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Preparation, Physical Properties and Reactions of Copper(I) -Triphenyl-M Complexes (M = P, As, Sb)

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General methods of preparation, chemical reactions and some physical properties of triphenylphosphine, arsine, and stibine-copper(I) complexes have been studied. The most general methods of preparation involve the reduction of copper(II) salts with triphenylphosphine or the direct reaction of this ligand with copper(I) salts. Displacement reactions on P_3CuCl *or* $[PCuCl]_4$ *(P = triphenylphosphine) by charged or uncharged ligands have been employed to prepare compounds such as:* $P_2CuSC_6H_5$, $P_2CuOC_6H_5$, $PCuC_5H_5$, $PCuC{\equiv}CC_6H_5$, $PCuCl \cdot pyr.$, $PCuN_3 \cdot pyr.$, $P_3CuB(C_6H_5)_4$, *etc.* P_3CuCl *adds polar molecules to yield* $P_3CuCl \cdot X$ *(X = 2* $CHCl_3$, *1* CS_2, *2 DMF, etc.). These complexes do not add carbon monoxide, olefins, or acetylenes to yield stable compounds.* P_2CuN_3 *in excess P decomposes smoothly to yield* $[P{=}N{-}Cu]_n$ *(250°) A study of the solution molecular weights suggests that many of these complexes have three coordinated copper(I). This coordination number of copper appears to be of appreciable stability.*

Introduction

Soft ligands such as phosphines, arsines, sulfides, etc., form complexes with copper(I) compounds. These have recently been reviewed.[1,2,3] The phosphine ligands form complexes of varying metal-ligand ratios.[4,5]

These complexes are colorless, air, moisture, and moderately heat stable substances. With exception of $P_4Cu^+ClO_4^-$,* which yields conducting solutions in nitrobenzene,[6] they are covalent substances which are fairly soluble in polar and non-polar solvents. They usually decompose at the mp and are dissociated in solution.[7,8]

The objective of this work was to examine the chemistry of the P_nCuX molecules, particularly the displacement reactions of P_3CuCl and $[PCuX]_4$, and to investigate the chemical and physical properties of the resulting products. A brief survey of various methods of preparing the starting materials is presented.

Experimental Section

The reagents and solvents employed were of the best quality commercially obtainable (Aldrich Chemical Co. and Alpha Inorganics, Inc.). The mp, taken in glass capillaries, frequently depends on the temperature at which the sample was placed into the mp device and the heating rate. The mp is generally accompanied by decomposition (browning, gas, cloudiness). This mp or dec. point is most often not a good measure of the compound's purity.

Removal of uncharged ligand (Table IV) was carried out in a sublimation tube which was externally heated by refluxing solvent. The x-ray powder patterns were run on a North American Phillips x-ray diffractometer using Cu–Kα radiation (Ni filtered) and recorded on film or a strip chart counter arrangement. The m.wt. were measured by the vapor phase osmometric technique at 37° in the solvents indicated (Table I) and at about 1 wt. % conc. level under N_2. The m.wt. of several compounds were extrapolated to zero conc. (four pts.). The infrared spectra were measured on samples as KBr pellets or (normally) Nujol mulls.

Tables II through XI summarize the experimental conditions employed in the preparation of the starting materials and their subsequent reactions. Only a select number of these are detailed below. Several are known compounds but the procedures employed here have with greater reliability yielded a pure product (as judged by elemental analyses). All reactions were carried out under a N_2 atmosphere and, where necessary, under anhydrous conditions. Elemental analyses and m. wt. are summarized in Table I.

Tris(triphenylphosphine) Copper(I) Chloride (P_3CuCl). Finely ground cuprous chloride (0.33 mol) was added to a clear solution of triphenylphosphine (1.315 mol) in about 2000 ml of chloroform. Within 2 hr the cuprous chloride had dissolved (with vigorous stirring) and the solution was filtered. The clear solution was evaporated (25°/vac) to 800 ml volume and the resulting slurry was filtered. The cake was washed (50 ml $CHCl_3$) and air dried; 318 g.

Anal. Calcd $C_{54}H_{45}P_3CuCl$: Cl, 4.01; Found: Cl,

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* Hereafter $P = (C_6H_5)_3P$, $As = (C_6H_5)_3As$, $Sb = (C_6H_5)_3Sb$.

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(7) E.W. Abel, R.A.N. Mclean, and I.H. Sablerwal, *J. Chem. Soc.*, (*A*), 133 (1969).

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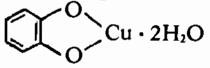
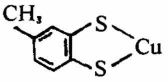
Table I. Analytical Results

