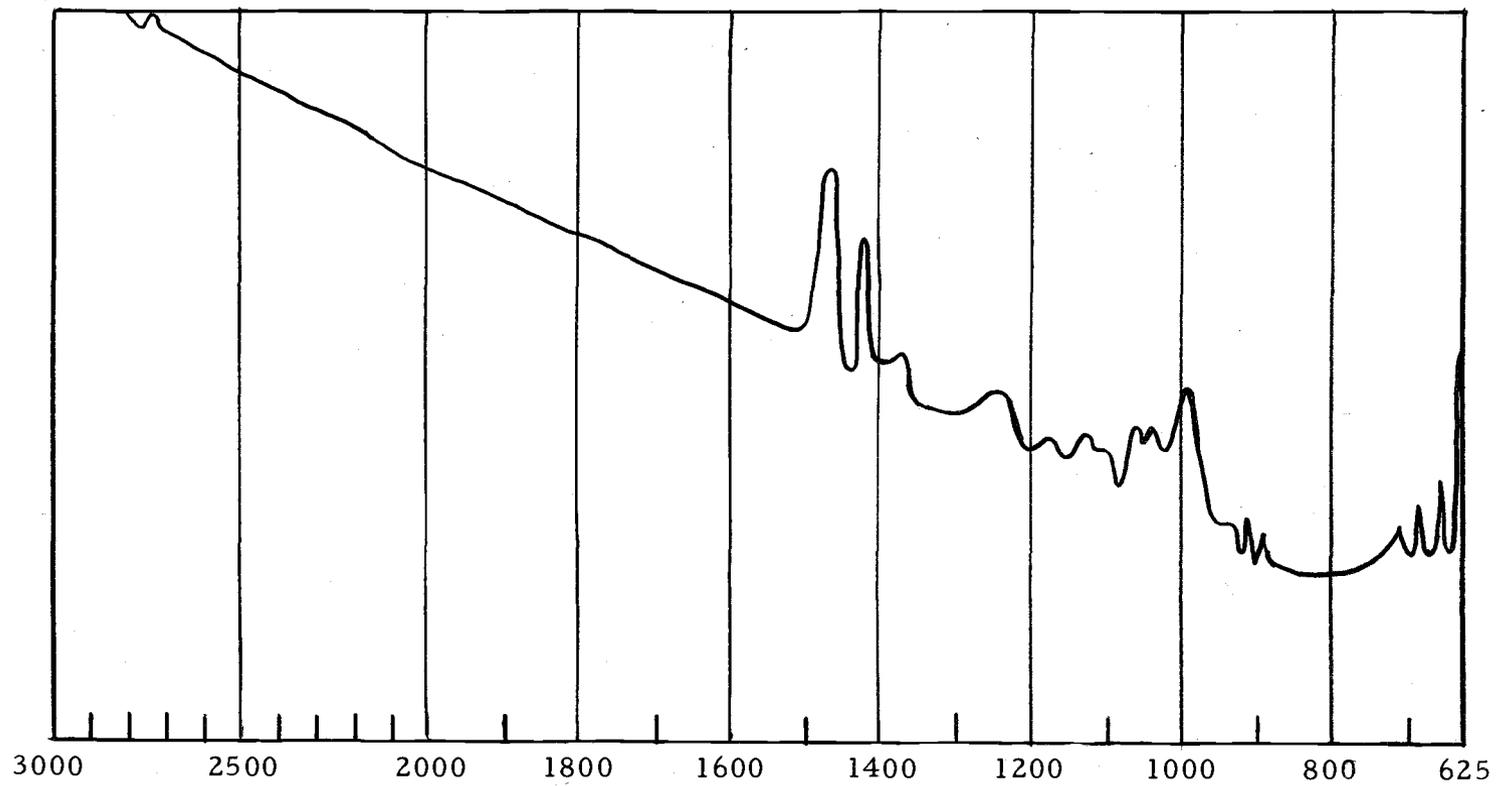


Figure 18. Raman spectrum (Δcm^{-1}) of the $(\text{C}_2\text{H}_5)_3\text{P}-\text{CuCl}_2$ oxidation-reduction products (mole ratio 3.5:1).

