

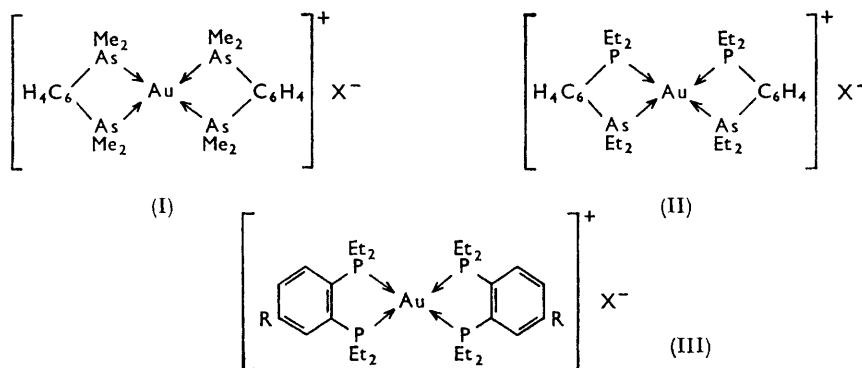
728. The Constitution of Complex Metallic Salts. Part XXII.¹ The Stereochemistry of Four-co-ordinated Gold(I) Salts and Some Related Gold(III) Salts.

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Certain unsymmetrically substituted chelating ditertiary phosphines have been co-ordinated to gold(I) halides to give salts having in the crystalline state a tetrahedral dissymmetric di(bisphosphine)gold(I) cation. Although numerous salts having the halide ion replaced by optically active anions have been prepared and repeatedly recrystallised, none has shown any evidence of optical resolution. The possible causes of this lack of optical activity are discussed.

A brief investigation of some of the corresponding gold(III) salts has been made. In certain compounds, dimethylformamide appears to co-ordinate with the gold(III) atom, which may thus become 6-co-ordinate.

STABLE salts of the 4-co-ordinate gold(I) atom, of type (I), were first prepared by Nyholm,² using *o*-phenylenebisdimethylarsine;³ some indication that the gold atom in such salts had the theoretically expected tetrahedral configuration was later obtained from *X*-ray powder photographs.⁴



The similar gold(I) salt (II) was prepared, using *o*-diethylphosphinophenyldiethylarsine,⁵ by Cochran, Hart, and Mann,⁶ who, however, could not resolve the cation of (II) into optically active forms by fractional recrystallisation of several salts having optically active anions. An *X*-ray examination of the iodide (II; X = I) showed decisively that the gold(I) atom had the tetrahedral configuration, and that the shortest distances between the iodine and the gold atoms were too great to allow bonding between these atoms, thus confirming the 4-co-ordinate condition of the gold. Furthermore, although the positions of the phosphorus or arsenic atoms were clearly defined, the atoms of the two elements could not be differentiated owing to an apparently random distribution in the crystal cell, quite distinct from the regular arrangement to be expected in a racemate.⁶ This factor would almost certainly have caused mixed-crystal formation of the diastereoisomers during attempted resolution, which must therefore have failed.

¹ Part XXI, Collier, Fox, Hinton, and Mann, *J.*, 1964, 1819.

² Nyholm, *Nature*, 1951, **168**, 705.

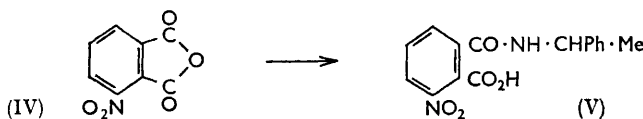
³ Chatt and Mann, *J.*, 1939, 610.

⁴ Nyholm and Stephenson, *Rec. Trav. chim.*, 1956, **75**, 687.

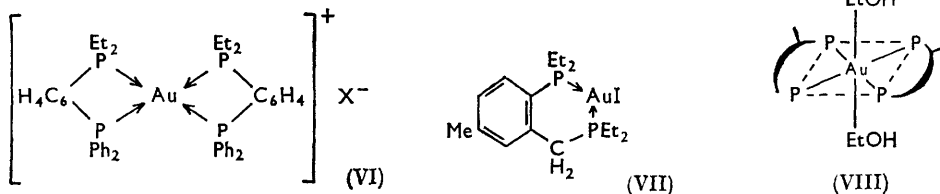
⁵ Emrys R. H. Jones and Mann, *J.*, 1955, 4472.