Compound	Elemental Analyses (Calc'd.) C	H	Other	Other	Molecular Wt.[a] Found, mg./g. Solvent (Calc'd.)
P_3CuCl	73.85 (73.21)	5.11 (5.09)	Cl-3.76 (4.01)	P-10.60 (10.51)	412, O, C_6H_5Cl (885)
$P_3Cu_2Cl_2$	65.77 (65.87)	4.68 (4.57)	—	—	524, O, $CHCl_3$ (985)
P_2CuCl	69.71 (69.33)	4.80 (4.82)	Cl-5.30 (5.70)	—	276, 7.6, 273, 7.9, $CHCl_3$ (623)
$[PCuCl]_4$	60.14 (59.83)	4.92 (4.15)	—	—	—
P_3CuBr	70.08 (69.71)	5.04 (4.85)	Br-10.61 (10.00)	—	—
P_3CuI	65.95 (66.36)	4.69 (4.61)	I-12.30 (13.00)	—	—
P_2CuSCN	68.10 (68.76)	4.68 (4.65)	S-4.79 (4.96)	N-2.14 (2.17)	Insol. $CHCl_3$
P_2CuCN	72.66 (72.31)	5.06 (4.90)	N-2.14 (2.29)	—	685, 11, 705, 13.6, $CHCl_3$ (611)
P_2CuNO_3	66.56 (66.50)	4.51 (4.60)	N-2.27 (2.16)	—	733, ~7, $CHCl_3$ (649)
P_4CuClO_4	70.86 (71.43)	4.82 (4.97)	Cl-3.12 (2.94)	—	—
P_3CuClO_4	68.01 (68.53)	4.49 (4.75)	Cl-3.78 (3.75)	—	—
P_4CuBF_4	71.86 (72.08)	5.34 (5.00)	P-9.63 (10.35)	F-8.79 (6.35)	1127, ~7, $CHCl_3$ (936)
P_2CuN_3	68.47 (68.61)	4.80 (4.76)	N-6.66 (6.68)	—	619, ~7, $CHCl_3$ (629)
$[PCuN_3]_n$	58.19 (58.76)	4.38 (4.08)	N-11.14 (11.44)	—	—
$[P_3Cu]_2SO_4$	74.00 (72.21)	5.60 (5.01)	S-1.73 (1.78)	P-9.87 (10.36)	—
$[P_2Cu]_2SO_4$	68.28 (67.79)	4.96 (4.72)	S-3.45 (2.52)	P-10.09 (9.76)	1175, ~7, $CHCl_3$ (1271)
P_2CuBH_4	71.86 (71.69)	6.07 (5.65)	—	—	—
$P_2CuO_2CCH_3$	70.75 (70.64)	5.84 (5.11)	—	—	637, ~7, $CHCl_3$ (646)
$P_2CuO_2CC_6H_5$	72.53 (72.37)	4.96 (5.02)	—	—	744, ~7, $CHCl_3$ (708)
$P_2CuO_2C_5H_7$ [b]	71.18 (71.73)	5.48 (5.38)	—	—	—
$P_2CuO_2C_5H_4F_3$ [b]	66.30 (66.45)	4.33 (4.59)	F-9.16 (7.69)	—	—
As_3CuCl	62.28 (63.82)	4.29 (4.42)	Cl-4.86 (3.49)	—	—
$[AsCuCl]_n$	54.96 (53.32)	3.98 (3.70)	—	—	—
Sb_3CuCl	55.63 (55.94)	4.03 (3.89)	Cl-2.87 (3.07)	—	—
$[P{=}N{-}Cu]_n$	66.22 (63.61)	4.58 (4.42)	N.3.80 (4.13)	—	495, ~7, $CHCl_3$ (339)
PCuCl · pyr.	62.69 (62.73)	4.71 (4.54)	N-8.70 (8.07)	—	401, ~7, 423, 6.1, $CHCl_3$ (440)
P_2CuCl · pyr.	70.04 (70.10)	5.08 (4.98)	Cl-5.22 (5.06)	N-1.88 (1.99)	—
PCuCl · bipyr.	65.58 (65.01)	5.15 (4.45)	N-5.08 (5.42)	Cl-6.38 (6.82)	573, ~, $CHCl_3$ (517)
$P_3CuCl \cdot CS_2$	68.60 (68.68)	4.91 (4.68)	Cl-3.84 (3.69)	S-7.38 (6.66)	—
$P_2CuO_2C_5H_7 \cdot CS_2$ [b]	65.80 (66.10)	4.27 (4.85)	S-8.69 (8.40)	—	—
$P_2CuOSC_5H_4F_3$ [b]	66.03 (65.01)	4.67 (4.49)	S-4.18 (4.23)	—	
$P_2CuO_2CCH_3 \cdot CS_2$	63.81 (64.78)	4.49 (4.56)	S-7.77 (8.86)	—	—
$P_2CuOC_6H_5 \cdot CS_2$	68.22 (68.21)	4.73 (4.63)	S-8.46 (8.46)	—	—
$P_2CuSC_6H_5 \cdot CS_2$	66.80 (66.81)	4.72 (4.51)	S-12.11 (12.43)	—	—
$P_2CuOC_6H_5$	74.23 (74.08)	5.21 (5.15)	Cl-0.0 (0.0)	—	450, 7.1; 565, 9.3, $CHCl_3$ (680)
$P_2CuSC_6H_5$	72.44 (72.39)	5.52 (5.02)	S-4.27 (4.59)	—	503, O, C_6H_5Cl (696)
$[PCuOC_6H_5]_2$	72.08 (68.77)	4.25 (4.78)	—	—	617, 13.1; 595, 7.8, C_6H_6 (418)
$[CuOC_6H_5]_n$	43.40 (45.98)	2.93 (3.20)	Cu-44.46 (40.60)	—	
$[PCuSC_6H_5]_2$	64.46 (66.25)	4.18 (4.61)	S-7.94 (7.37)	—	842, 859, ~7, $CHCl_3$ (435)
$[C_6H_5SCu]_n$	41.76 (41.90)	3.12 (2.90)	S-18.37 (18.45)-	—	—
	33.77 (34.70)	2.65 (3.85)	O-29.15 (30.85)	—	—
	40.70 (38.62)	3.04 (2.76)	—	—	—
$PCuC{\equiv}CC_6H_5$	72.75 (73.16)	4.50 (4.69)	S-0.0 (0.0)	P-7.68 (7.27)	1962, 13.4; 1968, 9.6, C_5H_6 (427)
P_2CuN_3 · pyr.	66.40 (69.43)	5.08 (4.94)	N-7.66 (7.91)	Cl-Neg.	—
$PCuN_3$ · pyr.	61.35 (61.80)	4.66 (4.48)	N-11.72 (12.56)	—	—
$[PCuBr]_n$	54.67 (54.24)	4.03 (3.69)	Br-19.35 (19.75)	—	—
$P_3CuB(C_6H_5)_4$	80.21 (80.11)	5.45 (5.57)	P-8.13 (7.96)	—	280, 6.6; 300, 14.7, THF (1166)
$(C_6H_5)_4P^+CuBr_2^-$	51.54 (51.19)	3.89 (3.55)	Br-26.1 (28.45)	Cl-Neg.	—
$(C_6H_5)_4P^+CuI_2^-$	38.69 (38.96)	2.87 (2.78)	I-37.7 (36.30)	Cl-Neg.	—
$(C_6H_5)_3PCH_2CH{=}CH_2{}^+Br^-$	64.12 (65.82)	4.99 (5.22)	Br-21.52 (10.87)	S-Neg.	—
$(C_6H_5)_3P^+CH_2C_6H_5 \,.\, CuCl_2^-$	61.43 (61.62)	4.70 (4.51)	Cl-14.77 (14.57)	—	—

[a] O concentration implies that the molecular wt. has been extrapolated (4 points) to zero concentration. [b] Acetonyl acetonate and acetonyl trifluoromethyl acetonate reaction products.

21.74. The product, therefore, contained about two mol of chloroform. This could be removed by drying 70°/vac, 20 hr, 251 g, 93% yield; mp 167-170° sharp, clear.*

Tris(triphenylarsine) Copper(I) Chloride (*As_3CuCl*). Cuprous chloride (0.02 mol) was added to a triphenylarsine (0.0817 mol) solution in chloroform (800 ml). The copper salt dissolved within about 1 hr (25°). After filtering, the solution was evaporated (25°/vac) to 35 ml volume. The solids were filtered off and washed twice with cold chloroform (20 ml each). The solids were dried 65°/vac/18 hr; 55.5% yield.

Tris(triphenylstibine) Copper(I) Chloride (*Sb_3CuCl*). Finely ground cuprous chloride (0.017 mol) was added to a chloroform solution (500 ml) of triphenylstibine and stirred at 25° for 1-1/2 hr. The solution

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* P_3CuCl appears to exist in two crystalline modifications (two different powder patterns), both modifications melt at 167-170°. No transitions could be detected by differential thermal analyses up to the mp. This complex slowly forms crystals in the melt ($P_3Cu_2Cl_2$ or $[PCuCl]_4$+P?).

was filtered and evaporated (25°/vac) to about 40 ml volume. The crystals were filtered off and washed once with cold chloroform (12 ml). Air dried solids; 16.5 g, 83.7% yield.