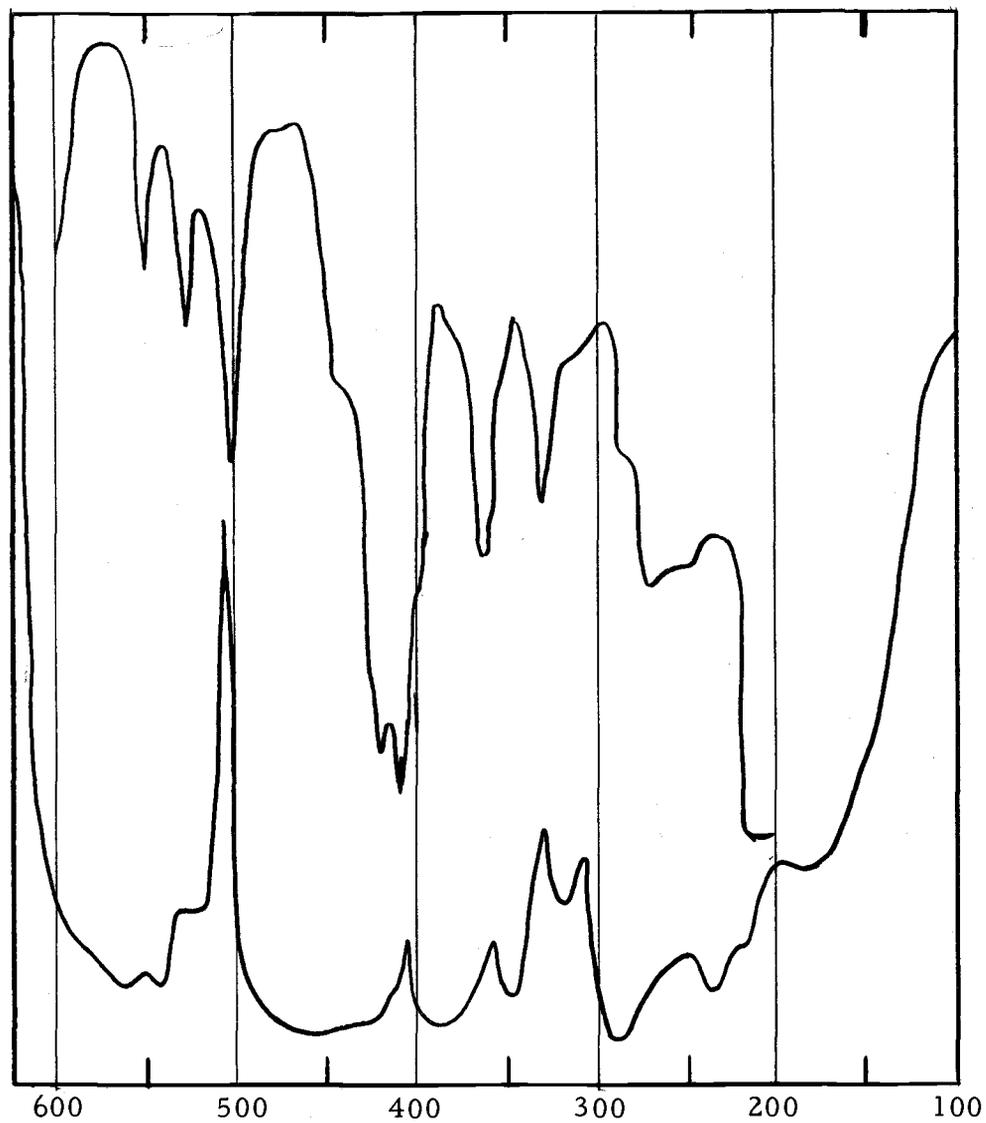


Figure 19. Far infrared (top, cm^{-1} , Nujol mull) and Raman (bottom, Δcm^{-1}) spectra of the $(\text{C}_2\text{H}_5)_3\text{P-CuCl}_2$ oxidation-reduction products (mole ratio 3.5:1).