⁶ Cochran, Hart, and Mann, *J.*, 1957, 2816.

In an attempt to prevent this random distribution, we have used 4-methyl-*o*-phenylenebis(diethylphosphine), 4-Me-C₆H₃(PEt₂)₂,^{7,8} which gave the stable, highly crystalline di(bisphosphine)gold iodide (III; R = Me, X = I). This salt has been converted into the (+)-camphorsulphonate, the (+)- α -bromocamphorsulphonate, the (+)-hydrogen tartrate, the (-)-hydrogen dibenzoyltartrate, the (+)-camphornitronate, the (+)-1-methylhexyl phthalate, the (-)-tricatechylarsenate, the (+)-antimonyl tartrate, and the (+)-2-carboxy-3-nitro-*N*-(1-phenylethyl)benzamide. The last salt was prepared from (+)-2-carboxy-3-nitro-*N*-(1-phenylethyl)benzamide (V), obtained by the action of (-)-1-phenylethylamine on 3-nitrophthalic anhydride (IV); it was assumed that this nucleophilic attack of the amine would occur on the least hindered carbonyl group of the anhydride.



To conserve material, the above salts were recrystallised several times, sufficient probably to detect partial resolution; certain of them then showed, in solution, a rotation very close to that of the anion alone. All of them, when treated in ice-cold solution with sodium iodide or picrate, gave the inactive iodide (III; R = Me, X = I) or picrate. Precipitation as the picrate was preferred to that as the iodide, in case the iodide ion co-ordinated momentarily with the gold, although no indication of this was obtained. This failure may have been caused by random distribution of the cation being unchecked by the small methyl substitution. Biphenylene-3,4-bis(diethylphosphine), Ph·C₆H₃(PEt₂)₂, was therefore similarly co-ordinated to give the di(bisphosphine)gold iodide (III; R = Ph, X = I).⁸ The small quantity available allowed the conversion of this salt only into the (+)- α -bromocamphorsulphonate, the (+)-hydrogen tartrate, and the (-)-hydrogen dibenzoyltartrate.



All attempts to resolve these salts by fractional crystallisation failed, and in view of this we finally employed *o*-diethylphosphinophenyldiphenylphosphine, C₆H₄(PEt₂)(PPh₂),⁹ kindly presented by Dr. F. A. Hart. This bisphosphine also gave a stable highly crystalline gold iodide salt (VI; X = I), which was converted into the (+)-camphorsulphonate, the (+)- α -bromocamphorsulphonate, the (+)-hydrogen tartrate, the (-)-hydrogen dibenzoyltartrate, the (+)-camphornitronate, and the unstable (-)-menthyloxyacetate. These salts also gave no evidence of optical resolution. It is noteworthy that the analogous iodide having two molecules of the bisarsine, *o*-C₆H₄(AsMe₂)(AsEt₂), could not be resolved.⁶

The use of (2-diethylphosphino-5-methylbenzyl)diethylphosphine, *o*-Me·C₆H₃(PEt₂)(CH₂·PEt₂),⁸ proved abortive, for this bisphosphine, even in excess, gave only the covalent 3-co-ordinate gold derivative (VII). Even if this bisphosphine had given a univalent spirocyclic cation of type (III) and (VI), its resolution would not have been of decisive significance, since some buckling of the two six-membered rings might alone have produced molecular dissymmetry.

⁷ Hart and Mann, *J.*, 1957, 3939.

⁸ Davis and Mann, preceding Paper.

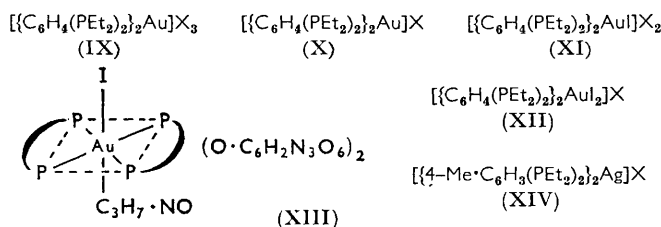
⁹ Hart, *J.*, 1960, 3324.

