

mined by Bennetto and Caldin. Furthermore, the Ni(II)-py bond could have a different energy from other Ni-solvent bonds. This energy difference could account for the apparent displacement of the activation parameter plot. One of the premises of the Bennetto-Caldin theory is that the enthalpy for the solvent-metal dissociative step is much the same from one solvent to another. This would seem to indicate that the composition of the primary solvation sphere of the metal ion is of little consequence in determining the overall activation parameters for the complexation reaction. Instead, the bulk solvent composition is probably very important. This model requires that many solvent molecules be involved in the activated complex. The concerted movements of these solvent molecules influence the activation parameters and the rate constants for complexation reactions.³⁴ Bennetto and Caldin proposed that the enthalpy of the metal-solvent dissociation step is much the same from one solvent to another and that the entropy change is small for this step. Any differences in activation parameters and in rate constants for metal ion complexation reactions in different solvents are a result of solvent properties.³⁴ Consequently, the different activation parameters for the Ni(II)-DPAP reaction in pyridine, in 6.20 M pyridine in nitromethane, and in 0.125 M pyridine in nitromethane can be interpreted using the Bennetto-Caldin model. The bulk solvent characteristics could account for the different activation parameters. The nitro group in nitromethane is free to rotate around the carbon-nitrogen bond, $\Delta H_{\text{rot}} = 0.53$. Nitromethane molecules are thus able to reorient quite easily while pyridine molecules are only able to reorient through motion of the entire molecule. The enthalpy and entropy of activation for a metal ion complexation reaction in solvents containing large amounts of pyridine should be higher than

(53) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969, p 41.

the corresponding activation parameters for the same reaction in solvents containing large amounts of nitromethane because pyridine is "stiffer" than nitromethane. The experimental values are in agreement with the predicted results.

The overall results of this work are consistent with the mechanism proposed by Bennetto and Caldin. The results do not exclude the Eigen-Wilkins mechanism, but a mechanism involving a five-coordinate intermediate is ruled out. The five-coordinate intermediate mechanism is not applicable to the reactions reported in this work for two reasons. First, the activation parameters for the reaction do not conform to those expected for the formation of a five-coordinate intermediate. Second, the solvent effects on the observed rate constants are not those expected for the formation of the five-coordinate intermediate Ni(py)₅²⁺ from Ni(py)₅nm²⁺ or Ni(py)₆²⁺. The applicability of the Eigen-Wilkins mechanism cannot be evaluated without a better knowledge of solvent-exchange rate constants for Ni(py)₆²⁺ and Ni(py)₅nm²⁺. The bimolecular rate constant for the reaction of Ni(py)₆²⁺ with DPAP is less than the upper limit established for the rate constant for pyridine exchange at Ni(py)₆²⁺.¹⁹ The Bennetto-Caldin model is a reasonable mechanism for the Ni(II) complexation reactions studied in this work. The variations in activation parameters for these reactions can be fit into the general relationship³⁴ of ΔH^\ddagger to ΔS^\ddagger proposed for this mechanism.

Registry No. Ni(py)₄(BF₄)₂, 15530-21-9; DPAP, 38894-49-4; NiDPAP²⁺, 38894-50-7; Ni(py)₆²⁺, 20037-72-3; Ni(py)₅nm²⁺, 38894-52-9.

Acknowledgment. The authors acknowledge support of this work through a grant (PRF-2177-A3,5) from the Petroleum Research Fund administered by the American Chemical Society. H. L. F. was the recipient of an NDEA fellowship and a University of California Regents fellowship during the course of this work.

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Coordination and Oxidation-Reduction in Copper(I) and -(II) Chloride-Triethylphosphine-Triethylchlorophosphonium Chloride (Triethyldichlorophosphorane) Systems¹

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Received November 27, 1972

Triethylphosphine is oxidized by copper(II) chloride above -45°, according to the following equations: (C₂H₅)₃P + 2CuCl₂ → (C₂H₅)₃PCl⁺[Cu₂Cl₃⁻]; (2n + 1)(C₂H₅)₃P + 2CuCl₂ → (C₂H₅)₃PCl₂ + 2(CuCl·nP(C₂H₅)₃), n = 1, 3. These products have been identified by comparison with complexes in copper(I) chloride-triethylphosphine-triethylchlorophosphonium chloride systems, using ¹H and ³¹P nmr spectra, infrared spectra, and phase studies. Chlorocuprate(I) salts with the triethylchlorophosphonium cation are additional examples of room-temperature fused salts.