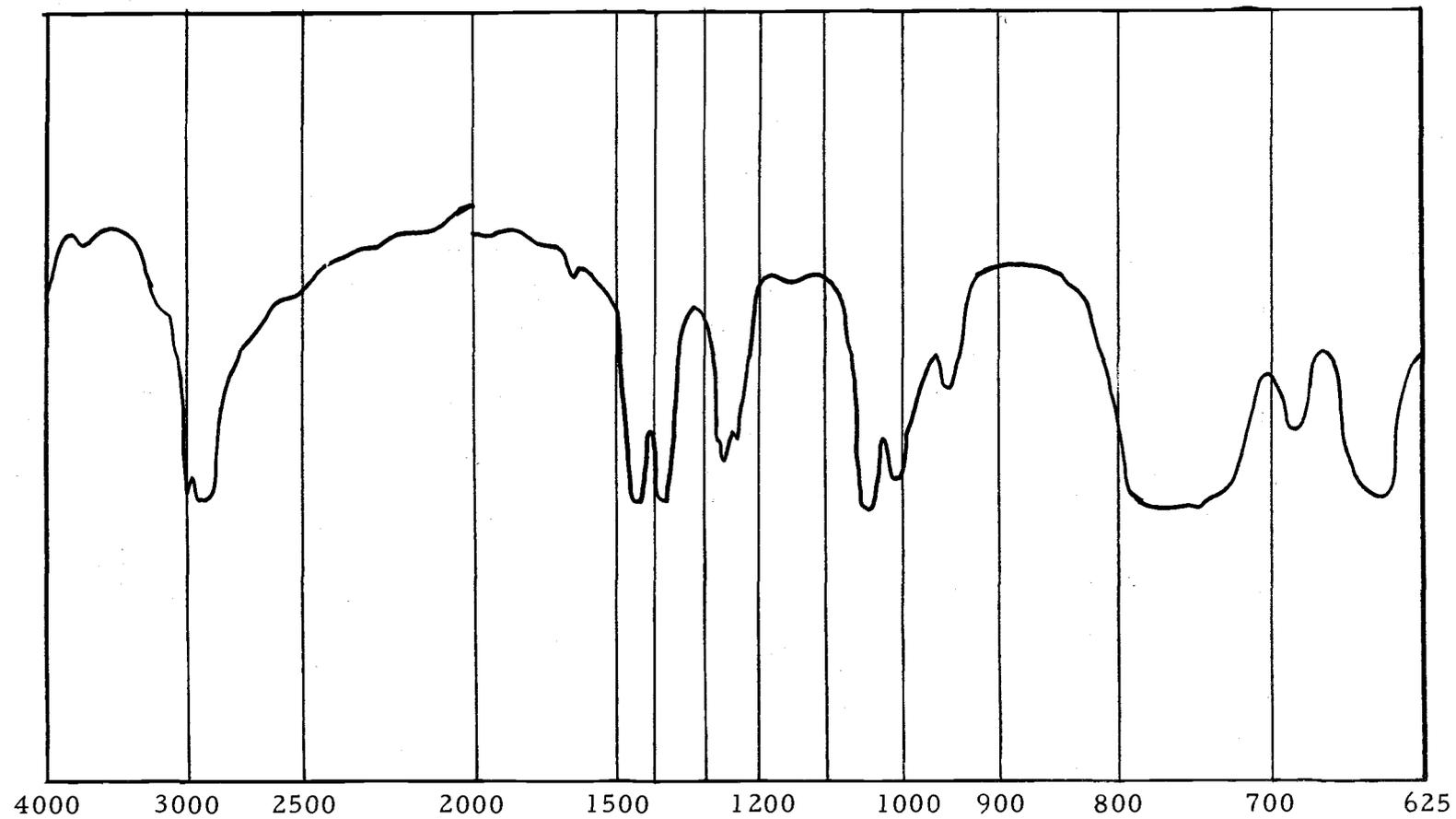
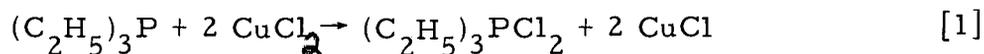


Figure 20. Infrared spectrum (cm^{-1}) of triethylphosphine-copper(II) chloride oxidation-reduction product (neat oil, mole ratio 0.5:1).

V. DISCUSSION

Mixtures of anhydrous copper(II) chloride and triethylphosphine undergo an exothermic oxidation-reduction reaction, slowly at -45° and more rapidly above -23° . Attempts to isolate a triethylphosphine-copper(II) coordination compound at a low temperature were unsuccessful. However, transient purple and brown colors were observed as frozen layers of triethylphosphine and of an ethanol solution of copper(II) chloride were allowed to thaw. This is indicative of an intermediate copper(II) complex.

The fundamental oxidation-reduction process is

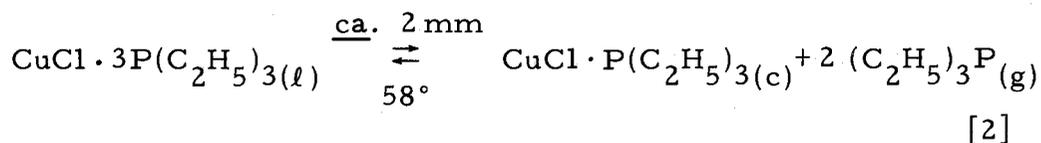


but these products then react with each other or with additional triethylphosphine. The reaction of triethylphosphine and copper(II) chloride in a 0.5:1 mole ratio yields a non-volatile, viscous dark green oil as the only reaction product. In contrast, the reaction between a large excess of triethylphosphine and copper(II) chloride yields colorless products. The volatile phosphine may then be easily removed in vacuo to a point corresponding to the retention of 3.5 moles of triethylphosphine per mole of copper(II) originally taken. The white solid material remaining at this point can be prepared more conveniently by starting with triethylphosphine and copper(II) chloride

in exactly 3.5:1 molar proportions. The resulting material will melt and lose part of its triethylphosphine content upon being heated to 58° and pumped on in vacuo. The final products after this treatment constitute a white solid in which 1.5 moles of triethylphosphine has been retained per mole of copper(II) originally taken.

The identification of the products of the copper(II) chloride-triethylphosphine oxidation-reduction reaction is based on comparison with the products of the reaction of copper(I) chloride, triethylphosphine, and triethylchlorophosphonium chloride. Such a comparison leads to an understanding of the triethylphosphine-copper(II) chloride combining ratios of 0.5:1, 1.5:1, and 3.5:1.