Tris(triphenylphosphine) Copper(I) Chloride-Carbon Disulfide Adduct ($P_3CuCl \cdot CS_2$). Four g of this copper complex were heated with carbon disulfide for 18 hr/100° in a small pressure bomb. The adduct was crystallized from 35 ml of hot carbon disulfide and air dried; 61.8% yield; mp crystals disintegrate 100° (popping), melt 165-200°.

Bis(triphenylphosphine) Copper(I) Phenoxide (P_2-$CuOC_6H_5$). Dry sodium phenoxide was prepared from phenol (0.30 mol) and a sodium dispersion (in toluene) in dry THF. To this was added P_3CuCl (0.20 mol) in toluene (1000 ml). The slurry was brought to reflux and the THF distilled out and refluxing continued overnight. The solution was filtered through a celite bed (dry box) and the crystals recrystallized from 250 ml hot benzene, 90.5% yield (product had a neg. qualitative test for Cl^-).

Reaction of Bis(triphenylphosphine) Copper(I) Phenoxide with Carbon Disulfide. One g of the copper compound was refluxed for 1 hr with 75 ml CS_2 and the solvent was gradually evaporated at r.t.; 1.10 g yellow crystals, 99% of theory, mp 152-5° w dec to d'red liquid (no gas evolution) dec. with gassing 165^{+o}.

Reaction of Bis(triphenylphosphine) Copper(I) Thiophenoxide and Phenylacetylene. Seven g of the complex and phenylacetylene (28.7 g) were heated at 100° for 30 hr under nitrogen. This resulted in a clear orange solution. Volatiles were pumped off at 40°/vac (pure phenylacetylene). The residue was a tan solid (9.75 g). This was washed twice with cold cyclohexane and air dried; 6.2 g light yellow crystals, mp 153-8°. These solids were crystallized twice from hot benzene yielding bright yellow-greenish, fluorescent crystals mp 198-202° w dec.

Reaction of Triphenylphosphine Copper(I) Chloride Pyridine Adduct with Anhydrous Hydrogen Chloride. Two g of the copper complex, in dry chloroform solution (25 ml), were sparged for 1/2 hr with anhydrous hydrogen chloride at 25°. A small amount of a white ppt appeared after 10 min and then redissolved. The clear solution was kept stoppered overnight and then evaporated to 15 ml with N_2. The resulting white, crystalline solid as filtered, washed with cold chloroform and air dried (1.15 g).

Anal. Calcd for $C_{41}H_{36}P_2Cu_2Cl_3N$: C, 58.75; H, 4.30; N, 1.67; Cl, 12.72. Found: C, 59.05; H, 4.33; N, 1.62; Cl, 12.99; ash, 17.86.

These crystals were insoluble in cold water (neutral slurry) and insoluble in ethanol. A KBr pressed disc showed a $N-H^+$ absorption at about 2800 cm^{-1} next to bands characteristic of the monosubstituted phenyl groups and possibly pyridine. The nmr spectrum (in dilute $CDCl_3$), despite 425 time averaging computer scans, showed no protons (down field from C_6H_6) other than the aromatic and pyridine protons. This may be due to broadening of the $N-H^+$ proton absorption because of the adjacent nitrogen quadrupole.

Thermal Decomposition of Bis(triphenylphosphine) Copper(I)Azide. The azide (2.0 g) and triphenylphosphine (7.0 g) were mixed in a small flask and heated under N_2 for 3 hr at 250°. There was vigorous gassing during the first hr which ceased after about 2-1/2 hr. Cooling and weighing showed a loss of 0.100 g (0.089 g N_2 theory). Some of this solid (4.09 g) was subjected to sublimation (137°/vac/24 hr). This left a dark, green-brown crystalline residue, 0.46 g (0.494 g theory for $(C_6H_5)_3P{=}N{-}Cu$). This substance had a poorly defined mp fused 205-225°, clear, dark brown melt by 245°.

Results

Copper(I)-triphenylphosphine complexes can be prepared by a number of simple methods:

1. Reaction of a copper(I) compound with the phosphine (Table II):

$$3P+CuCl \xrightarrow{CHCl_3} P_3CuCl \tag{1}$$

This method worked well for all copper(I) compounds tested except Cu_2O, Cu_2S or Cu_3P. Triphenyl-

Table II. Preparation of $(C_6H_5)_3M$ - Copper(I) Complexes from $(C_6H_5)_3M$ and Copper(I) Compounds[a]

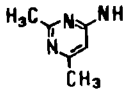
Product	Reagents	Reaction Conditions	Product mp. (°)	Lit. mp. (°)
P_3CuCl	$P+CuCl$	$CHCl_3$, r.t., crystals dried 65°/vac.	167-70 dec.	166 (5)
P_3CuBr	$P+CuBr$	$CHCl_3$, r.t., crystals dried 70°/vac.	165-7 dec.	164-7 (5)
P_3CuI	$P+CuI$	$CHCl_3$, r.t., crystals dried 60°/vac.	144-50 dec.	150-1 (5)
P_2CuCl[b]	$P+[PCuCl]_4$	C_6H_6, refl. 1/2 hr., crystals dried 50°/vac.	180-230 dec.	—
P_2CuCl[b]	$2P+CuCl$	C_6H_6, refl. 24 hr., crystals dried 50°/vac.	180-230 dec.	—
$P_3Cu_2Cl_2$	$3P+2CuCl$	$CHCl_3$, refl. 1 hr., cryst. $CHCl_3$-EtOH	237-9 dec.	241 (5)
$[PCuCl]_4$	$P+CuCl$	C_6H_5Cl, refl. 1 hr.	234-45 dec.	236-7 (5)
$P_2CuO_2CCH_3$	$P+CuO_2CCH_3$	$C_6H_5CH_3$, refl. 1/2 hr.	183-7 dec.	—
$P_2CuO_2CC_6H_5$	$P+CuO_2CC_6H_5$	$CHCl_3$, r.t. 1 hr., cryst. C_6H_{12}—C_6H_6	195-205 dec.	—
P_2CuCN	$3P+CuCN$	$CHCl_3$, r.t. 1/2 hr., cryst. C_6H_6	178-80	182-4(10)
P_2CuSCN	$3P+CuSCN$	$CHCl_3$, r.t. 1/2 hr.	236-7	210-13 (11)
As_3CuCl	$4As+CuCl$	$CHCl_3$, r.t., crystals dried 60°/vac.	152-5 dec.	—
Sb_3CuCl	$4Sb+CuCl$	$CHCl_3$, r.t.	148-53 dec.	—

[a] CuCl or CuI did not react with $(C_6H_5)_3Bi$, $(C_6H_5)_3N$, $(C_6H_5)_2S$; $(C_6H_5)_3P$ did not react with Cu_2O, Cu_2S or $CuF_2+Cu°$, Cu_3P.
[b] The x-ray powder pattern of P_2CuCl when prepared by either method was identical but different from mixtures of the starting materials or of P_3CuCl (both forms) and $P_3Cu_2Cl_2$.