Introduction

The reduction of copper(II) chloride by triethylphosphine was reported by Jensen³ to give the known⁴ copper(I) com-

plex, CuCl·P(C₂H₅)₃, presumably tetrameric by analogy to the iodide.⁵ The oxidation product has not been characterized, although tertiary phosphine oxides have been obtained

(1) Presented in part at the 27th Northwest Regional Meeting of the American Chemical Society, Corvallis, Oreg., June 1972. Taken from the Ph.D. dissertation of D. D. A., Oregon State University, 1973.

(2) NSF Trainee, 1967-1971.

(3) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **229**, 282 (1936).

(4) A. E. Arbutov, *Zh. Russ. Fiz.-Khim. Obshchest.*, **38**, 293 (1906).

(5) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).

from similar reactions in wet systems.⁶

Copper(II) chloride oxidizes the primary, secondary, and tertiary ethylamines by dehydrogenation,^{7,8} with polymerization of the resulting vinylamines. An alternative oxidation mechanism with alkylphosphines would be oxidation of the phosphorus center. Cohn and Parry⁹ obtained *N,N*-dimethylaminodichlorodifluorophosphorane from the copper(II) chloride oxidation of *N,N*-dimethylaminodifluorophosphine.

We have characterized all the products of the copper(II) chloride-triethylphosphine oxidation-reduction reaction in detail and have identified them by comparison with complexes formed in copper(I) chloride-triethylphosphine-triethylchlorophosphonium chloride (triethyldichlorophosphorane) systems.

Experimental Section

Instrumentation and Analyses. Infrared spectra were obtained with Beckman IR8 and Perkin-Elmer 621 spectrophotometers. Nmr spectra were measured with a Varian HA 100 instrument; ³¹P nmr spectra were obtained at 40.5 MHz. ³¹P chemical shifts, reported in ppm vs. H₃PO₄, were referenced to H₃PO₄ by tube interchange or to an internal capillary of P₂O₅. Chloride was determined gravimetrically, and copper was determined by EDTA back-titration using PAN indicator. C, H, and P microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

Materials. Oxygen- and moisture-sensitive compounds were handled by high-vacuum-line and Schlenk techniques or under nitrogen in a Forma stainless steel glove box equipped with an evacuable lock and a water and catalytic oxygen removal purification train.¹⁰ Freshly purified samples of the copper chlorides¹¹ and of triethylphosphine¹² were used. Other reagents and solvents were purified by standard methods. In the following, whenever physical data are presented for a composition based on several components, without analytical data, the composition specified is based on precise weighing of the analyzed components and is exact to three significant figures.

Copper(I) Chloride-Triethylphosphine System. At 25° and a triethylphosphine:copper(I) chloride mole ratio greater than 5, the system is a homogeneous liquid in equilibrium with triethylphosphine vapor. The ¹H nmr of the neat solution (mole ratio 20) consists of two complex multiplets, δ 1.17 and 0.82, while triethylphosphine itself has a very broad and complex multiplet¹³⁻¹⁵ centered at δ 1.13. The ³¹P nmr signal, +18.3 ppm, is a broad singlet below room temperature, is partly structured at 31°, and at 50° is an apparent octet (like the +19.5-ppm resonance of triethylphosphine itself). Limited isothermal pressure-composition studies of this system were carried out, using previously described techniques.¹⁶ The excess of triethylphosphine was removed in portions by distillation from a vacuum-line reaction assembly, accompanied by separation of a white solid and by a drop in the equilibrium pressure. As the mole ratio decreased to 3.0, the last of the liquid phase disappeared and the pressure dropped to less than 1 mm. The sample was then heated to 58°. It melted and the equilibrium pressure rose to about 2.5 mm. Additional amounts of triethylphosphine were pumped off at 58°, until a mole ratio of 1.0 was reached. At this point, the system again consisted only of a white solid and the pressure dropped to less than 1 mm. These phase studies indicate the existence of the solid compounds CuCl·3P(C₂H₅)₃ and CuCl·P(C₂H₅)₃.

