

353. *The Constitution of Complex Metallic Salts. Part XXI.¹ The Copper(I), Silver(I), and Gold(I) Derivatives of 2-Phenylisophosphindoline.*

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2-Phenylisophosphindoline gives four distinct types of copper(I), silver(I), and gold(I) derivatives. For type (I), $(R_3P, MX)_n$ ($M = \text{metal}$, $X = \text{halogen}$), the copper(I) iodide member forms the expected tetramer, the silver(I) bromide member in solution has a value $n \approx 2.1$, and the three gold(I) halides are stable monomers. For type (II), $(R_3P)_2MX$, the copper(I) and silver(I) iodide members are associated; the compound $(R_3P)_2AuI$ is covalent in organic solvents but ionised in the crystal form. For type (III), $(R_3P)_3MX$, the three gold(I) members are stable; otherwise only the copper(I) iodide and the silver(I) perchlorate members were isolated, the latter being ionised in solution. For type (IV), $[(R_3P)_4M]X$, no silver(I) or gold(I) derivatives were isolated, and in the copper(I) series only the nitrate and perchlorate.

The stabilities and structures of these derivatives are discussed.

IN view of the strong co-ordinating power of 2-phenylisophosphindoline, $o\text{-C}_6\text{H}_4(\text{CH}_2)_2\text{PPh}$, which enables it to form compounds with certain metallic halides in which the metal shows an unusual co-ordination number,^{1,2} we have investigated its co-ordinated derivatives with copper(I), silver(I), and gold(I) halides, and with certain other salts of these metals.

The copper(I) derivatives fall into the expected four classes, having one, two, three, and four molecules of the phosphine to each metallic atom (I—IV, where R_3P represents



2-phenylisophosphindoline, M the metal, and X the halide or an anion); no silver(I) or gold(I) derivatives of type (IV) were isolated. The formation of the copper(I) members of these four classes, by co-ordination with methyldiphenylarsine, has been reported by Nyholm.³

The main points of interest of our members of each class will be discussed in turn.

Type (I).—The copper(I) members (I; $M = \text{Cu}$, $X = \text{Cl}$, Br , or I) and the silver(I) members (I; $M = \text{Ag}$, $X = \text{Cl}$ or Br) were readily prepared as colourless crystals of sharp melting point. Surprisingly, the compound (I; $M = \text{Ag}$, $X = \text{I}$) could not be isolated, although the iodo-members in analogous compounds are often more stable than the chloro- and bromo-members.

Copper(I) and silver(I) iodides, with simple trialkyl-phosphines and -arsines, form

¹ Part XX, Collier and Mann, preceding paper.

² Collier, Mann, D. G. Watson, and H. R. Watson, *J.*, 1964, 1803.

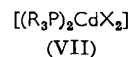
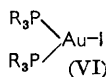
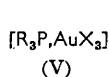
³ Nyholm, *J.*, 1952, 1257.

tetramers having a unique structure.^{4,5} We find that the compound (I; M = Cu, X = I) shows a molecular weight in dichloromethane solution indicating a stable tetramer. The compound (I; M = Ag, X = Cl) is probably tetrameric in the solid state, but its molecular weight in dichloromethane gives a value for n of 2.1. This value most probably arises from partial dissociation of the tetramer in solution, and not, for example, to the formation of a bridged complex of type $[\text{R}_3\text{P}, \text{AgCl}_2, \text{Ag}, \text{R}_3\text{P}]$.

The crystalline gold(I) members (I; M = Au, X = Cl, Br, or I) all proved, as expected,⁵ to have normal monomeric molecular weights in dichloromethane.

The compounds (I; M = Cu, X = I), (I; M = Ag, X = Cl) and (I; M = Au, X = I) gave nitrobenzene solutions which were virtually non-conducting.