Table III. Preparation of $(C_6H_5)_3P$ - Copper(I) Complexes Via Reductive Procedure[a]

Product	Reagents	Reaction Conditions	Product mp. (°)	Lit. mp. (°)
P_3CuCl	$P+CuCl_2\cdot 2H_2O$	EtOH, r.t., 20 hr.	166-9	166 (5)
P_3CuBr	$P+CuBr_2$	$CHCl_3$, r.t.	165-7	164-7 (5)
P_2CuNO_3	$P+Cu(NO_3)_2\cdot 3H_2O$	EtOH, r.t., 24 hr., Cryst. cold C_6H_6	240-2 dec.	237 (6)
$P_2CuAcAc$	$P+Cu(AcAc)_2$	Xylene, reflux 24 hr., Cryst. C_6H_6	181-4 dec.	182-4 dec. (13)
$P_2CuAcAcF_3$	$P+Cu(AcAcF_3)_2$	CH_3CN, reflux, 24 hr.	154-7	—[b]
$[P_3Cu]_2SO_4$	$P+Cu(SO_4)_2\cdot 5H_2O$	EtOH, r.t., 24 hr.	110-5-dec.	—
P_4CuClO_4	$P+Cu(ClO_4)_2\cdot 6H_2O$	EtOH, r.t., 24 hr., Cryst. C_6H_6	274-5 dec.	275 dec. (6)
P_4CuBF_4	$P+Cu(BF_4)_2$	dimethoxyethane, r.t., 1/2 hr., Cryst. C_6H_6—$CHCl_3$	285-6 dec.	—

[a] $(C_6H_5)_3P$ would not react with CuO, CuS $(C_6H_5)_3P$ and CuF_2+Cu° (CH_3CN, reflux, 72 hr.) yielded:



[b] This compound has been prepared by another method[14].

Table IV. Uncharged Ligand Loss on Heating or Crystallization of $[(C_6H_5)_3M]_nCuX$

Product	Starting Material	Reaction Conditions[a]	Product mp. (°)	Lit. mp. (°)
$P_3Cu_2Cl_2$	P_3CuCl	137°, vac., 20 hr., Cryst. hot C_6H_5Cl	238-9 dec.	241 (5)
$[PCuCl]_4$	P_3CuCl	180°, vac., 20 hr.	220-30 dec.	236-7 (5)
$[PCuI]_n$	P_3CuI	180°, vac., 20 hr.	258-60 dec.	266 (4)
P+dec.	$P_2CuO_2CC_6H_5$	180°, vac., 48 hr. (137°, vac., N.R.)	—	—
Cu_2O+P	$P_2CuO_2CCH_3$	137°, vac., 20 hr.	—	—
$CuCN+P$	P_2CuCN	180°, vac., 24 hr.	—	—
$CuSCN+P$	P_2CuSCN	137°, vac., 20 hr.	—	—
$[P_2Cu]_2SO_4$	$[P_3Cu]_2SO_4$	100°, vac., 60 hr.	184-7 dec.	—
$[P_2Cu]_2SO_4$	$[P_3Cu]_2SO_4$	Cryst. hot. C_6H_{12}	188-9 dec.	—
P+dec.	P_4CuBF_4	180°, vac., 24 hr.	—	—
$(PCuSC_6H_5)_2$	$P_2CuSC_6H_5$	116°, vac., 48 hr.	155-180	—
$(CuSC_6H_6)_n$	$(PCuSC_5H_5)_2$	170°, vac., 30 hr.	dec.	—
$[PCuOC_6H_5]_2$	$P_2CuOC_6H_5$	126°, vac., 72 hr.	177-82	—
$(CuOC_6H_5)_n$[b]	$PCuOC_6H_5$	170°, vac., 72 hr.	300 dec.	285 dec. (12)
$C_5H_5N+P+?$	$P_2CuCl\cdot C_5H_5N$	108°, vac., 8 hr.	—	—
$C_5H_5N+[PCuCl]_4$	$PCuCl\cdot C_5H_5N$	80°, vac., 24 hr.	225 dec.	236-7 (5)
P_3CuClO_4	P_4CuClO_4	Cryst. hot. EtOH	173-4	193 (4)
$[AsCuCl]_n$	As_3CuCl	Cryst. hot. C_6H_5Cl	206-8	—
$CuCl+As$	As_3CuCl	137°, vac., 24 hr.	—	—
$[SbCuCl]_n$	Sb_3CuCl	100°, vac., 18 hr.	160 dec.	—
$CuCl+Sb$	Sb_3CuCl	108°, vac., 60 hr.	—	—

[a] Vac. was ~ 0.01 mm. Hg; [b] *Partially* decomposed.

arsine (As) or stibine (Sb) yielded adducts, while triphenylamine, bismuth and diphenylsulfide did not.

2. Reduction[9] of a copper(II) compound (Table III):

$$7P+2CuCl_2 \xrightarrow{EtOH} 2P_3CuCl+(C_6H_5)_3PCl_2 \qquad (2)$$

This procedure seems to work very well and is probably applicable to most copper(II) compounds. The CuO and CuS did not react.

3. The loss of uncharged ligand on heating (vacuum) or on crystallization (Table IV) can take place stepwise:

$$P_3CuCl \xrightarrow[-P]{137^\circ/vac} P_3Cu_2Cl_2 \xrightarrow[-P]{180^\circ/vac} [PCuCl]_4 \qquad (3)$$

The uncharged ligands of these complexes may be selectively removed, the extent of removal and the product phosphine-copper ratio depends upon the rigor of the conditions and the nature of the removed ligand.* Thus P_3CuCl yields only $P_3Cu_2Cl_2$ at 137°/vac, while the arsine analog suffers a total loss of ligand at this temperature. The stibine compound yields only Sb+CuCl at 108°/vac. Crystallization from a solvent can also result in loss of ligand: $(P_3Cu)_2SO_4$, P_4CuClO_4, As_3CuCl.

Several of these complexes refused to lose their ligands to yield products with a lower ligand-copper ratio and instead, decomposed to triphenylphosphine and copper(I) salts (P_2CuCN, P_2CuSCN, $P_2CuO_2CCH_3$, $P_2CuO_2CC_6H_5$). Under these circumstances, compounds with a phosphine-copper ratio of one do not appear to be stable.** It appears that these P_2CuL complexes with bidentate charged ligands ($L = NO_3^-$, ClO_4^-, RCO_2^-) decompose rather than lose uncharged ligand.

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* Thermal gravitimetric curves do not yield sharply defined steps in the time vs wt. loss or time vs temp. curves. The ligand loss is slow and approaches the new compound's composition asymptotically over a period of many hours.