Chlorotris(triethylphosphine)copper(I). A sample was prepared as described above (mole ratio 3.0); mp (sealed tube) 49-51°; ¹H nmr (CDCl₃); δ 1.60 (m), 1.09 (m); ³¹P nmr (CDCl₃): +14.7 ppm. The ir spectrum is given in Figure 1.

(6) For example, H. D. Caughman and R. C. Taylor, *Inorg. Nucl. Chem. Lett.*, **6**, 623 (1970).

(7) J. F. Weiss, G. Tollin, and J. T. Yoke, *Inorg. Chem.*, **3**, 1344 (1964).

(8) J. R. Clifton and J. T. Yoke, *Inorg. Chem.*, **7**, 39 (1968).

(9) K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968).

(10) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

(11) J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963).

(12) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 475 (1962).

(13) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).

(14) J. B. Hendrickson, *et al.*, *Tetrahedron*, **20**, 449 (1964).

(15) S. F. Spangenberg and H. H. Sisler, *Inorg. Chem.*, **8**, 1006 (1969).

(16) W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, **1**, 463 (1962).

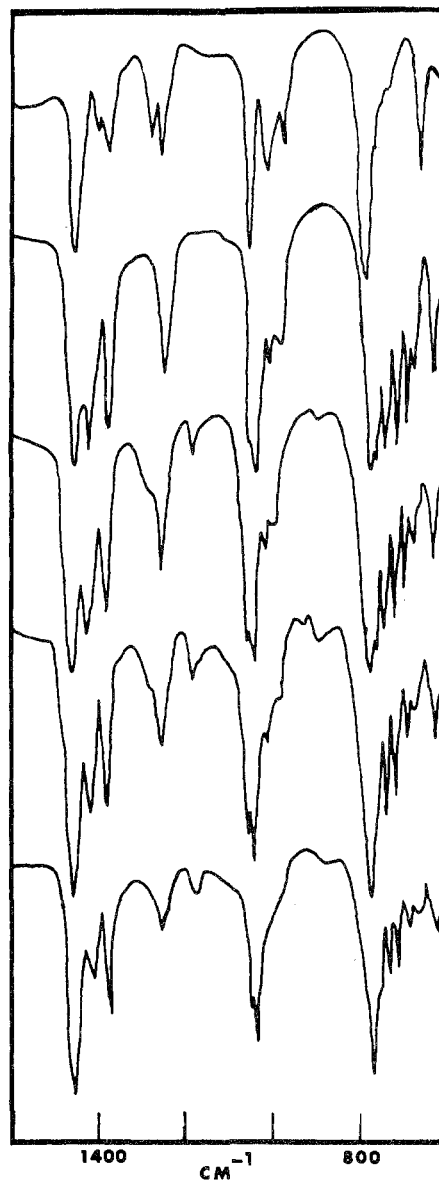


Figure 1. Infrared spectra (Nujol) of (from the top) (C₂H₅)₃PCL₂, CuCl·3P(C₂H₅)₃, product from (C₂H₅)₃PCL₂ + 2(CuCl·3P(C₂H₅)₃), product from (C₂H₅)₃PCL₂ + 6(C₂H₅)₃P, and product from 7(C₂H₅)₃P + 2CuCl₂.