Stable 3-co-ordinate gold compounds of type (VII) are sometimes formed with mono-phosphines, although the molecule therefore lacks the extra stabilising effect of the chelated group; for example, bis-(2-phenylisophosphindoline)iodogold.¹

This inability to demonstrate optical activity in the cations of type (III) and (VI), in spite of their almost certain tetrahedral configuration in the crystalline state, and the considerable number of apparently suitable salts investigated, cannot be decisively explained. Several dissymmetric compounds have in the past stubbornly resisted resolution for many years. Apart from this chance factor, it is possible that the changes in the structure of the chelating bisphosphines employed are still insufficient to prevent the particular type of random distribution of the cations in the crystal cell shown by salts of type (II). Alternatively, it is noteworthy that, although the numerous salts of the cations (III; R = Me or Ph) and (VI) have varying solubilities in different solvents, a very considerable proportion have an exceptionally high solubility in cold ethanol and (slightly lower) in methanol. This may indicate that the cation has united with ethanol to give, for example, an octahedral cation represented diagrammatically as (VIII) which is stable in the solution but which discards the ethanol on crystallisation, with the regeneration of the original racemic salts. A cation (VIII), having unsymmetrically substituted diphosphine molecules as indicated, could exist in *cis*- and *trans*-forms, the *cis*-form having two planes of symmetry and the *trans*-form one such plane and a centre of symmetry. It is difficult to prepare the salts now recorded in the complete absence of hydroxylic solvents, and the formation of such a cation would clearly render attempts at resolution fruitless. On the other hand, no 6-co-ordinated gold(I) compounds have apparently been recorded, although gold(III) derivatives are known.^{4,10}

We have briefly investigated some of the gold(III) derivatives of the bisphosphines; since 4-methyl-*o*-phenylenebis(diethylphosphine) might give *cis-trans*-isomers of the planar gold(III) complexes, we have used chiefly *o*-phenylenebis(diethylphosphine), *o*-C₆H₄(PEt₂)₂,⁹ also kindly supplied by Dr. F. A. Hart. The corresponding bisarsine derivatives have been studied by Nyholm and his co-workers, who have produced considerable evidence that the gold(III) atom may be 4-, 5-, or 6-co-ordinate, according to the anions available.^{4,10}

The stability to reduction of the gold(III) halides is shown clearly when a cold ethanolic solution of chloroauric acid is treated with the bisphosphine (3 mol.), giving a



yellow solution from which petroleum precipitates the colourless gold(III) trichloride (IX; X = Cl); if the yellow solution is boiled under reflux for 30 minutes and then cooled before addition of the petroleum, the gold(I) chloride (X; X = Cl) is precipitated. If, however, the initial cold ethanolic solution is treated with aqueous potassium bromide or iodide, reduction rapidly occurs with deposition of the salt (X; X = Br or I). This rapid reduction is not caused by the action of water, because treatment with aqueous lithium chloride precipitates the trichloride (IX; X = Cl). For the normal preparation of the latter, only 2 molecules of the bisphosphine are used.

The greenish-yellow gold(III) tribromide can be prepared by treatment of the ethanolic trichloride (IX; X = Cl) with lithium bromide or of the monochloride (X; X = Cl) with bromine (1 mol.) in carbon tetrachloride; the orange gold(III) tri-iodide, probably of structure (XI; X = I) (see p. 3794), can be similarly prepared from the trichloride, or by

¹⁰ Harris and Nyholm, *J.*, 1957, 63.

treating the chloride or bromide (X; X = Cl or Br) with iodine (1 mol.). The formation of mixed halogen derivatives, which occurs so readily when the covalent monophosphine-monohalogeno-gold(I) compounds are treated with other halogens,¹¹ does not apparently occur in the present series of salts. The trichloride with aqueous sodium picrate and perchloric acid gives the yellow tripicrate (IX; X = O·C₆H₂N₃O₆) and the colourless triperchlorate (IX; X = ClO₄), respectively.

The reactions of the tri-iodide are of particular interest. It is only slightly soluble in cold ethanol, but the solution with sodium picrate gave the above tripicrate. In hot aqueous solution the tri-iodide, with 60% aqueous perchloric acid, gave the yellow iodide diperchlorate (XI; X = ClO₄).