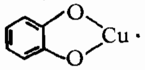
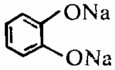
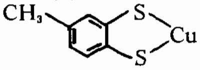
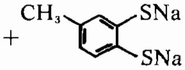
** The reaction of $[PCuCl]_4+AgNO_3$ (Table VII) yielded only P_2CuNO_3 which also seems to indicate that $[PCuNO_3]_n$ is probably not stable.

Table V. Displacement of Uncharged Ligand by Another[a]

Product	Reagents[b]	Reaction Conditions	Product mp. (°)
$P_2CuCl \cdot C_5H_5N$	$P_3CuCl + C_5H_5N$	C_5H_5N, reflux, 1 hr., solids dried 80°, vac.	160 dec.
$PCuCl \cdot$ bipyr.	$P_3CuCl +$ bipyr.	C_6H_6, reflux, 2 hr.	185-90 dec.[d]
$P_3CuCl \cdot 2DMF$	$P_3CuCl + DMF$	DMF, reflux, 6 hr.	145-65 dec.
$P_3CuCl \cdot C_6H_5NH_2$	$P_3CuCl + C_6H_5NH_2$	$C_5H_5NH_2$, 180°, 4 hr.	163-77 dec.
$PCuCl \cdot C_5H_5N$	$[PCuCl]_4 + C_5H_5N$	C_5H_5N, 116°, 1 hr.	154-60 dec.
$PCuCl \cdot$ bipyr.	$[PCuCl]_4 +$ bipyr.	bipyr., 250°, 1/2 hr., cryst. hot C_6H_{12}	187-95 dec.[d]
$PCuCl \cdot TMED$	$[PCuCl]_4 + TMED$	TMED, reflux, 18 hr.	dec. > 170
$[PCuCl]_4 \cdot DMF$[c]	$[PCuCl]_4 + DMF$	DMF, 100°, 6 min.	195-218 dec.

[a] P_3CuCl did not react with: bicycloheptadiene (150°), diphenylacetylene (250°), triethylamine (100°), TMED (121°). $[PCuCl]_4$ did not react with: bicycloheptadiene (90°), diphenylacetylene (230°), benzonitrile (191°), diphenylsulfide (250°), triethylamine (100°), CO (1500 psi, 150°, C_6H_6). [b] DMF = N,N'-*dimethylformamide*, bipyr. = 2,2'-bipyridyl. [c] Also some copper metal. [d] Ref. (9) gives m.p. 198°.

Table VI. Displacements of Charged Ligands on $[(C_6H_5)_3M]_3CuCl$[a]

Product(s)	Reagents	Reaction Conditions	Product mp. (°)	Lit. mp. (°)
P_2CuN_3	$P_3CuCl + NaN_3$	H_2O/THF, reflux, 18 hr.	208-11 dec.	185 dec. (11)
$P_2CuOC_6H_5$	$P_3CuCl + C_6H_5ONa$	$THF/C_6H_5CH_3$, reflux, 18 hr.	156-8 dec.	—
P_2CuNO_3	$P_3CuCl + AgNO_3$	$EtOH/CH_3CN$, reflux, 18 hr.	230-3	237 (6)
Cu_2S	$P_3CuCl + H_2S/NH_3$ (or aqu. Na_2S)	$CHCl_3$, r.t.	—	—
Cu_2O	$P_3CuCl + KOH$(aqu.)	EtOH, reflux	—	—
P_2CuBH_4	$P_3CuCl + NaBH_4$	$EtOH/CHCl_3$, r.t.	163.5-4.5 dec.	167 (4)
$Cu^\circ + P$	$P_3CuCl + CH_3ONa$	THF, r.t.	—	—
 $\cdot 2H_2O$	$P_3CuCl +$ 	THF, reflux, 4 hr.	—	—
$P_2CuSC_6H_5$	$P_3CuCl + C_6H_5SNa$	$THF/C_6H_5CH_3$, reflux, 18hr.	160-2	
$Cu_2S(?) + P$	$P_3CuCl +$ i–buSNa	$THF/C_6H_5CH_3$, reflux, 18hr.	—	—
	$P_3CuCl +$ 	$THF/C_6H_5CH_3$, reflux, 18 hr.	—	—
$CuSC_6H_5$	$As_3CuCl + C_6H_5SNa$	$THF/C_6H_5CH_3$, reflux, 18 hr.	300 dec.	285 dec. (12)
$CuSC_6H_5$	$Sb_3CuCl + C_6H_5SNa$	$THF/C_6H_5CH_3$, reflux, 18 hr.	300 dec.	285 dec. (12)
PCucpd[b]	$P_3CuCl +$ cpdNa	THF, r.t., 18hr., Cryst. hot. C_6H_{12}	195-205 dec.	(17)
$PCuC \equiv CC_6H_5$	$P_3CuCl + C_6H_5C \equiv CLi$	$Et_2O/C_6H_5CH_3$, reflux, 3hr.	195-7 dec.	212-14 dec. (16)
N.R.(No $(C_6H_5)_2$)	$P_3CuCl + C_6H_5Li$. TMED	dimethoxyethane, reflux, 18 hr.	—	—
$Cu^\circ + P$	$P_3CuCl + C_6H_5Na$	hexane/THF, reflux	—	—
N.R.	$P_3CuCl + (Allyl)_4Sn$	Neat, 200°	—	—
$Cu^\circ + P$	$P_3CuCl +$ Allyl–MgBr	Et_2O, r.t.	—	—
P_2CuN_3	$P_4CuClO_4 + NaN_3$	CH_3CN/H_2O, reflux, 1/2 hr.	209-17 dec.	185 dec. (11)
$P_3CuB(_6H_5)_4$	$P_3CuCl + (C_6H_5)_4BNa$	CH_3CN, excess P, reflux,1/2 hr.	150-65 dec.	—

[a] P_3CuCl did not react with: $NaF(THF/H_2O)$, NaF (glyme), $AgF(CH_3CN)$, $NaCN(THF/H_2O)$, NaCN(pyridine). [b] cpd = cyclopentadiene anion.

4. Displacement of uncharged ligand by another[9] (Table V):

$$P_3CuCl + C_5H_5N \xrightarrow{116^\circ} P + P_2CuCl \cdot C_5H_5N \qquad (4)$$

A number of nitrogen bases displace phosphine from P_3CuCl or add to $[PCuCl]_4$. Pyridine forms $P_2CuCl \cdot C_5H_5N$, $PCuCl \cdot C_5H_5N$ and bipyridine $PCuCl \cdot (C_5H_4N)_2$. Tetramethylethylenediamine (TMED) does not react with P_3CuCl but it adds to $[PCuCl]_4$ to give $PCuCl \cdot TMED$. Triethylamine does not react with either compound. Neither carbon monoxide, bicycloheptadiene, tolane, benzonitrile nor diphenylsulfide would react with these copper-phosphine complexes, even at temperatures as high as 250°.