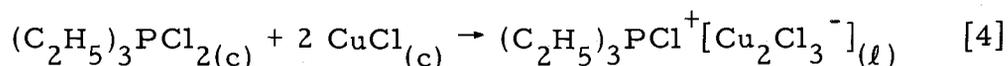
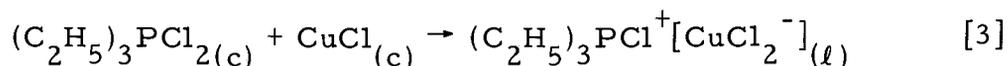
The reaction of copper(I) chloride with triethylphosphine yields two neutral complexes, chloro(triethylphosphine)copper(I), and chlorotris(triethylphosphine)copper(I). The complexes are related by the equilibrium



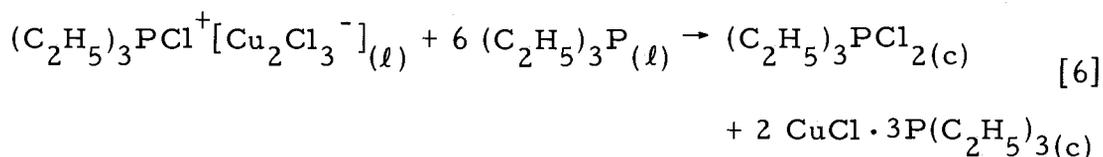
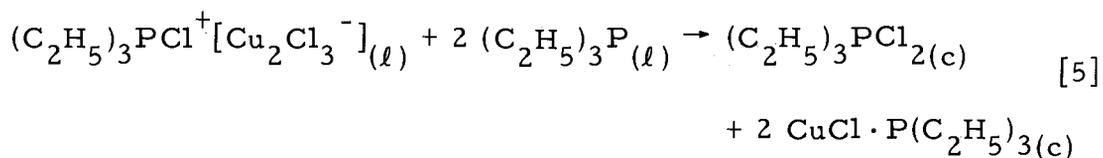
The complex $\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ is presumably tetrameric (8, 11, 12), while $\text{CuCl} \cdot 3\text{P}(\text{C}_2\text{H}_5)_3$ is presumably monomeric with four-coordinate copper(I) (8, 17). The infrared spectra of these compounds closely resemble those of free triethylphosphine. The large discrepancy between previously reported values of the melting point of

$\text{CuCl} \cdot \text{P}(\text{C}_2\text{H}_5)_3$ and that obtained in this work is no doubt due to the use of open capillary tubes by the earlier workers which would allow reaction with air.

Copper(I) chloride will react at room temperature under nitrogen with triethylchlorophosphonium chloride even in the absence of a solvent to produce compounds containing complex chlorocuprate(I) anions. The formal compositions depend on the mole ratios of the reactants used. Although these compounds are written with salt-like formulations, they are oils at room temperature.

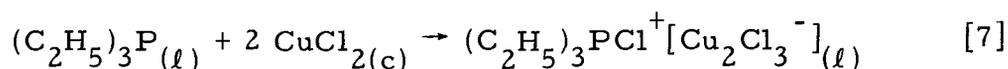


The dark green oil of composition $(\text{C}_2\text{H}_5)_3\text{PCl}^+[\text{Cu}_2\text{Cl}_3^-]$ reacts stoichiometrically with triethylphosphine by nucleophilic displacement, giving triethylchlorophosphonium chloride and the neutral triethylphosphine-copper(I) chloride complexes.

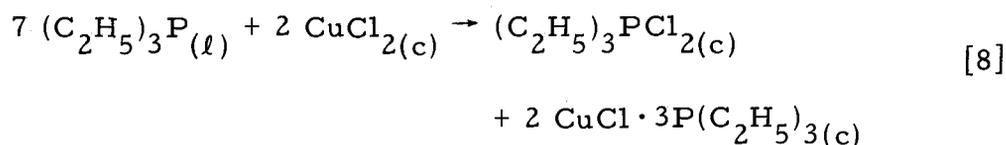


The infrared spectra of the reaction products (Figures 14, 17) are the sum of the spectra of triethylchlorophosphonium chloride and the neutral copper(I) complexes.

The products of the copper(II) chloride-triethylphosphine oxidation-reduction reaction can now be identified. Thus, when one-half mole of triethylphosphine is used per mole of copper(II) chloride, the product is a non-volatile, viscous green-black liquid corresponding to the sum of reactions [1] and [4].



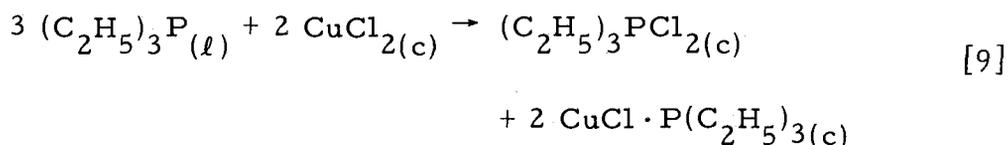
When an excess of triethylphosphine is used, and the unreacted amount is then pumped off, 3.5 moles of triethylphosphine are retained in the white solid per mole of copper(II) chloride used, corresponding to the sum of reactions [6] and [7].