It is noteworthy that the compounds (I; M = Cu, X = Cl or Br) when treated in cold chloroform solution with chlorine and bromine, respectively, appeared to undergo general decomposition, and the corresponding copper(II) compounds cannot be obtained in this way. The gold(I) compounds (I; M = Au, X = Cl or Br), when similarly treated, gave the stable crystalline gold(III) compounds (V; M = Au, X = Cl or Br); many similar compounds have been previously made,⁶ and X-ray crystal analysis shows that the 4-coordinate gold(III) atom has a planar configuration in these compounds.⁷



Type (II).—In this class, the three halogen members in both the copper(I) and silver(I) series were stable compounds which could be recrystallised from organic solvents, although the compound (II; M = Ag, X = NO₃) was light-sensitive. In the gold(I) series the chloride was too unstable to be isolated, the bromide was stable in the crystalline state but dissociated in hot organic solvents to give the compound (I; M = Au, X = Br) and the free phosphine, and the iodide had considerable stability. The compounds are covalent, for the members (II; M = Cu, X = I), (II; M = Ag, X = I or NO₃), and (II; M = Au, X = I) gave nitrobenzene solutions having negligibly low conductivities.

Previous work on compounds of this general class gave a variety of results. Nyholm³ considered that his arsine-copper(I) halide compounds of composition $(\text{R}_3\text{As})_2\text{CuX}$ in the solid state probably formed salts of type $[(\text{R}_3\text{As})_4\text{Cu}][\text{CuX}_2]$ but in solution underwent extensive dissociation, forming non-electrolytes most probably of the type $[(\text{R}_3\text{As})_3\text{CuX}]$ and $(\text{R}_3\text{As}, \text{CuX})_4$. Cass, Coates, and Hayter⁸ obtained compounds of type $(\text{R}_3\text{P})_2\text{CuI}$, which were stable but too insoluble for molecular weight determinations, and of type $(\text{R}_3\text{P})_2\text{AgI}$ which were stable soluble compounds, monomeric and un-ionised in benzene solutions. Hart and Mann,⁹ using the ligand *o*-diethylphosphinophenyldiethylarsine, C₆H₄(PEt₂)(AsEt₂), obtained a compound of type $(\text{P-As})_2\text{CuCl}$, which had Λ_m 21.1 mhos in nitrobenzene, and hence was almost certainly a uni-univalent salt of type $[(\text{P-As})_2\text{Cu}][\text{CuCl}_2]$; the corresponding silver iodide derivative had Λ_m 16.4 mhos, and was probably a similar salt incompletely ionised in solution.

Our present isophosphindoline compounds of this class show two unexpected points of interest. The compounds (II; M = Cu, X = I), (II; M = Ag, X = Cl), and (II; M = Ag, X = I) in dichloromethane solution at 23° show molecular weights which are, respectively, 43, 29, and 41% greater than that of the monomeric form. The reason for this is unknown; these compounds may exist in solution as an equilibrium mixture of the monomeric $(\text{R}_3\text{P})_2\text{MX}$ and the bridged $(\text{R}_3\text{P})_2\text{MX}_2\text{M}(\text{R}_3\text{P})_2$ forms, but there is at present no evidence for this.

⁴ Mann, Purdie, and Wells, *J.*, 1936, 1503.

⁵ Mann, Wells, and Purdie, *J.*, 1937, 1828.

⁶ Mann and Purdie, *J.*, 1940, 1235.

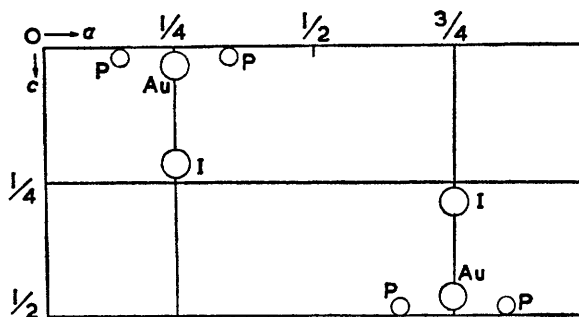
⁷ Perutz and Weisz, *J.*, 1946, 438.

⁸ Cass, Coates, and Hayter, *J.*, 1955, 4007.

⁹ Hart and Mann, *J.*, 1957, 2816.