Both dimethylformamide and aniline *add* to P_3CuCl to yield 2:1 and 1:1 complexes, respectively and $[PCuCl]_4$ yields an adduct $DMF \cdot [PCuCl]_4$.

5. Displacement of charged ligand by another (Table VI and VII):

$$P_3CuCl + cpdNa \xrightarrow{THF} 2P + PCucpd \qquad (5)$$

As expected, the chloride ions in P_3CuCl and $[PCuCl]_4$ are readily displaced by other anions. Table VI shows the wide variety of anions which react with P_3CuCl. The sulfide and hydroxide ions yield only Cu_2S or Cu_2O, respectively.

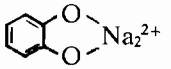
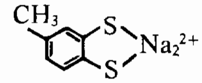
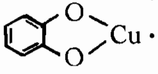
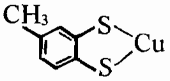
The sodium phenoxide and thiophenoxide yield $P_2CuMC_6H_5$ (M = S, O) while similar reagents CH_3ONa, i–C_4H_9SNa,  and  yield copper metal, Cu_2S,  $\cdot 2H_2O$, and  respectively. Excess sodium thiophenoxide does not lead to $P_2Cu(SC_6H_5)_2^-Na^+$ as might be expected (vide infra). Sodium cyclopentadiene and lithium phenylacetylide result in stable products while other carbanions (C_6H_5Na, allyMgBr, $C_6H_5Li \cdot TMED$)

Table VII. Displacement of Charged Ligand on $[PCuCl]_4$[a]

Reagents	Products	Reaction Conditions	Product mp (°)	Lit. mp (°)
$[PCuCl]_4+NaN_3$	$[PCuN_3]_n$	THF, reflux, 48 hr.	184-204 dec.	—
$[PCuCl]_4+AgNO_3$	P_2CuNO_3	CH_3CN/C_6H_5Cl reflux, 2 min. crystallized dimethoxyethane	229 dec.	237 (6)
$[PCuCl]_4+NaBH_4$	$Cu^\circ+P$	THF/EtOH r.t.	—	—
$[PCuCl]_4+C_6H_5SNa$	$[PCuSC_6H_5]_2$	$C_6H_5CH_3$, reflux, 2 hr.	—	—
$[PCuCl]_4+cpdNa$	PCucpd	THF, r.t., 18 hr.	150 dec.	—
$[PCuCl]_4+C_6H_5Li$	$Cu^\circ+P_3CuCl$	$THF/C_6H_5CH_3$, reflex, 18 hr.	167	166 (5)
$[PCuCl]_4+AgO_2CCH_3$	$P\cdot[Cu(O_2CCH_3)_2]_2$[b]	CH_3CN, reflux, 1 hr.	189-92 dec.	—
$[PCuCl]_4+C_6H_5CH_2Cl$	$(C_6H_5)_3P^+CH_2C_6H_5\cdot CuCl_2^-$	$C_6H_5CH_2Cl$, reflux	164-6 dec.	—
$[PCuCl]_4+C_6H_5Br$	$(C_6H_5)_4P^+\cdot CuBr_2^-$[c]	C_6H_5Br, reflux, 48 hr.	206-8 dec.	—
$[PCuCl]_4+C_6H_5I$	$(C_6H_5)_4P^+\cdot CuI_2^-$[c]	C_6H_5I, reflux, 48 hr.	210-11 dec.	216-19 (15)

[a] $[PCuCl)_4$ did not react with: $AgCN(CH_3CN)$, $(C_6H_5)_2Hg$ (210°), CH_3CO_2H (116°), NaO_2CCH_3 (THF). [b] dark green crystals. [c] also C_6H_5Cl as product (vpc).

Table VIII. Miscellaneous reactions of $P_2CuMC_6H_5$ (M=O,S)[a]

Product	Reagents	Reaction Conditions	Product mp (°)
$PCuC\equiv CH_6H_5$	$P_2CuSC_6H_5+C_6H_5C\equiv CH$	100°, neat, 30 hr.	198-202 dec.
$[(C_6H_5)_3P^+—CH_2—CH=CH_2]Br^-$	$P_2CuSC_6H_5+CH_2=CH—CH_2Br$	r.t., 72 hr.	223-5[b]
$[C_6H_5NCO]_3$	$P_2CuSC_6H_5+C_6H_5NCO$	r.t., exothermic reaction	273-6[c]
polymer (low m. wt.)	$P_2CuSC_6H_5+C_6H_5NCS$	100°, neat, 6 hr.	—
$P_2CuSC_6H_5\cdot CS_2$	$P_2CuSC_6H_5+CS_2$	refluxing CS_2	105-115 dec.[d]
$[PCuBr]_n$	$P_2CuSC_6H_5+C_6H_5Br$	refluxing dimethyl ether of diethylene glycol (164°)	—
$P_2CuOC_6H_5\cdot CS_2$	$P_2CuOC_6H_5+CS_2$	refluxing CS_2	152-5 dec.
$P_2CuOC_6H_5\cdot\sim 0.1C_5H_5N$	$P_2CuOC_6H_5+C_5H_5N$	refluxing C_5H_5N	—
$(C_6H_5)_3P=O+?$	$P_2CuOC_6H_5+O_2$	refluxing C_6H_6, 2 hr.	—
$Cu^\circ+P$	$P_2CuOC_6H_5+CO_2$	125°, C_6H_6 (N.R. at 75°)	—
polymer	$P_2CuOC_6H_5+C_6H_5NCS$	100°, neat, 6 hr.	—

[a] $P_3CuOC_6H_5$ would not react with: CO (1000 psi, 75°, C_6H_6), tolane (220°), bicycloheptadiene (90°). $P_2CuSC_6H_5$ would not react with: CO_2 (100°, C_6H_6), CO (1000 psi, 75°, C_6H_6), tolane (220°), pyridine (116°), bicycloheptadiene (90°, 1 hr.), chlorobenzene (in dimethyl ether of diethylene glycol, 164°). [b] Lit. (19) mp 209-14°. When this molecule is prepared from triphenylphosphine and allyl bromide (100°, neat) and cryst. twice from benzene, mp 226-7°. [c] Lit. (20) mp 275° (trimer of C_6H_5NCO). [d] Decomposes to $P_2CuSC_6H_5$ mp 154-5°.

either caused reduction or resulted in unstable products. Interestingly, sodium tetraphenylborate (with excess P) yielded $P_3CuB(C_6H_5)_4$ instead of the expected $P_4CuB(C_6H_5)_4$. The As_3CuCl and Sb_3CuCl complexes formed only $(CuSC_6H_5)_n$ with sodium thiophenoxide. The $(CuSC_6H_5)_n$ appears to complex only with triphenylphosphine and the stability of these complexes appears to be: $P \gg As > Sb$ which is in accord with the thermal behavior (Table IV). Cyanide is normally an excellent nucleophile but it would not react under a variety of conditions; as did neither NaF nor AgF.