When, however, saturated ethanolic sodium picrate was added to a dimethylformamide solution of the tri-iodide, yellow crystals of the iodide-dipicrate-dimethylformamide separated. The presence of one molecular equivalent of the amide was shown by analysis, and by the characteristic carbonyl bands in the infrared spectrum. This compound also crystallised when dimethylformamide solutions of the tri-iodide (1 mol.) and the tripicrate (2 mol.) were mixed and diluted with ethanol. A dimethylformamide solution of this compound was pale yellow when cold, but became progressively deeper orange on heating, the original colour being restored on cooling. The formation of this type of compound is not peculiar to this bisphosphine, for the analogous compound has been similarly prepared using 4-methyl-*o*-phenylenebis(diethylphosphine). It is probable that in these compounds, the gold(III) atom has become 6-co-ordinate by direct linking to the amide molecule as in (XIII); the Λ_m value for the 4-methyl analogue also indicates a uni-bivalent salt (see Table). Co-ordination of dimethylformamide to the heavier metals is not infrequent.¹²

The dimethylformamide dipicrate (XIII), when recrystallised from ethyl methyl ketone containing *ca.* 1% of water, gave the iodo-dipicrate trihydrate, in which one molecule of water may have evicted the co-ordinated amide molecule. Both these iodo-dipicrates were unaffected when heated at 65°/0.1 mm. for 6 hours. Insufficient material precluded their further study.

The triperchlorate (IX) was too slightly soluble in nitrobenzene for conductivity measurements. The Λ_m value for the iodo-diperchlorate (XI; X = ClO₄) accords well

Conductivity in nitrobenzene solution at 23°.

	<i>M</i>	Concn. (<i>M</i> × 10 ⁻⁴)	Λ_m (mho cm. ²)
[{C ₆ H ₄ (PEt ₂) ₂ }] ₂ AuI]I ₂	1086	6.73	35.8
[{C ₆ H ₄ (PEt ₂) ₂ }] ₂ AuI](ClO ₄) ₂	1031	8.92	52.7
[{4-Me·C ₆ H ₃ (PEt ₂) ₂ }] ₂ AuI, C ₃ H ₇ NO](C ₆ H ₂ N ₃ O ₇) ₂	1391	10.64	42.8
[{4-Me·C ₆ H ₃ (PEt ₂) ₂ Ag][Ag ₂].....	1008	16.78	24.8

with a uni-bivalent salt having therefore 5-co-ordinate gold. The value for the tri-iodide falls between those expected for a uni-univalent and a uni-bivalent salt, and may indicate that in nitrobenzene the tri-iodide gives an equilibrium between the two forms (XI; X = I) and (XII; X = I). This is not unexpected, for the tri-iodide presumably exists in cold ethanol as (IX; X = I) since it gives a tripicrate, and in hot aqueous solution as (XI; X = I) since it gives a diperchlorate; hence the solvent may determine the particular structure or equilibrium of structures adopted by the tri-iodide.

When 4-methyl-*o*-phenylenebis(diethylphosphine) (2 mol.) was shaken with silver iodide (1 mol.) in aqueous potassium iodide, a mixed crystalline product was deposited. Ethanol extracted the di(bisphosphine)silver iodide (XIV; X = I), which readily gave a picrate; the residue from the extraction, when recrystallised from dimethylformamide, furnished the corresponding di-iodoargentite (XIV; X = AgI₂), the ionic structure of which was confirmed by its conductivity (see Table).

¹¹ Mann and Purdie, *J.*, 1940, 1235.

¹² *E.g.*, Poller, *Proc. Chem. Soc.*, 1963, 312.

EXPERIMENTAL

Unless otherwise stated, all compounds were colourless except the yellow picrates. All rotations were determined with Na_D light (λ 5893 Å), using (unless otherwise stated) a 4 dcm. tube.

(+)-2-Carboxy-3-nitro-N-(1-phenylmethyl)benzamide (V).—A solution of 3-nitrophthalic anhydride¹³ (1.93 g.) and (–)-1-phenylethylamine (1.21 g., 1 mol.) in ether (100 ml.) was boiled under reflux for 1 hr., evaporated to *ca.* 25 ml., and diluted with light petroleum (b. p. 40–60°) until crystallisation started. The acid (V) (2.0 g., 65%) had m. p. 169° (from aqueous ethanol) (Found: C, 61.2; H, 4.6; N, 8.7. $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_5$ requires C, 61.2; H, 4.5; N, 8.9%). A 1.908% ethanolic solution had α +0.16°, $[M] +7.4^\circ$.