The gold(I) compound (II; $M = Au$, $X = I$) is of particular interest. It has a normal monomeric molecular weight in dichloromethane solution and its nitrobenzene solution has Λ_m 1.01 mhos; it is soluble in various organic solvents but insoluble in water, and in benzene solution has a dipole moment 8.05 D. We are indebted for this determination and report to Mrs. I. Borrow, working under the direction of Dr. J. Chatt, F.R.S., at the Imperial Chemical Industries Limited Akers Research Laboratories. "The compound in benzene solution at 25° had μ 8.05 \pm 0.2 D (error probably much less), the atom polarisation being taken as 15% of the electron polarisation. Determinations were carried out at three concentrations, and doubling the concentration caused a 10% decrease in the moment. It is certain that this does not occur from association, but from a decrease in "activity" with greater concentration, an effect which is quite normal for molecules of this general type. The above value, derived from extrapolation to infinite dilution, is in fact very little different from that derived from the measured concentrations. The estimated dipole moment, if the molecule had the trigonal plane structure (VI), is 8 D."

A brief X-ray crystal structure examination, undertaken by Dr. G. A. Mair and Mr. H. M. Powell, F.R.S., at the Chemical Crystallography Laboratory of the University of Oxford, shows, however, that the P-Au-P atoms are nearly linear (see Figure). The y -co-ordinates have not been determined, but, because the Au and the I atoms lie in special positions, the y -co-ordinates for these atoms must differ either by zero or by half the length of the b -axis (*i.e.*, by 3.21 Å). In the first case the closest Au-I distance is 3.18 Å and the I atom is in the same plane as that formed by the Au atom and its attached P atoms; in the second case the Au-I distance is 4.52 Å, and no such coplanarity exists. The sum of the ionic radii of Au^+ and I^- is *ca.* 3.53 Å, whereas the covalent Au-I bond is *ca.* 2.67 Å. It is clear, therefore, that in the solid state this compound has largely (and possibly completely) an ionic structure, $[(R_3P)_2Au]^+I^-$. A complete crystal analysis of this compound and of its copper(I) and silver(I) analogues would be of great interest.



Compound (II; $M = Au$, $X = I$). Diagram of the [010] projection.

Our compound differs in its physical properties from the compound which Cass *et al.*⁸ formulate as $[(p-Me_2N \cdot C_6H_4 \cdot PMe_2)_2Au]I$, which can be recrystallised from benzene but in nitrobenzene solution has a molal conductance of 12.5 mhos, and hence is apparently partly ionised in this solvent; its molecular weight in organic solvents has not been recorded.

Type (III).—The compound (III; $M = Cu$, $X = I$) was the only copper(I) member isolated; its molecular weight in dichloromethane showed that it was a monomer, and its nitrobenzene solution was non-conducting. All attempts to prepare the compounds (III; $M = Ag$, $X = Cl$, Br , or I) unexpectedly failed. The silver(I) compound (III; $M = Ag$, $X = ClO_4$) was the only silver compound isolated. In nitrobenzene solution it had Λ_m 23.0 mhos, and must, therefore, be a salt of type $[(R_3P)_3Ag]^+ClO_4^-$.

In contrast to the copper(I) and silver(I) compounds, the three gold(I) compounds (III; $M = Au$, $X = Cl$, Br , or I) were readily isolated and recrystallised; the bromo-member in dichloromethane showed a molecular weight 7% above the monomer value.

There is little doubt that in covalent compounds of this class the metal occupies the centre of a tetrahedron with the four co-ordinated groups at the apices.

Type (IV).—We have obtained only the compounds (IV; $M = \text{Cu}$, $X = \text{NO}_3$ or ClO_4), which gave nitrobenzene solutions having Λ_m 25.0 and 25.5 mhos, respectively, and which were, therefore, the expected uni-univalent salts. Attempts to convert them into the corresponding iodides by the action of sodium iodide in solution gave solely the corresponding derivative of type (III) and the free phosphine. This is similar to Nyholm's experience with his analogous dimethylphenylarsine derivatives;³ the strongly co-ordinating iodide ion evicts a phosphine molecule from the cation in these type (IV) compounds, which can be stabilised only by very weakly co-ordinating anions such as NO_3^- and ClO_4^- .