A mixture of this composition can be prepared three ways: (a) by the oxidation-reduction reaction [8], (b) by the nucleophilic displacement reaction [6], (c) by the removal of solvent from an acetonitrile solution of the authentic components of the mixture in the exact molar proportions. The proton and ^{31}P nmr spectra of these preparations

are very nearly identical. The ^{31}P nmr clearly show the $(\text{C}_2\text{H}_5)_3\text{PCl}^+$ and the coordinated $(\text{C}_2\text{H}_5)_3\text{P}$ species. The infrared spectra ($1600\text{-}625\text{ cm}^{-1}$), shown in Figure 17 are identical and correspond to the sum of the spectra of triethylchlorophosphonium chloride and chlorotris(triethylphosphine)copper(I).

Additional triethylphosphine can be pumped from the above oxidation-reduction products at 58° . This corresponds to reaction [2], and gives a final mixture retaining 1.5 mole of triethylphosphine per mole of copper(II) originally used. Therefore, a third equation can be written for the oxidation-reduction reaction, corresponding to the sum of reactions [5] and [7].



One can suppose a catalytic cycle for the autoxidation of triethylphosphine, based on re-oxidation of the copper(I) species with oxygen and complete hydrolysis of triethylchlorophosphonium chloride to triethylphosphine oxide. The liquid chlorocuprate(I) salts, in particular, are very sensitive to oxygen. Such a process, based on the intermediate oxidation of triethylphosphine by copper(II) chloride, is in interesting contrast to the cobalt(II) chloride-catalyzed triethylphosphine autoxidation previously studied by Schmidt (26). In that

system, the mechanism involved formation of an intermediate O_2 adduct of the stable cobalt(II) chloride-triethylphosphine complex.

There is no evidence for an alkyl group dehydrogenation mechanism in the copper(II) chloride oxidation of triethylphosphine. This is in sharp contrast to the oxidative pathway previously reported for the ethylamines.

The triethylchlorophosphonium dichlorocuprate(I) and trichlorodocuprate(I) oils are additional examples of room temperature "fused salts" based on chlorocuprate(I) complex anions. The first example was the triethylammonium dichlorocuprate(I) of Weiss (22). Other examples based on organic ammonium salts have been prepared in conjunction with this work by Porterfield (42) and by Porterfield and Good (51), and include N-ethylpiperidinium, tri-n-butylammonium, and tri-n-octylammonium dichlorocuprates(I). These contrast with the mono-, di-, tri-, and tetra-methylammonium, the mono-, di-, and tetra-ethylammonium, and the quinuclidinium salts, which are solids and are prepared by crystallization from a solvent. For these, such melting points as have been recorded are in excess of 100° .

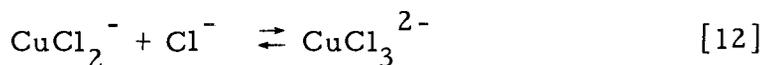
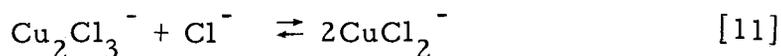
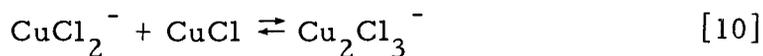
In addition to its reaction with triethylchlorophosphonium chloride, $(C_2H_5)_3PCl^+Cl^-$, copper(I) chloride will also react in the absence of a solvent with triethylphosphonium chloride,

$(C_2H_5)_3PH^+Cl^-$, to give similar "fused salts" at room temperature.

Oils of formal compositions $[(C_2H_5)_3PH^+]_2[CuCl_3^{2-}]$,

$(C_2H_5)_3PH^+[CuCl_2^-]$, and $(C_2H_5)_3PH^+[Cu_2Cl_3^-]$ have been prepared. The low-frequency vibrational spectra of these oils give information relevant to the actual nature of the complex anions, after absorptions due to the cations have been identified. The anion Raman spectra presented here have all been normalized to constant intensity of the strong C-P absorption at $625-636\text{ cm}^{-1}$, and the spectrum of triethylphosphonium chloride then subtracted. (The corresponding spectra of the triethylchlorophosphonium compounds are not useful in this regard, due to severe cation interferences with the anion frequencies of interest.) The conclusions based on study of the triethylphosphonium compounds are supported by similar studies on the alkylammonium chlorocuprates(I) made by Porterfield (42) and by Porterfield and Good (51).

The results of the low-frequency infrared and Raman studies may be discussed in terms of a complex equilibrium system in which a chloride ion transfer mechanism is operative:



Taking the oils of formal anionic composition $CuCl_2^-$ as a starting point, systems containing additional copper(I) chloride (a chloride ion

acceptor) are "chloride-poor," and mixtures containing added chloride ion are "chloride-rich."