The acid (0.4567 g.) was added to a solution of sodium hydroxide (0.580 g., 1 mol.) in water (10 ml.), and the resulting solution made quite neutral to litmus with dilute nitric acid. Silver nitrate (0.2500 g., 1 mol.) in water (5 ml.) was added, and the precipitated *silver salt*, when rapidly collected, washed, and dried, had m. p. 255° (decomp.) (Found: C, 45.1; H, 3.1; N, 6.7; Ag, 25.0. $\text{C}_{16}\text{H}_{13}\text{AgN}_2\text{O}_5$ requires C, 45.6; H, 3.1; N, 6.7; Ag, 25.6%).

Di-[4-methyl-o-phenylenebis(diethylphosphine)]gold(I) Salts (III; R = Me).—The iodide (III; R = Me, X = I), m. p. 240–241.5°, has been briefly recorded;⁷ the following detailed preparation is typical of all analogous salts containing our various bisphosphines. The bisphosphine (4.15 g., 3 mol.) in ethanol (15 ml.) was added to a solution of chloroauric acid (2.0 g.) in water (3 ml.) and ethanol (15 ml.). The initial bright yellow precipitate rapidly redissolved to give a clear pale green solution. Ethanol (20 ml.) was added, the solution heated to *ca.* 60°, and a solution of an excess of potassium iodide (6 g.) in water (10 ml.) added. The mixture was diluted dropwise with hot water until a crystalline precipitate began to separate, and was then cooled. The collected dried iodide (4.2 g., 94%), on recrystallisation from ethanol-light petroleum (b. p. 60–80°), formed prisms, m. p. and mixed m. p. 241–242°. Solutions of the iodide in methanolic methyl iodide, and in ethanolic ethyl iodide, were boiled under reflux for 1 hr.; the unchanged iodide was recovered.

An ethanolic solution of the iodide, when (a) added to aqueous sodium picrate deposited the *picrate* [III; R = Me, X = $\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$], m. p. 171° (from aqueous ethanol, 3 : 2 v/v) (Found: C, 45.0; H, 5.8; N, 4.65. $\text{C}_{36}\text{H}_{54}\text{AuN}_3\text{O}_7\text{P}_4$ requires C, 44.9; H, 5.65; N, 4.4%), (b) treated with aqueous silver nitrate, stirred, warmed, filtered, and evaporated, gave the *nitrate dihydrate*, m. p. 244° (from ethyl methyl ketone) after drying at 50°/0.1 mm. for 4 hr. (Found: C, 43.35; H, 7.2; N, 1.7. $\text{C}_{30}\text{H}_{52}\text{AuNO}_3\text{P}_4\cdot 2\text{H}_2\text{O}$ requires C, 43.3; H, 6.8; N, 1.7%), (c) treated with dilute sulphuric acid (acid : water, 1 : 3 v/v) slowly deposited the *hydrogen sulphate* (III; R = Me, X = HO_4S), m. p. 239° (from water containing a trace of ethanol) (Found: C, 40.5; H, 6.45. $\text{C}_{30}\text{H}_{53}\text{AuO}_4\text{P}_4\text{S}$ requires C, 40.85; H, 6.3%). This salt was prepared in this way to see if the use of silver salts in the following preparations could, when advisable, be avoided.

A solution of the iodide (0.4 g.) in ethanol (20 ml.) was treated with silver (+)-camphorsulphonate (0.178 g., 1 mol.), shaken in the dark for 1 hr., and filtered. Evaporation to dryness gave the (+)-*camphorsulphonate monohydrate* (III; R = Me, X = $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3$), m. p. 291–293°, increased to 295–296° by 5 recrystallisations from water containing a trace of ethanol (Found: C, 48.5; H, 7.1. $\text{C}_{40}\text{H}_{67}\text{AuO}_4\text{P}_4\text{S}\cdot\text{H}_2\text{O}$ requires C, 48.8; H, 7.1); a 0.9193% aqueous ethanolic solution had α +0.23°, $[M] +60^\circ$. The camphorsulphonate ion in this solvent has $[M] +55^\circ$. The salt gave an inactive picrate, m. p. and mixed m. p. 170°.

The (+)- α -*bromocamphorsulphonate monohydrate*, similarly prepared and recrystallised, had m. p. 228–231° (Found: C, 45.4; H, 6.8. $\text{C}_{40}\text{H}_{66}\text{AuBrO}_4\text{P}_4\text{S}\cdot\text{H}_2\text{O}$ requires C, 45.2; H, 6.5%); a 0.681% ethanolic solution had α +0.86°, $[M] +330^\circ$, whereas a 0.480% ethanolic solution of the silver sulphonate had α +1.46°, $[M] +332^\circ$. It gave an inactive picrate.