Chloro(triethylphosphine)copper(I). This was prepared more readily by interaction of equimolar quantities of the components in acetonitrile in a vacuum-line reaction bulb, followed by removal of the solvent *in vacuo*. *Anal.* Calcd for CuClC₆H₁₅P: Cu, 29.26; Cl, 16.32; C, 33.18; H, 6.96. Found: Cu, 29.09; Cl, 16.14; C, 32.89; H, 6.77. ¹H nmr (CH₂Cl₂): δ 1.11 (m), 1.61 (m). The ir spectrum (Nujol) was essentially the same as that of the free ligand,^{17,18} with some simplification in the 900-1200-cm⁻¹ region attributed to the presence of only one rotational isomer of the ligand.¹⁹ The compound CuCl·P(C₂H₅)₃ was found to melt at 222-224° (sealed tube) and to be insoluble in carbon tetrachloride, petroleum ether, acetone, and alcohol and slightly soluble in chloroform, benzene, toluene, and acetonitrile. These properties do not agree with the previous report of Arbuzov.⁴ He gave a melting point of 103-104° dec²⁰ and reported quite different solubility properties. The solubility was insufficient to permit detection of the ³¹P nmr in a single scan, but a spectrum of low quality was obtained in 211 repetitive scans, using a P₂O₅ lock.

(17) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, **15**, 360 (1959).

(18) M. van den Akker and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **86**, 275 (1967).

(19) J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 137 (1968).

Triethylchlorohydroxyphosphorane. A solution of triethylphosphine oxide²¹ [³¹P nmr: in CCl₄, -46.8 ppm; in C₆H₆, -46.6 ppm (lit.²² -48.3 ppm)] in benzene was saturated with hydrogen chloride and evaporated to dryness *in vacuo* leaving a white solid, mp 129–134°; ir (Nujol) (cm⁻¹): 2380–2300 (w), 1555 (m), 1270 (m), 1238 (m), 1145 (m), 1068 (w), 1047 (s), 1010 (s), 970 (m), 815 (m), 777 (s), 756 (s), 666 (vw); ¹H nmr (CH₃CN, concentration dependent): δ 14.10 (s), 1.96 (m), 1.20 (m); ¹H nmr (CDCl₃): δ 12.49 (s), 2.18 (m), 1.28 (m); ³¹P nmr (CDCl₃): -82.6 ppm (s). An identical material was obtained during attempted preparations of triethylchlorophosphonium chloride^{15,23} when protection from moisture was inadequate. *Anal.* Calcd for (C₂H₅)₃PClOH: C, 42.24; H, 9.45; P, 18.15; Cl, 20.78. Found: C, 42.00; H, 9.80; P, 18.32; Cl, 20.95.

Triethylchlorophosphonium Chloride (Triethylchlorophosphorane). This was prepared from triethylphosphine and phosphorus trichloride (mole ratio 3:2) in benzene, according to the procedure of Spangenberg and Sisler,^{15,24} and was recrystallized from toluene; mp 238–243° dec (lit.²⁴ mp 242–247° dec). *Anal.* Calcd for C₁₆H₁₅PCl₂: C, 38.11; H, 7.99; P, 16.38. Found: C, 38.33; H, 8.07; P, 16.49. ¹H nmr (CDCl₃): δ 3.35 (m), 1.45 (m); ³¹P nmr: -110 ppm [lit.²⁴ ¹H nmr: δ 3.36 (m), 1.44 (m); ³¹P nmr: -114 ppm]. The ir spectrum is given in Figure 1.

Triethylchlorophosphonium Chloride-Copper(I) Chloride System. Exactly equimolar quantities of the two white solids reacted on contact at room temperature to give a light green oil, of composition (C₂H₅)₃PCl⁺[CuCl₂⁻]. Ir (neat) (cm⁻¹): 2980 (m), 2923 (s), 2893 (s), 1452 (s), 1388 (s), 1263 (m), 1239 (m), 1045 (s), 1015 (sh), 1007 (m), 955 (w), 777 (s), 752 (sh), 645 (m). When a mole ratio of exactly 1:2 was used, a dark green-black oil formed spontaneously at room temperature, of composition (C₂H₅)₃PCl[Cu₂Cl₃]. ¹H nmr (neat): δ 3.99 (m), 2.44 (m); ³¹P nmr: -110 ppm; ir (neat) (cm⁻¹): 2975 (m), 2925 (s), 2885 (s), 1457 (s), 1387 (s), 1261 (m), 1242 (sh), 1045 (s), 1016 (w), 952 (w), 778 (vs), 768 (sh), 753 (m), 647 (m).