In good agreement with the assignments of the previous workers (48, 49, 50) for a linear dichlorocuprate(I) ion, the spectra of triethylphosphonium dichlorocuprate(I) show ν_3 at 410 cm^{-1} (infrared) and ν_1 at 302 cm^{-1} (Raman). The ν_3 absorption is not greatly affected in either the chloride-rich or chloride-poor systems, although there is considerable broadening and overlap with a cation absorption in the latter case. The ν_1 frequency in the Raman spectrum (Figure 21) is very greatly affected, however. It is maintained in the chloride-rich system (Equation 11), with some increased intensity in the $320\text{-}345 \text{ cm}^{-1}$ region possibly due to some CuCl_3^{2-} species in the oil of this formal composition (Equation 12). In the chloride-poor system (Equation 10), the 302 cm^{-1} absorption is greatly decreased, broadened, and shifted to lower frequency, presumably due to the formation of Cu_2Cl_3^- (and possibly higher polynuclear complexes) in the oil of this formal composition.

A Cu_2Cl_3^- ion may be expected to have C_{2v} symmetry, with linear bonds Cl-Cu-Cl at two-coordinate copper(I) and a bent geometry Cu-Cl-Cu due to the lone pairs on the bridging chloride. The very broad and unresolved absorption in the region $240\text{-}310 \text{ cm}^{-1}$ may be attributed to dinuclear (and possibly polynuclear) species. The terminal chloride-metal stretch in such species is apparently little changed

from the ν_3 frequency of CuCl_2^- , though significantly broadened.

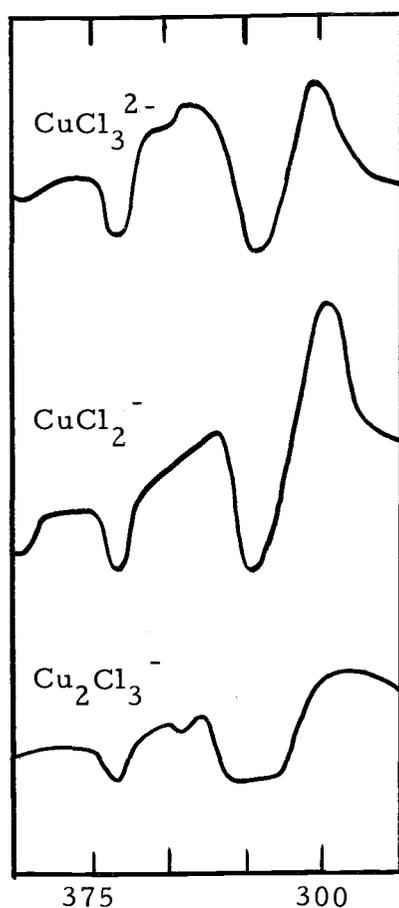


Figure 21. Anion Raman spectra (Δcm^{-1}) of triethylphosphonium chlorocuprates(I).

Comparing the cations which give room temperature liquid chlorocuprate(I) salts with those which give solids, it appears that trialkyl (ethyl or larger) substitution in the phosphonium or ammonium ion is important. A steric effect on the lattice energy may be significant. A major factor stabilizing the liquid state in the room temperature oils is the melting point depression of mixed species, arising

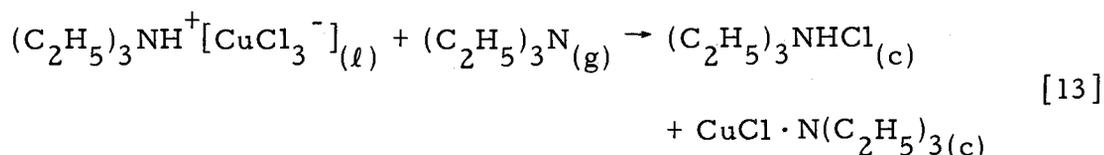
through the operation of Equations 10-12. The various chlorocuprate(I) oils are viscous and form glasses on cooling. The specific conductance ($\text{ohm}^{-1} \text{cm}^{-1}$) of neat triethylphosphonium dichlorocuprate(I) at 25° , 1.35×10^{-2} , may be compared with 3.84×10^{-3} for neat triethylammonium dichlorocuprate(I) at 25° (42), 3.27 for molten copper(I) chloride at 430° (71), and 2.77×10^{-3} for 0.02M aqueous potassium chloride at 25° .

Although the liquid chlorocuprate(I) oils are very sensitive to oxygen, and darken rapidly if protection is inadequate, their yellow-to-green color is not due to contamination with copper(II) species. As has been shown by Porterfield (42) for triethylammonium dichlorocuprate(I), and by Russian workers (72) for aqueous chlorocuprate(I) species, the visible absorption is the tail of an intense ultraviolet band, which shifts to higher wavelengths in the more highly condensed species. That the green-black oil of composition $(\text{C}_2\text{H}_5)_3\text{PCl}^+[\text{Cu}_2\text{Cl}_3^-]$ is by far the darkest of all the chlorocuprate(I) oils studied suggests that in it the equilibrium lies farthest on the side of di- and poly-nuclear complexes.