The ethanolic iodide, treated with finely powdered silver (–)-hydrogen dibenzoyltartrate (1 mol.),¹⁴ gave, on filtration and evaporation, a sticky solid which crystallised when rubbed with acetone. Three recrystallisations from acetone gave the (–)-*hydrogen dibenzoyltartrate di-acetonate* (III; R = Me, X = $\text{C}_{18}\text{H}_{13}\text{O}_8$), m. p. 85° (effervescence) (Found: C, 53.5; H, 6.5. $\text{C}_{48}\text{H}_{65}\text{AuO}_8\text{P}_4\cdot 2\text{C}_3\text{H}_6\text{O}$ requires C, 53.7; H, 6.5%). It gave the inactive iodide.

The (+)-*hydrogen tartrate monohydrate*, similarly prepared from the silver hydrogen salt,¹⁴ had m. p. 220° after 3 recrystallisations from acetone containing *ca.* 2% of water (Found: C, 45.4; H, 6.7. $\text{C}_{34}\text{H}_{57}\text{AuO}_6\text{P}_4\cdot\text{H}_2\text{O}$ requires C, 45.3; H, 6.6%); it gave the inactive iodide.

¹³ *Org. Synth.*, Coll. Vol. 1, 2nd edn., 1941, p. 410.

¹⁴ Coyne, McEwen, and VanderWerf, *J. Amer. Chem. Soc.*, 1956, **78**, 3061.

The (+)-*camphorvitronate* (III; R = Me, X = C₁₀H₁₄NO₃), prepared from the silver salt, had m. p. 244° (decomp.) after 3 recrystallisations from water containing ca. 10% of ethanol (Found: C, 51.5; H, 7.1. C₄₀H₆₆AuNO₃P requires C, 51.6; H, 7.1%); it gave the inactive picrate.

The use of silver (+)-1-methylhexylphthalate gave, on evaporation, a residue which crystallised in massive rhombs when a solution in acetone-ethyl acetate was allowed to evaporate slowly. These were recrystallised 5 times from ether-benzene, giving the (+)-1-methylhexylphthalate (III; R = Me, X = C₁₅H₁₉O₄), m. p. 177–179° (Found: C, 53.2; H, 7.3. C₄₅H₇₁AuO₄P₄ requires C, 53.2; H, 7.3%); it gave the inactive picrate.

A solution of the iodide (0.3888 g.) in ethanol (10 ml.) was treated with powdered silver sulphate (0.0710 g., 0.5 mol.), shaken for 2 hr., filtered through a sintered filter, treated with barium (-)-tricatechylarsenate¹⁵ (0.2600 g., 0.5 mol.) in ethanol (5 ml.). The mixture was vigorously shaken, filtered, warmed, and treated with hot water. The white powder which separated was recrystallised from ethanol, giving the (-)-tricatechylarsenate diethanolate (III; R = Me, X = C₁₈H₁₂AsO₆), m. p. 176° (effervescence) (Found: C, 51.2; H, 6.2. C₄₈H₈₄AsAuO₆P₄.2C₂H₆O requires C, 51.1; H, 6.2%); it gave an inactive picrate.

The (+)-*antimonyltartrate* (III; R = Me, X = C₄H₄O₇Sb), prepared from the silver salt,¹⁵ and once recrystallised from aqueous ethanol, had m. p. 225–227°, unchanged by 5 more recrystallisations (Found: C, 40.4; H, 5.6. C₃₄H₅₆AuO₇P₄Sb requires C, 40.1; H, 5.5%). A 0.166% ethanolic solution had $\alpha + 0.103^\circ$, $[M] + 158^\circ$. It gave an inactive picrate.

The (+)-2-carboxy-3-nitro-N-(1-phenylethyl)benzamide (III; R = Me, X = C₁₆H₁₃N₂O₅), prepared from the silver salt of the acid (V) and thrice recrystallised from toluene, had m. p. 90° (Found: C, 52.3; H, 6.3; N, 2.8. C₄₆H₆₅AuN₂O₅P₄ requires C, 52.8; H, 6.2; N, 2.7%). It gave the inactive picrate.