Triethylchlorophosphonium Trichlorocuprate(I)-Triethylphosphine System. An excess of triethylphosphine was distilled onto 1.16 mmol of dark (C₂H₅)₃PCl[Cu₂Cl₃] 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, giving a white solid with a negligible dissociation pressure, with the gain in weight corresponding to retention of 6.88 mmol of triethylphosphine (mole ratio (C₂H₅)₃P:Cu = 2.97). This melted on heating to 58°, and the equilibrium pressure rose to about 2 mm, permitting further removal of triethylphosphine until the pressure again fell to a negligible value leaving a white solid in which 2.36 mmol of triethylphosphine had been retained (mole ratio (C₂H₅)₃P:Cu = 1.02), composition (C₂H₅)₃PCl₂·2CuCl·2(C₂H₅)₃P. The ir spectrum corresponded to the sum of the spectra of (C₂H₅)₃PCl₂ and CuCl·P(C₂H₅)₃. To a portion of this, exactly enough triethylphosphine was added to regenerate the first solid, of composition (C₂H₅)₃PCl₂·2CuCl·6(C₂H₅)₃P. ¹H nmr (CDCl₃): δ 3.31 (m), 1.58 (m), 1.10 (m); ³¹P nmr: +14.9 (s), -112 ppm (s). The ir spectrum is given in Figure 1.

Triethylchlorophosphonium Chloride-Chloro(triethylphosphine)-copper(I) System. These two white solids, in exactly 1:2 molar quantities, were dissolved in the minimum amount of acetonitrile, and the solvent was removed *in vacuo* leaving a white residue of composition (C₂H₅)₃PCl₂·2CuCl·2(C₂H₅)₃P. The ir spectrum corresponded to the sum of the spectra of (C₂H₅)₃PCl₂ and CuCl·P(C₂H₅)₃.

Triethylchlorophosphonium Chloride-Chlorotris(triethylphosphine)copper(I) System. These two white solids, in exactly 1:2 molar proportions, were dissolved in the minimum amount of acetonitrile, and the solvent was removed *in vacuo* leaving a white residue of composition (C₂H₅)₃PCl₂·2CuCl·6(C₂H₅)₃P. ¹H nmr (CDCl₃): δ 3.36 (m), 1.60 (m), 1.13 (m); ³¹P nmr: +14.1 ppm. The ir spectrum is given in Figure 1.

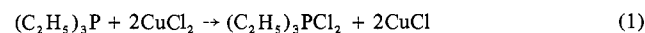
Copper(II) Chloride-Triethylphosphine Redox Reaction. The reaction was observed in benzene, acetonitrile, and ethanol but was usually carried out by allowing neat triethylphosphine-anhydrous

copper(II) chloride mixtures to warm from -196° to room temperature with magnetic agitation. At sufficiently low triethylphosphine:copper(II) chloride reactant mole ratios (e.g., 0.52), the products were dark greenish black (see Results and Discussion), but addition of more triethylphosphine to these or use of an excess initially gave completely colorless products—a white solid, plus a colorless liquid if the mole ratio exceeded 3.5. The excess triethylphosphine could be readily pumped off in the vacuum line at 25° to a mole ratio of 3.5 (weight basis of reactants) and more difficultly at 58° to a mole ratio of 1.5, leaving white solids. A 2.035-g (17.22-mmol) quantity of triethylphosphine was condensed at -196° onto 0.6605 g (4.912 mmol) of copper(II) chloride (mole ratio 3.506), and the reaction mixture was allowed to warm to room temperature and stand for several hours, giving only a white solid. ¹H nmr (CDCl₃): δ 3.35 (m), 1.56 (m), 1.08 (m); ³¹P nmr (CDCl₃): +14.9 ppm (s), -112 ppm (s). The ir spectrum is given in Figure 1.

Results and Discussion

Mixtures of anhydrous copper(II) chloride and triethylphosphine undergo an exothermic oxidation-reduction reaction, slowly at -45° and more rapidly above -23°. No reaction was observed at -78° in 6 months and attempts to isolate a triethylphosphine-copper(II) coordination compound at a low temperature were unsuccessful.²⁵ Transient purple and brown colors, observed as frozen layers of triethylphosphine and of a solution of copper(II) chloride in ethanol were allowed to thaw, are indicative of an intermediate copper(II) complex.