The triethylchlorophosphonium chlorocuprate(I) oils are cases where there can be no cation-anion hydrogen bonding. However, hydrogen bonding can occur in triethylphosphonium (and -ammonium) systems, and may play a role in the reduction of the symmetry of the complex anions. The large shift to higher frequency of the

triethylphosphonium $\nu_{\text{P-H}}$ frequency passing from the simple chloride salt to the oils with complex chlorocuprate(I) anions demonstrates that there is much less hydrogen bonding in the oils. Comparison of the ^1H nmr chemical shifts of the cation acidic proton in $(\text{C}_2\text{H}_5)_3\text{PHCl}$ and in $(\text{C}_2\text{H}_5)_3\text{PH}^+[\text{CuCl}_2^-]$ leads to the same conclusion. In comparable alkylammonium systems (51), hydrogen bonding in the chlorocuprate(I) oils has been found to be intermediate between that in chlorides and in tetraphenylborates. The greater anion perturbation in the nitrogen systems is also indicated by the Raman activity of the $\nu_3 \text{CuCl}_2^-$ frequency, which was not observed in the phosphorus systems.

The reaction of triethylphosphonium dichlorocuprate(I) with triethylphosphine is more complicated than is the reaction of triethylchlorophosphonium dichlorocuprate(I) with triethylphosphine (Equations 5 and 6) or the reaction of triethylammonium dichlorocuprate(I) with triethylamine, previously reported by Weiss (43)



That the products of reaction [13] are as shown is demonstrated by the X-ray diffraction pattern of the reaction mixture (Table V and Figure 22), which corresponds to the sum of the powder patterns of

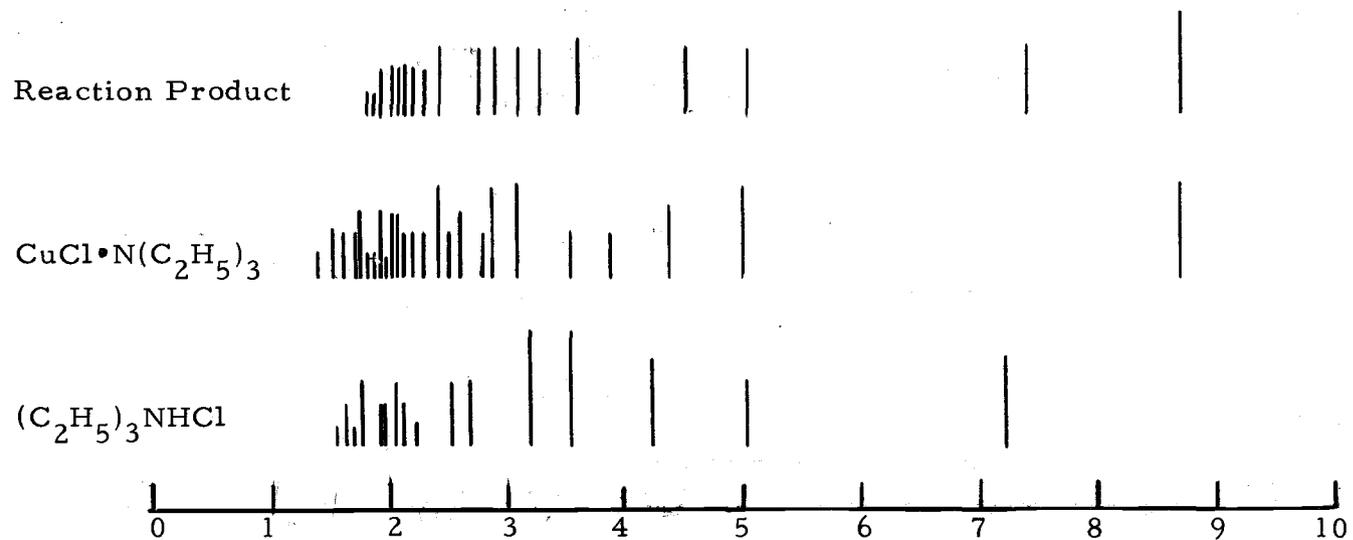
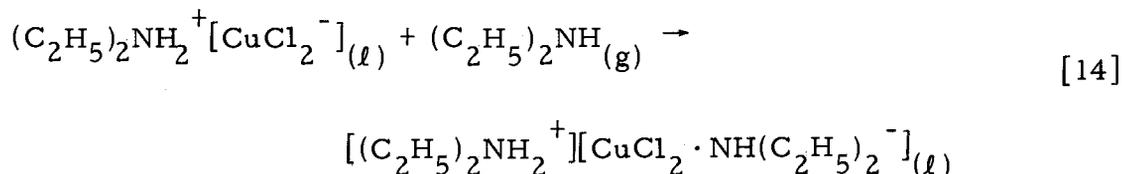
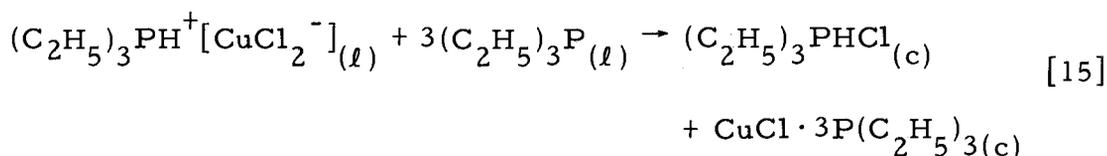


Figure 22. Comparison of X-ray powder diffraction patterns—triethylamine system.