Even the use of these anions did not furnish any silver or gold(I) compounds of type (IV). Stable gold(I) halide compounds of type (IV) can be readily prepared if chelating diarsines¹⁰ or arsine-phosphines⁹ are used, the enhanced stability being caused by the much stronger co-ordinating power of these groups when in the chelated ring system. This chelation is clearly not essential for stable copper(I) and silver(I) derivatives of type (IV), for, in addition to the above copper(I) compounds, stable salts having the $[\text{Cu}(\text{PPh}_3)_4]^+$ and $[\text{Ag}(\text{PPh}_3)_4]^+$ cations and the ClO_4^- , BrO_3^- , and NO_3^- anions have been prepared.¹¹

In the compounds described in this Paper, the power of the phosphine to stabilise metallic complexes in which the metal has an unusual co-ordination number or valency is less pronounced than in the derivatives of the Group VIII metals described earlier,^{1,2} but the copper–silver–gold series clearly offers less scope for the exercise of this power.

The compounds of the phosphine with the cadmium halides have been briefly investigated. The phosphine (2 Equivalents) combined with cadmium bromide and iodide to give the bis(phosphine)dibromocadmium (VII; $X = \text{Br}$) and the more stable di-iodo-derivative (VII; $X = \text{I}$), respectively. Attempted preparation of the corresponding dichloro-derivative gave a mixed product, apparently because the unstable derivative (VII; $X = \text{Cl}$) lost phosphine with the formation of the bridged compound $(\text{R}_3\text{P})\text{ClCdCl}_2\text{CdCl}(\text{R}_3\text{P})$, which was the only pure chloro-derivative isolated.

EXPERIMENTAL

The term "the phosphine" is applied throughout to 2-phenylisophosphindoline (preparation in ref. 12). Compounds were colourless unless otherwise stated. Molecular weights were determined in dichloromethane solution by the vapour-pressure thermistor technique at 30°. Molar conductivities (Λ_m) were measured in nitrobenzene solution.

Type (I).—*Mono(phosphine)monochlorocopper* (I; $M = \text{Cu}$, $X = \text{Cl}$). The phosphine (0.318 g., 1.5 mol.) in ethanol (3 ml.) was added dropwise with shaking to a solution of copper(I) chloride dihydrate (0.170 g.) in ethanol (5 ml.). The green colour faded as the deliquescent crystalline *monochloro-compound* separated, m. p. 142.5–143° (from acetone–ethanol) (Found: C, 54.0; H, 4.4. $\text{C}_{14}\text{H}_{13}\text{ClCuP}$ requires C, 54.0; H, 4.2%). The *bromo-compound*, similarly prepared and recrystallised, had m. p. 134–135° (Found: C, 47.15; H, 3.9. $\text{C}_{14}\text{H}_{13}\text{BrCuP}$ requires C, 47.2; H, 3.7%). The phosphine (0.212 g., 1 mol.), in ethanol (5 ml.), when added to a solution of copper(I) iodide (0.190 g.) in aqueous potassium iodide, gave a heavy white precipitate which was collected, washed with water, dissolved in a minimum of hot acetone–ethanol (2 : 3 v/v) and boiled with copper(I) iodide to remove any compound of type (II). The filtered, cooled solution gave the *iodo-compound*, m. p. 195.5–196° (Found: C, 42.0; H, 3.5%; M , 1590. $\text{C}_{14}\text{H}_{13}\text{CuIP}$ requires C, 41.7; H, 3.3%; M , for the tetramer, 1610).

Mono(phosphine)monochlorosilver (I; $M = \text{Ag}$, $X = \text{Cl}$) The phosphine (0.212 g., 1 mol.) in acetone (5 ml.) was added to a suspension of silver chloride (0.144 g.) in ethanol (10 ml.), which was boiled under reflux until almost clear, filtered, and cooled; the *monochloro-compound* which separated had m. p. 150–151° (from acetone–ethanol; 1 : 1) (Found: C, 48.6; H, 4.1%;

¹⁰ Nyholm, *Nature*, 1951, 118, 705; Nyholm and Stephenson, *Rec. Trav. chim.*, 1956, 75, 687.

¹¹ Cotton and Goodgame, *J.*, 1960, 5267.

¹² Mann, Millar, and Watson, *J.*, 1958, 2516.

M, 755. $C_{14}H_{13}AgClP$ requires C, 48.4; H, 3.7%; *M*, for monomer, 355). The *bromo-compound*, similarly prepared and purified, had m. p. 152—153° (Found: C, 41.9; H, 3.5. $C_{14}H_{13}AgBrP$ requires C, 42.0; H, 3.3%).