The chloride ion in $[PCuCl]_4$ also participates in such displacement reactions (Table VII). Organic halides (C_6H_5Br, C_6H_5I, $C_6H_5CH_2Cl$) form quarternary phosphonium salts (CuX_2^- anion), the borohydride and phenyllithium yield copper metal, silver nitrate yields the rearranged product P_2CuNO_3, and sodium azide gives $(PCuN_3)_n$. Again fluoride and cyanide do not react.

These chloride displacement reactions generally proceeded with ease. Quite frequently reduction to copper metal is the favored route, particularly with $[PCuCl]_4$. With P_3CuCl, sodium borohydride yields P_2CuBH_4,[4] with $[PCuCl]_4$ only copper metal was obtained. Organic halides and d^{10} transition metal complexes frequently undergo oxidative additions at elevated temperatures,[18] in which the metal is oxidized. Here, the phosphorus ligand is oxidized instead of the copper ion. $[PCuCl]_4$ when reacted with benzyl chloride yields $(C_6H_5)_3P^+CH_2C_6H_5\cdot CuCl_2^-$. Both azide and thiophenoxide, due to their high nucleophilicities, lead to good yields of product. The azides are very stable substances, they resist shock and decompose only gradually at the mp.

$P_2CuOC_6H_5$ and $P_2CuSC_6H_5$ were subjected to a number of reactions (Table VIII). Carbon disulfide forms adducts which appear to lose the donor reversibly ($P_2CuOC_6H_5\cdot CS_2$ decomposes at about 100-110°). Pyridine does not add nor displace triphenylphosphine; phenylthiocyanate seems to yield low molecular weight polymers, the corresponding isocyanate the cyclic trimer. Phenylacetylene and $P_2CuSC_6H_5$ gave $PCuC\equiv CC_6H_5$ while allyl bromide resulted in a quarternary phosphonium salt. Non-reactive were carbon monoxide, tolane, bicycloheptadiene, pyridine, carbon dioxide and chlorobenzene.

Carbon disulfide seems to have a strong affinity for these copper-phosphine complexes (Table IX). Next to the above mentioned phenoxide compounds it reacted with the thiophenoxide and the acetonylacetonates. In case of the trifluoromethylacetylacetonate one oxygen of the ligand exchanged forming presumably;

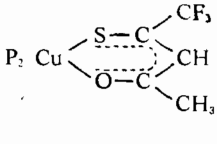


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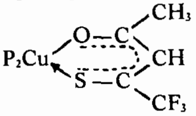
Table IX. Reaction of Phosphine Complexes with Carbon Disulfide

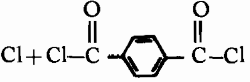
Product [a]	Reagents	Reaction Conditions	Product mp (°) [b]
$P_2CuOC_6H_5 \cdot CS_2$	$P_2CuOC_6H_5 + CS_2$	Refluxing CS_2 in excess	152-5 dec.
$P_2CuSC_6H_5 \cdot CS_2$	$P_2CuSC_6H_5 + CS_2$	Refluxing CS_2 in excess	105-115 dec. [c]
$P_2CuO_2CCH_3 \cdot 0.9CS_2$	$P_2CuO_2CCH_3 + CS_2$	Refluxing CS_2 in excess	130-5 dec.
	$P_2CuAcAcF_3 + CS_2$	Refluxing CS_2 in excess	167-78 dec.
$P_2CuAcAc \cdot CS_2$	$P_2CuAcAc + CS_2$	Refluxing CS_2 in excess	160-2 dec.
$P_3CuCl \cdot CS_2$	$P_3CuCl + CS_2$	Refluxing CS_2 in excess	165-200 dec.
$P_2CuCN \cdot 0.1CS_2$	$P_2CuCl + CS_2$	100°, CS_2 in excess	—

[a] There was no reaction of refluxing CS_2 with P_2CuSCN, P_2CuBF_4, P_2CuNO_3, $PCuCl \cdot$pyr., $[PCuCl]_4$ (6 hr., 125°).
[b] These all melt to red liquids excepting $P_2CuSC_6H_5 \cdot CS_2$. [c] dec. to $P_2CuSC_6H_5$ mp 154-5°.

Table X. Reactions of $P_nCuCl \cdot C_5H_5N$ (n=1,2)

Products	Reagents	Reaction Conditions	Product mp (°)
$P_2CuN_3 \cdot C_5H_5N$	$P_2CuCl \cdot C_5H_5N + NaN_3$	Pyridine, 116°	120 dec.
$C_5H_5N + [PCuCl]_4$	$P_2CuCl \cdot C_5H_5N + (C_6H_5)_2C_2$	Neat, 195°, 4 hr.	220 dec.
$P_2CuCl \cdot C_5H_5N \cdot HCl$	$P_2CuCl \cdot C_5H_5N + HCl$ (anhydr.)	dry $CHCl_3$, 1/2 hr.	—
$PCuN_3 \cdot C_5H_5N$	$PCuCl \cdot C_5H_5N + NaN_3$	Pyridine, 116°	119-26 dec.
$(CuSC_6H_5)_n$	$PCuCl \cdot C_5H_5N + C_6H_5SNa$	Pyridine, 116°, 18 hr.	300 dec.
$(PCuCl)_2 \cdot C_5H_5N \cdot HCl$	$PCuCl \cdot C_5H_5 + HCl$ (anhydr.)	dry $CHCl_3$, r.t.	—
$PCuC{\equiv}CC_6H_5$	$PCuCl \cdot C_5H_5N + C_6H_5C{\equiv}CH$	Neat, 142°, 2 1/2 hr.	200 dec.
$C_5H_5N + (C_6H_5)_2C_2 + [PCuCl]_4$	$PCuCl \cdot C_5H_5N + (C_6H_5)_2C_2$	Neat, 185°, 1 hr.	190-215 dec.

Table XI. Miscellaneous Reactions of Phosphine Complexes [a]

Products	Reagents	Reaction Conditions
P_2CuBF_4	$P_2CuBH_4 + HF$	$CHCl_3$, aqu. HF
$(C_6H_5)_3P{=}O$	$[PCuCl]_4 + NO$	
N.R.	$P_3CuCl +$ 	
$[(C_6H_5)_3P{=}N{-}Cu]_n$	$P_2CuN_3 + P$	250°, Neat
$[PCuBr]_4 + N_2$	$P_2CuN_3 + C_6H_5Br$	180°, refluxing C_6H_5Br

[a] There was no reaction with: $P_2CuO_2CCH_3 + C_6H_5Cl$ (131°), $P_2CuO_2CCH_3 + C_5H_5N$ (116°), $P_3CuCl + h\nu(C_6H_{12}$, r.t.). P_3CuCl could not be reduced to a Cu° complex with N_2H_4/EtOH, $(n{-}bu)_3SnH$, Na(Hg), Na(Pb), Zn, e– (DMF, $bu_4N^+ClO_4^-$) polarograph, Na (NH_3,l), Mg, $CaH_2 \cdot (C_6H_5)_3P$ did not react with copper powder 275°, 12 hr., neat.