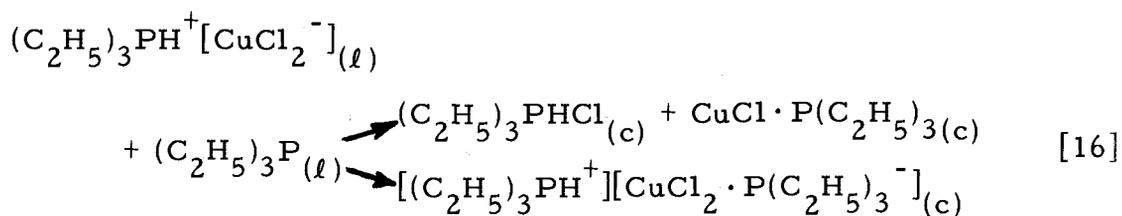
the components. The reaction is a nucleophilic displacement of chloride ion by triethylamine from the coordination sphere of copper(I). Similar behavior has been observed in the analogous ethylamine system (23). In contrast, a liquid product was obtained in the analogous diethylamine system and was formulated as an ionic complex (16), based on addition of the nucleophile to the coordination sphere of copper(I) without displacement of chloride ion.



Liquid triethylphosphonium dichlorocuprate(I) is found to react with three molar equivalents of triethylphosphine by nucleophilic displacement to give solid products. The infrared spectrum of the products is the sum of the spectra of triethylphosphonium chloride and of chlorotris(triethylphosphine)copper(I).



However, the reaction of equimolar amounts of triethylphosphonium dichlorocuprate(I) and triethylphosphine yields a more complicated mixture of solid products, apparently by two pathways,



Only lines of chloro(triethylphosphine)copper(I) can be identified in the poorly defined X-ray powder pattern of the reaction product (Table IV and Figure 23). The infrared spectrum (Figure 8) clearly shows two types of triethylphosphonium cations in the product. One of the cations is strongly hydrogen bonded to chloride ion, and one has the P-H stretch shifted to higher frequency as in a complex anion salt. The ^{31}P nmr spectrum shows a singlet at +10.8 ppm typical of coordinated triethylphosphine, in addition to the triethylphosphonium cation doublet at -20.1 ppm. It can be concluded that the chlorocuprate(I) anions react with nucleophiles either by displacement or by addition; in Equation 16 both processes take place.

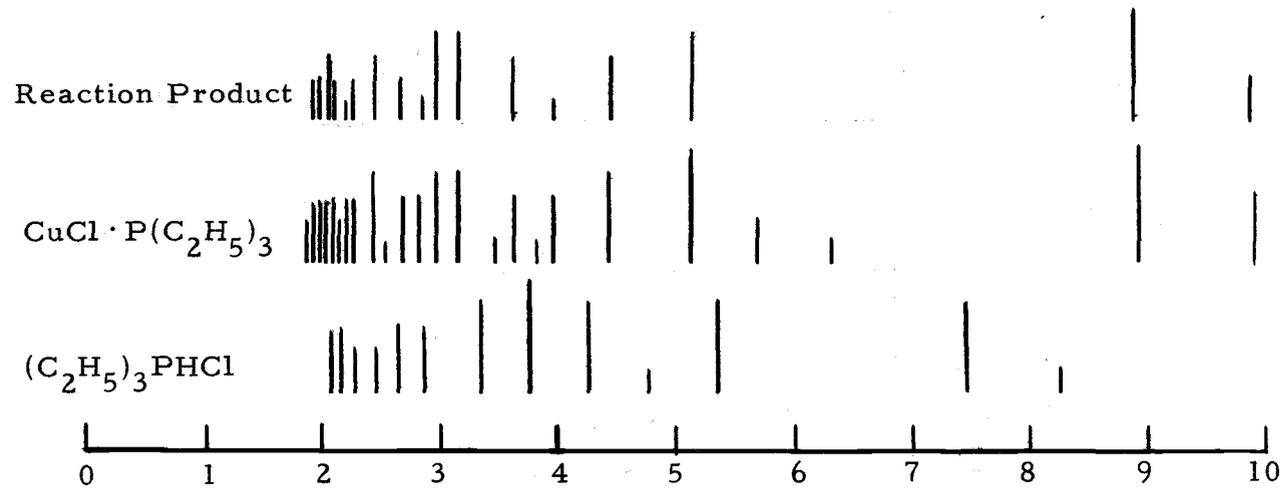


Figure 23. Comparison of X-ray powder diffraction patterns—triethylphosphine system.

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