Mono(phosphine)monochlorogold (I; *M* = Au, *X* = Cl). The phosphine (1 g., 2 mol.), in ethanol (5 ml.), was added dropwise to a solution of sodium chloroaurate dihydrate (0.9 g.) in water (3 ml.) and ethanol (5 ml.) under nitrogen. The initial yellow precipitate slowly re-dissolved, and the monochloro-compound separated, m. p. 192—194° (lit.,¹³ 193°) (from acetone) (Found: C, 37.5; H, 2.7%; *M*, 450. Calc. for $C_{14}H_{13}AuClP$ C, 37.8; H, 2.9%; *M*, 444).

A saturated aqueous acetone solution of sodium bromide (2 ml.) was added to a solution of the monochloro-compound (0.2 g.) in acetone (15 ml.); the mixture was boiled under reflux for 10 min., and hot water added until precipitation started. The *bromo-compound* had m. p. 195—197° (from acetone) depressed to below 160° by admixture with the chloro-compound (Found: C, 33.8; H, 3.0%; *M*, 493. $C_{14}H_{13}AuBrP$ requires C, 34.3; H, 2.7%; *M*, 489). Repetition of this experiment, using sodium iodide in place of the bromide, gave the *iodo-compound*, m. p. 181—182° (Found: C, 32.0; H, 2.5%; *M*, 550. $C_{14}H_{13}AuIP$ requires C, 31.3; H, 2.4%; *M*, 536).

Type (II).—*Bis(phosphine)monochlorocopper* (II; *M* = Cu, *X* = Cl). The phosphine (0.265 g., 2.5 mol.) in acetone (4 ml.) was added to a solution of copper(II) chloride dihydrate (0.085 g.) in water (2 ml.) and acetone (3 ml.); the white precipitated *monochloro-compound* had m. p. 151—152° (Found: C, 63.7; H, 5.4. $C_{28}H_{26}ClCuP_2$ requires C, 64.1; H, 5.0%). The *bromo-compound*, m. p. 156—157° (Found: C, 58.7; H, 4.4. $C_{28}H_{26}BrCuP_2$ requires C, 59.1; H, 4.6%), and the *iodo-compound*, m. p. 168—169° (Found: C, 54.4; H, 4.8%; *M*, 880. $C_{28}H_{26}CuIP_2$ requires C, 54.7; H, 4.3%; *M*, 614), were similarly prepared. The three compounds were recrystallised from acetone-ethanol.

Bis(phosphine)monochlorosilver (II; *M* = Ag, *X* = Cl). The compound (I; *M* = Ag, *X* = Cl) (0.173 g.) was dissolved in an acetone-ethanol solution of the phosphine (0.106 g., 1 mol.), which, when boiled under reflux for 15 min. and cooled, deposited the *monochloro-compound*, m. p. 154—155°, mixed m. p. with (I; *M* = Ag, *X* = Cl) 130° (Found: C, 59.1; H, 4.9. $C_{28}H_{26}AgClP_2$ requires C, 59.3; H, 4.6%). The *bromo-compound* was prepared (a) by boiling a suspension of silver bromide (0.095 g.) in ethanol (10 ml.) with the phosphine (0.212 g., 2 mol.) in acetone (5 ml.) for 30 min., when the filtered, cooled solution deposited the compound, m. p. 156—157° (Found: C, 54.4; H, 4.9%; *M*, 790. $C_{28}H_{26}AgBrP_2$ requires C, 54.9; H, 4.3%; *M*, 612; (b) by the action of the phosphine (1 mol.) on the compound (I; *M* = Ag, *X* = Br), as above. A mixture of the two monobromo-compounds had m. p. 125°. The *iodo-compound*, similarly prepared from silver iodide, had m. p. 154—155° (Found: C, 51.0; H, 4.2%; *M*, 928. $C_{28}H_{26}AgIP_2$ requires C, 50.9; H, 3.95%; *M*, 659). These three compounds were recrystallised from acetone-ethanol. The *nitrate-compound* (II; *M* = Ag, *X* = NO₃) crystallised when solutions of silver nitrate (0.170 g.) in ethanol (3 ml.) with a trace of water, and of the phosphine (0.424 g., 2 mol.) in ethanol (5 ml.), were mixed and cooled in ice-salt. The compound had m. p. 173—174° (from ethanol) (Found: C, 56.55; H, 4.8. $C_{28}H_{26}AgNO_3P_2$ requires C, 56.6; H, 4.4%), Λ_m 0. Exposure to light caused the colour to change from white to pale buff.