The P_3CuCl also yielded an adduct. The cyanide appeared to be marginally reactive while the thiocyanide, tetrafluoroborate, nitrate, $PCuCl \cdot C_5H_5N$, and $[PCuCl]_4$ were unreactive even under strenuous conditions (125°).

The pyridine adducts of these copper(I)-phosphine complexes also undergo a number of reactions (Table X). With $PCuCl \cdot C_5H_5N$, sodium thiophenoxide yields only $(CuSC_6H_5)_n$, sodium azide yields the respective $P_2CuN_3 \cdot C_5H_5N$, $PCuN_3 \cdot C_5H_5N$; phenylacetylene yields $PCuC{\equiv}CC_6H_5$ and tolane decomposes $PCuCl \cdot C_5H_5N$ to pyridine and $[PCuCl]_4$. Anhydrous hydrogen chloride and $PCuCl \cdot C_5H_5N$ seems to lead to $[PCuCl]_2 \cdot C_5H_5N \cdot HCl$. Carbon disulfide and bicycloheptadiene proved to be non-reactive.

Table XI gives the results of a number of miscellaneous reactions. P_2CuBH_4 and hydrogen fluoride yield P_2CuBF_4; the P_2CuN_3 decomposes in excess triphenylphosphine at 250° to yield $[(C_6H_5)_3P{=}N{-}Cu]_n$ and in refluxing bromobenzene this azide formed $[PCuBr]_4$ and nitrogen. P_3CuCl does not decarboxylate aromatic acid chlorides;[21] $[PCuCl]_4$ and nitric oxide yields triphenylphosphine oxide.

Discussion

The coordination number of copper(I) complexes is two (linear sp) or more generally four (tetrahedral sp^3).[22,23,24] This arises naturally from the d^{10} configuration of the ion; the charged and uncharged ligands fill the 4 s–p orbitals to form variously hybridized complexes. The coordination number three also exists. $KCu(CN)_2$,[25] copper(I)-olefin (cyclooctatetraene),[26] the bis-thiourea adduct[27] and the molecule $(P_3Cu_2Cl_2$[28] all have planar, three coordinated copper(I) ions. In

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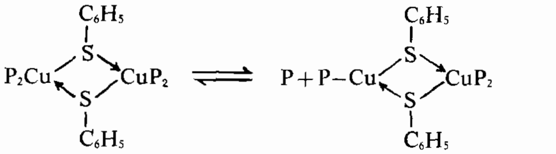
this work the solution molecular weights of the compounds P_2CuCN, P_2CuN_3, $P_2CuMC_6H_5$, $[P_2CuMC_6H_5]_2$ (M=S, O) and PCuCl·pyr. all appear to be approximately monomeric (in dilute solution). These molecules are either true monomers (*e.g.* P_2CuX) or dissociated bridged dimers* in solution. In either case the solutions must have molecules in which the metal coordination is three. It might be most reasonable to suppose that these compounds are dissociated dimers in view of the known tendency for bridging which these charged ligands have. For example, copper(I) thiophenoxide is clearly a polymer (insoluble in solvents, very high mp), $(PCuSC_6H_5)_2$ is a dimer in solution, while $P_2CuSC_6H_5$ strangely appears monomeric. An equilibrium such as,

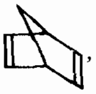


(7)

would resolve this apparent anomaly. The corresponding oxygen system $(PCuOC_6H_5)_2$ and $P_2CuOC_6H_5$ also fits this scheme. On the other hand, similar d^{10} systems appear to have three coordinated, monomeric molecules in solution: tris(tri-*o*-tolyl phosphite) nickel(0)[30] and ethylene bis(tri-*o*-tolyl phosphite) nickel(0)[31] as well as some silver(I)-ligand complexes.[32]

It would appear to be reasonable that an empty 4p orbital on a three coordinated d^{10} atom would accept other ligands to become fully saturated. $P_2CuSC_6H_5$ (and the others) does *not* react with additional charged ligands to become four-coordinated.

$$P_2CuSC_6H_5 + L \not\longrightarrow P_2CuSC_6H_5 \cdot L \qquad (8)$$

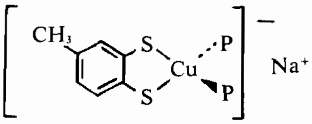
L=

, $C_6H_5C{\equiv}CC_6H_5$, CO, C_5H_5N, $(C_6H_5)_3P$, $C_6H_5S^-$

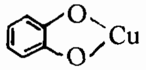
even under stringent conditions. The compound $P_3CuB(C_6H_5)_4$, which is highly dissociated in dilute solution (Table I), does not appear to have phenyl groups on boron interacting with the copper ion (π (h^6)–bonding) as judged by the absence of the 1460 and 1390 cm^{-1} bands (halocarbon mull or KBr disc) which are said to be characteristic of this type of bonding.[33]

Chelating ligands frequently yield more stable complexes than analogous non-chelating ligands do. When the reaction,

(9)

was carried out the stable copper(II) toluene–3,4–dithiolate was obtained and not the expected complex:



Similarly, catechol disodium salt and P_3CuCl leads to


$\cdot 2H_2O$. It is quite clear that the coordination number of three in these copper(I) complexes represents a fairly stable one and that even « good » ligands do not add to yield four coordinated species.

A rigorous explanation of the preference of copper(I) ion for the coordination numbers two, three, or four in these various complexes is not known. It appears to be clear that the metal coordination number of three in the complexes $P_2CuMC_6H_5$, $(PCuMC_6H_5)_2$ (M=O, S), P_2CuN_3, P_2CuCN and PCuCl·pyr. is one of considerable stability; the metal evidently prefers it to a coordination number of two or four. The coordination number of three must therefore be classified as an important one in copper(I) complex chemistry.

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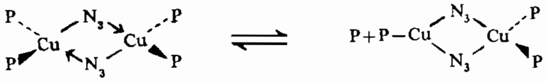
* An *apparent* monomeric molecular weight can result from the dissociation of a tetracoordinated, bridged dimer,[29]



(6)

if the dissociation is substantial. The resulting product $PCu(N_3)_2CuP_2$ must have one three coordinated copper atom. An actual example of such a molecule $P_3Cu_2Cl_2$.[28]

(29) P_2CuN_3 is «monomeric» in dilute solution[11] but a bridged dimer in the solid state: R.F. Ziolo, A.P. Gangham, Z. Dori, C.G. Pierpont, and R. Eisenberg, *J. Am. Chem. Soc.*, *92*, 738 (1970).

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