The (-)-N-1-phenylethylphthalamate,¹⁵ the (-)-menthyloxyacetate, and the (-)-quininate did not crystallise satisfactorily.

Di[biphenylene-3,4-bis(diethylphosphine)]gold(I) Salts (III; R = Ph).—The iodide, m. p. 313–315° (decomp.) and the picrate, m. p. 191–192°, have been recorded.⁸

The (+)- α -bromocamphorsulphonate (III; R = Ph; X = C₁₀H₁₄BrO₄S), prepared as usual and recrystallised four times from acetone-ether, formed leaflets, m. p. 253–254° (Found: C, 51.5; H, 6.2. C₅₀H₇₀AuBrO₄P₄S requires C, 51.4; H, 6.1%); a 0.203% ethanolic solution had $\alpha + 0.237^\circ$, $[M] + 341^\circ$. The anion alone in ethanol has $[M] + 332^\circ$.

The (+)-hydrogen tartrate monohydrate (III; R = Ph, X = C₄H₆O₆), when 5 times recrystallised from ethanol-light petroleum (b. p. 60–80°), formed pale yellow needles, m. p. 203–205° (effervescence) (Found: C, 51.3; H, 6.5. C₄₄H₆₁AuO₆P₄.H₂O requires C, 51.5; H, 6.2%).

The (-)-hydrogen dibenzoyltartrate (III; R = Ph, X = C₁₈H₁₃O₈) was initially obtained, by evaporation of its solution, as a glassy solid which when dissolved in acetone and set aside deposited pale yellow crystals, m. p. 172° (effervescence), unchanged by recrystallisation from aqueous acetone (Found: C, 57.3; H, 5.7. C₅₈H₆₉AuO₈P₄ requires C, 57.4; H, 5.7%).

The above three salts gave inactive picrates.

Bis-(o-diethylphosphinophenyl)diphenylphosphine)gold(I) Salts (VI).—The iodide (VI; X = I), prepared in the usual way and recrystallised from ethanol-light petroleum (b. p. 60–80°), formed prisms (95%), m. p. 278–279° (Found: C, 51.1; H, 4.5. C₄₄H₄₈AuIP₄ requires C, 51.5; H, 4.7%); it gave a picrate dihydrate, needles, m. p. 167–168° (from aqueous ethanol) (Found: C, 51.8; H, 4.5; N, 3.7. C₅₀H₅₀AuN₃O₇P₄.2H₂O requires C, 51.7; H, 4.6; N, 3.6%).

All the following salts, after the described recrystallisations, were converted into the above picrate, which was inactive.

The (+)-camphorsulphonate (VI; X = C₁₀H₁₅O₄S), prepared from the silver sulphate in aqueous ethanol, crystallised slowly from the cold filtrate; the needles, m. p. 232° (effervescence) in 0.457% chloroform solution had $\alpha + 0.14^\circ$, $[M] + 87^\circ$, camphorsulphonic acid at approximately this concentration having $[M] + 86^\circ$. The needles, recrystallised five times from ether-chloroform, separated as a monochloroformate, m. p. 233° (effervescence) (Found: C, 52.2; H, 5.2. C₅₄H₆₃AuO₄P₄S.CHCl₃ requires C, 52.8; H, 5.2%); the presence of chloroform was confirmed.

The (+)- α -bromocamphorsulphonate (VI; X = C₁₀H₁₄BrO₄S), prepared as before, was isolated, by evaporation, as a residue which crystallised when rubbed with acetone; 4 recrystallisations from acetone-light petroleum (b. p. 80–100°) gave needles, m. p. 235–236°

¹⁵ Mann and Watson, *J.*, 1947, 505.

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(Found: C, 53.6; H, 5.2. $C_{54}H_{62}AuBrO_4P_4S$ requires C, 53.7; H, 5.2%). A 0.473% ethanolic solution had $\alpha + 0.50^\circ$, $[M] + 320^\circ$, the anion in this solvent having $[M] + 332^\circ$.

The (+)-*hydrogen tartrate monohydrate*, prepared as before and recrystallised 4 times from ethanol-ether, had m. p. 268° (decomp.) (Found: C, 54.3; H, 5.5. $C_{48}H_{53}AuO_6P_4 \cdot H_2O$ requires C, 54.2; H, 5.2%).