Bis(phosphine)monobromogold (II; *M* = Au, *X* = Br). The compound (I; *M* = Au, *X* = Br) (0.09 g.) was dissolved in a hot solution of the phosphine (0.043 g., 1 mol.) in acetone (10 ml.); the mixture was boiled for 10 min., and then cautiously diluted with boiling water to initiate crystallisation of the *monobromo-compound*, m. p. 163—164° (Found: C, 47.9; H, 3.8. $C_{28}H_{26}AuBrP_2$ requires C, 47.9; H, 3.7%). The *iodo-compound*, similarly prepared and recrystallised from diethyl carbonate, had m. p. 154—155° (Found: C, 44.5; H, 3.6%; *M*, 735. $C_{28}H_{26}AuIP_2$ requires C, 44.9; H, 3.5%; *M*, 748), Λ_m 1.01 mhos.

Type (III).—*Tris(phosphine)monoiodocopper* (III; *M* = Cu, *X* = I). The compound (II; *M* = Cu, *X* = I) (0.165 g.) was added to a hot solution of the phosphine (0.056 g., 1 mol.) in ethanol-acetone (5 ml.), and the mixture boiled for 10 min. and allowed to cool. The *mono-iodo-compound* which separated had m. p. 180.5—181° (from ethanol-acetone) (Found: C, 61.0; H, 5.0%; *M*, 790. $C_{42}H_{39}CuIP_3$ requires C, 61.0; H, 4.7%; *M*, 826), Λ_m at 23° 0.28 mho.

Tris(phosphine)silver perchlorate (III; *M* = Ag, *X* = ClO₄). Silver perchlorate (0.109 g.), dissolved in hot ethanol (3 ml.), when added dropwise to a solution of the phosphine (0.32 g.,

¹³ Mann, Millar, and Stewart, *J.*, 1954, 2832.

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3 mol.) in ethanol (5 ml.) gave an immediate oily precipitate which solidified on cooling. After purification by repeated precipitation from acetone solution by ether, the light-sensitive *perchlorate* (0.3 g.) had m. p. 167—168° (Found: C, 59.2; H, 4.9. $C_{42}H_{39}AgClO_4P_3$ requires C, 59.6; H, 4.6%), Λ_m at 20° 23 mhos.

Tris(phosphine)monochlorogold (III; M = Au, X = Cl). The compound (I; M = Au, X = Cl) (0.18 g.) was dissolved in boiling acetone (10 ml.) containing the phosphine (0.18 g., 2.2 mol.). The *monochloro-compound* which separated on cooling had m. p. 180—182° (from acetone containing free phosphine) (Found: C, 57.7; H, 4.7. $C_{42}H_{39}AuClP_3$ requires C, 58.0; H, 4.5%). The *bromo-compound*, m. p. 196—198° (from acetone) (Found: C, 54.4; H, 4.2%; M, 970. $C_{42}H_{39}AuBrP_3$ requires C, 55.2; H, 4.3%; M, 913), and the *iodo-compound*, m. p. 185—186° (from ethanol) (Found: C, 52.5; H, 4.4. $C_{42}H_{39}AuIP_3$ requires C, 52.5; H, 4.1%), were similarly prepared. The iodo-compound was also prepared by treating a boiling acetone solution of the phosphine with the compound (II; M = Au, X = I) and with aqueous sodium iodide; after boiling for 10 min., the solution was poured into water. The precipitated gummy iodide solidified when rubbed with acetone, and was then recrystallised as before.

Type (IV).—*Tetakis(phosphine)copper(i) nitrate* (IV; M = Cu, X = NO₃). The phosphine (0.48 g., 4.6 mol.), in ethanol (6 ml.) at 0°, was added to a solution of cupric nitrate hexahydrate (0.148 g.) in ethanol (3 ml.) at 0°, and the mixture set aside overnight at 0°. The *nitrate*, when collected and recrystallised from ethanol containing a trace of phosphine, had m. p. 80—81° (Found: C, 68.3; H, 5.8. $C_{56}H_{52}CuNO_3P$ requires C, 68.4; H, 5.4%), Λ_m at 23° 25.0 mhos.