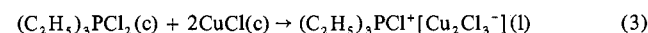
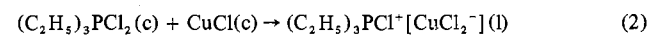
The fundamental oxidation-reduction process is



but these products then react with each other or with additional triethylphosphine.

The ³¹P nmr of (C₂H₅)₃PCl₂ in chloroform corresponds to that observed for the (C₂H₅)₃PCl⁺ cation with a complex anion and so we name this compound as triethylchlorophosphonium chloride in preference to triethylchlorophosphorane. In contrast to a previous study with related compounds,²⁶ we were able to obtain triethylchlorohydroxyphosphorane, (C₂H₅)₃PClOH, by limited hydrolysis of this compound, as well as by addition of hydrogen chloride to triethylphosphine oxide.

Equimolar amounts of triethylchlorophosphonium chloride and copper(I) chloride react, merely on contact of the white powders, to give a light green oil, and an additional mole of copper(I) chloride can be dissolved in this oil at room temperature, giving a very dark green viscous liquid, *i.e.*



These are two additional examples of the remarkable chlorocuprate(I) salts which are "fused salts" at room temperature. The first example¹¹ was triethylammonium dichlorocuprate(I). Several other examples have also been prepared recently, and a study of the vibrational spectra, conductance, and other properties of these liquids is being reported separately.²⁷ For each formal composition specified, they contain an equilibrium mixture of mono- and polynuclear chlorocuprate(I) complexes. Their color is due to the visible tail of a uv charge-transfer band, which is shifted to longer wavelengths in the more condensed species. The dark oil of composition (C₂H₅)₃PCl⁺[Cu₂Cl₃⁻] reacts stoichiometrically with triethylphosphine by nucleophilic displacement, giving

(20) F. H. Jardine, L. Rule, and A. G. Vohra, *J. Chem. Soc. A*, 238 (1970), also prepared this compound by Jensen's method³ and reported a melting point of 116° dec. These lower decomposition temperatures are no doubt due to the use of open capillary tubes, allowing reaction with air.

(21) D. D. Schmidt and J. T. Yoke, *Inorg. Chem.*, **9**, 1176 (1970).

(22) M. M. Crutchfield, *et al.*, "P³¹ Nuclear Magnetic Resonance," Wiley-Interscience, New York, N. Y., 1967, p 284.

(23) J. N. Collie and F. Reynolds, *J. Chem. Soc.*, **107**, 367 (1915).

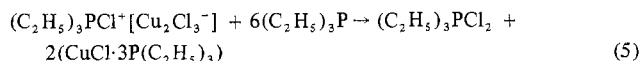
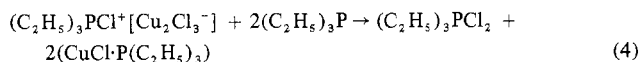
(24) S. F. Spangenberg, Dissertation, University of Florida, 1968.

(25) The first such complex of copper(II) hexafluoroacetylacetonate was reported recently: R. A. Zelonka and M. C. Baird, *Chem. Commun.*, 780 (1971).

(26) K. Issleib and W. Seidel, *Z. Anorg. Allg. Chem.*, **288**, 201 (1956).

(27) D. D. Axtell, B. W. Good, W. W. Porterfield, and J. T. Yoke, submitted for publication.

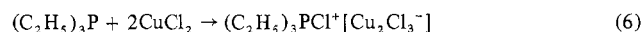
triethylchlorophosphonium chloride and the neutral triethylphosphine-copper(I) chloride complexes, *i.e.*



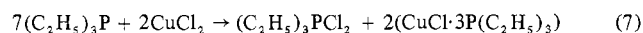
The complex $\text{CuCl}\cdot\text{P}(\text{C}_2\text{H}_5)_3$ is presumably tetrameric,⁵ while $\text{CuCl}\cdot 3\text{P}(\text{C}_2\text{H}_5)_3$ is presumably monomeric with four-coordinate copper(I). We did not observe an intermediate $\text{CuCl}\cdot 2\text{P}(\text{C}_2\text{H}_5)_3$ species.²⁸