The similar use of cupric perchlorate (0.132 g.) and the phosphine (0.48 g., 4.6 mol.) gave the *perchlorate*, m. p. 102—104° (Found: C, 66.0; H, 5.8. $C_{56}H_{52}ClCuO_4P$ requires C, 66.5; H, 5.2%; Λ_m at 25° 25.5 mhos.

Treatment of silver perchlorate in ethanol with the phosphine (5 mol.) afforded only the compound (III; M = Ag, X = ClO₄).

Gold(III) Compounds.—*Mono(phosphine)trichlorogold* (V; X = Cl). Chlorine was bubbled for 5 min. through a solution of the compound (I; M = Au, X = Cl) (0.2 g.) in chloroform (10 ml.) at 0°. Evaporation gave yellow plates which effloresced in the air; the residue, when recrystallised from chloroform and dried in a vacuum, gave the *trichloro-compound*, m. p. 141—141.5° (Found: C, 32.7; H, 2.5. $C_{14}H_{13}AuCl_3P$ requires C, 32.6; H, 2.5%). The orange *tribromo-compound*, similarly prepared, had m. p. 130—131° (Found: C, 26.4; H, 2.3. $C_{14}H_{13}AuBr_3P$ requires C, 25.9; H, 2.0%).

Cadmium Compounds.—*Bis(phosphine)dibromocadmium* (VII; X = Br). The phosphine (0.110 g., 2.1 mol.) in ethanol (4 ml.), when added to a solution of cadmium bromide tetrahydrate (0.086 g.) in 50% aqueous ethanol (2 ml.) with ice cooling, gave the white crystalline *dibromo-compound*, m. p. 222—223° after rapid recrystallisation from ethanol (Found: C, 47.8; H, 3.8. $C_{28}H_{26}Br_2CdP_2$ requires C, 48.2; H, 3.7%). The di-iodo-compound, similarly prepared and purified, had m. p. 124—125° (Found: C, 42.6; H, 3.4%; M, 807. $C_{28}H_{26}CdI_2P_2$ requires C, 42.5; H, 3.3%; M, 790. The phosphine (0.25 g., 1.1 mol.) in ethanol (3 ml.), when added to a solution of cadmium chloride (0.24 g.) in 50% aqueous ethanol (2 ml.), gave an immediate white precipitate, which after repeated recrystallisation from ethanol afforded *di-μ-chloro-dichlorobis(phosphine)dicalcium*, m. p. 266—267° (Found, in independent preparations: C, 42.1, 42.55; H, 3.9, 3.5. $C_{28}H_{26}Cd_2Cl_4P_2$ requires C, 42.5; H, 3.3%). It was insufficiently soluble in dichloromethane for molecular weight determinations.

Crystal Data.—The following data for the compound (II; M = Au, X = I), limited to the elucidation of its essential stereochemistry, have been supplied by Dr. G. A. Mair. $C_{28}H_{26}AuIP_2$, $M = 748.1$, orthorhombic, $a = 20.8(7)$, $b = 6.4(1)$, $c = 19.7(7)$ Å. Density determinations were not highly accurate because of high solubility, but they showed that $Z = 4$. Space group, *Pccn*. Absences, (i) $0kl$ when l odd, (ii) $h0l$ when l odd, (iii) $hkh0$ when $h + k$ odd. Cu K_α radiation, single-crystal photographs.

The $h0l$ reflections were collected from zero-layer Weissenberg photographs of a crystal rotating about the b -axis. The multiple film technique was used, and intensities were read by visual comparison with a standard intensity scale. These were corrected for Lorentz and polarisation factors but not for absorption.

The highest peak on the vector map was assumed to be due to the Au–Au vector and from its position co-ordinates for gold and iodine atoms were obtained.

A set of structure factors for the $h0l$ reflections based on contributions from the gold and

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iodine atoms alone was calculated and gave an R value of 40%. Refinement by successive difference syntheses and structure factor calculations reduced this factor to 30%. The next set of structure factors included the contributions of the phosphorus atoms, and gave an R value of 26%. Two rounds of least-squares calculations were carried out, and in these the three positional and six thermal parameters for each atom were refined, reducing the R value to 21%.

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