The solution of copper(I) chloride in neat triethylphosphine as solvent presumably contains the highest possible complex as the solute species. Only one ³¹P nmr signal was observed, in keeping with the expected lability of copper(I) complexes. The loss of structure of this signal on cooling the solution may be due to a decrease in the rate of exchange to a point permitting additional splitting by the copper nuclei.²⁸

The identification of the products of the copper(II) chloride-triethylphosphine oxidation-reduction reaction is based on comparison to the products of reaction of copper(I) chloride, triethylchlorophosphonium chloride, and triethylphosphine. Thus, when 0.5 mol of triethylphosphine is used per mole of copper(II) chloride, the product is a viscous green-black liquid, corresponding to



When an excess of triethylphosphine is used and the unreacted amount is then pumped off, 3.5 mol of triethylphosphine is retained in the solid white product per mole of copper(II) chloride used, corresponding to

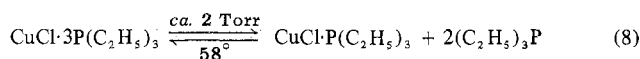


A mixture of this composition can be prepared three ways: (a) by reaction 7; (b) by reaction 5; (c) by the removal of solvent from an acetonitrile solution of the authentic components in the exact molar proportions. The ¹H and ³¹P nmr spectra of these preparations are very nearly identical; the ³¹P nmr clearly show the $(\text{C}_2\text{H}_5)_3\text{PCl}^+$ and the coordinated

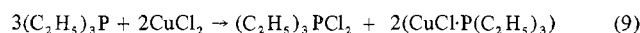
(28) For $\text{L} = (\text{CH}_3)_3\text{P}$, the complexes $[\text{CuCl}\cdot\text{L}]_4$, $[\text{CuCl}\cdot 2\text{L}]_2$, $[\text{CuCl}\cdot 3\text{L}]$, and $[\text{CuL}_4]\text{Cl}$ have been reported: H. Schmidbauer, J. Adlkofer, and K. Schwirten, *Chem. Ber.*, **105**, 3382 (1972).

$(\text{C}_2\text{H}_5)_3\text{P}$ species. The vibrational spectra of the three preparations, shown in Figure 1, are also identical and correspond to the sum of the spectra of triethylchlorophosphonium chloride and chlorotris(triethylphosphine)copper(I).

Additional triethylphosphine can be pumped at 58° from the above oxidation-reduction products, giving a final mixture containing 1.5 mol of triethylphosphine consumed per mole of copper(II) chloride used. This corresponds to the process



Therefore, a third equation can be written for the oxidation-reduction reaction, corresponding to the stoichiometry



One can suppose a catalytic cycle for the autoxidation of triethylphosphine, based on reoxidation of the copper(I) species with oxygen and complete hydrolysis of triethylchlorophosphonium chloride to the phosphine 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.²⁹ There, the mechanism involved formation of an intermediate O_2 adduct of the stable cobalt(II)-triethylphosphine complex.

Registry No. $(\text{C}_2\text{H}_5)_3\text{P}$, 554-70-1; CuCl_2 , 7447-39-4; HCl , 7647-01-0; $(\text{C}_2\text{H}_5)_3\text{PO}$, 597-50-2; $(\text{C}_2\text{H}_5)_3\text{PClOH}$, 38960-87-1; $(\text{C}_2\text{H}_5)_3\text{PCl}_2$, 16616-89-0; CuCl , 7758-89-6; $\text{CuCl}\cdot\text{P}(\text{C}_2\text{H}_5)_3$, 38966-47-1; $\text{CuCl}\cdot 3\text{P}(\text{C}_2\text{H}_5)_3$, 38894-56-3; $[(\text{C}_2\text{H}_5)_3\text{PCl}][\text{CuCl}_2]$, 38894-57-4; $[(\text{C}_2\text{H}_5)_3\text{PCl}][\text{Cu}_2\text{Cl}_3]$, 37333-31-6; $(\text{C}_2\text{H}_5)_3\text{PCl}_2$, 38894-58-5.

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