The (-)-*hydrogen dibenzoyltartrate* (VI; $X = C_{16}H_{13}O_6$) was obtained initially as an oil; its ethanolic solution, when diluted with ether and set aside, deposited large rosettes, which after 2 recrystallisations from ethyl methyl ketone formed needles, m. p. $150-151^\circ$, of the *ketonate* (Found: C, 61.1; H, 5.1. $C_{66}H_{61}AuO_8P_4 \cdot C_4H_8O$ requires C, 61.1; H, 5.1%). A 0.189% ethanolic solution had $[M] - 465^\circ$. The anion in water has $[M] - 469^\circ$.¹⁴

The (+)-*camphornitronate* (VI; $X = C_{10}H_{14}NO_3$) after 6 recrystallisations from acetone-ether containing ca. 2% of ethanol, formed prisms, m. p. $208-210^\circ$ (Found: C, 59.0; H, 5.7. $C_{54}H_{62}AuNO_3P_4$ requires C, 59.3; H, 5.7%).

An ethanolic solution of the iodide, when shaken with powdered silver (-)menthyloxyacetate (1 mol.) for $1\frac{1}{2}$ hr., filtered, and evaporated, yielded an oil which initially could not be crystallised. A solution in ethyl acetate, when set aside for 2 weeks, deposited prisms, which when twice rapidly recrystallised gave the (-)-menthyloxyacetate (VI; $X = C_{12}H_{21}O_3$), m. p. $220-222^\circ$, too unstable for satisfactory analysis. It was therefore converted forthwith into the picrate.

(2-*Diethylphosphino-5-methylbenzyl*)*diethylphosphineiodogold* (VII).—The redistilled bisphosphine (0.465 g., 3.2 mol.) in ethanol (5 ml.) was added to chloroauric acid (0.195 g.) in ethanol (5 ml.), which was gently warmed for 3–4 min. and then diluted with aqueous sodium iodide. The oil which separated was removed and dissolved in acetone (10 ml.); the filtered solution, when allowed to evaporate slowly, gave pale yellow-green crystals, which on recrystallisation from toluene gave the *compound* (VII), pale yellow needles, m. p. $225-226^\circ$ (Found: C, 31.8; H, 4.9. $C_{16}H_{28}AuIP_2$ requires C, 31.7; H, 4.7%); in nitrobenzene at 23° , Λ_m 9.1 mho $cm.^2$ at molar concentration of 1.85×10^{-3} M. The compound is therefore almost wholly covalent; its low solubility in suitable solvents precluded molecular weight determinations. If the compound had been a salt, $[(C_{16}H_{28}P_2)_2Au]AuI_2$, it would have had Λ_m ca. 25–27 mho $cm.^2$, for the comparable compounds $[(C_6H_4(AsMe_2)_2)_2Au]AuI_2$ and $[(C_6H_4(AsMe_2)_2)_2Au]CuI_2$ have Λ_m 25.3 and 27.4 mho $cm.^2$ in nitrobenzene.⁴

Di-[o-phenylenebis(diethylphosphine)]gold(I) Salts (X).—The bisphosphine (4.8 g., 3.1 mol.) in ethanol (50 ml.) was added to chloroauric acid (2.26 g.) in ethanol (14 ml.), which was boiled under reflux for 30 min., and cooled. (a) One portion of the solution, when diluted with light petroleum (b. p. $60-80^\circ$), deposited an oil which when removed and stirred with aqueous lithium chloride gave the *chloride tetrahydrate* (X; $X = Cl$), needles, m. p. $313-315^\circ$ (from water) (Found: H_2O , 8.6. $C_{28}H_{48}AuClP_4 \cdot 4H_2O$ requires H_2O , 8.8%). Heating at $120^\circ/0.2$ mm. gave the anhydrous *chloride*, m. p. 317° (Found: C, 45.4; H, 6.7. $C_{28}H_{48}AuClP_4$ requires C, 45.3; H, 6.5%). (b) A second portion, diluted with aqueous potassium bromide, deposited the *bromide monohydrate* (X; $X = Br$), needles, m. p. $251-252^\circ$ (from aqueous ethanol) (Found: C, 41.6; H, 6.6. $C_{28}H_{48}AuBrP_4 \cdot H_2O$ requires C, 41.8; H, 6.3%); heating at $100^\circ/0.2$ mm. gave the anhydrous *bromide*, of unchanged m. p. (Found: C, 42.3; H, 6.4. $C_{28}H_{48}AuBrP_4$ requires C, 42.7; H, 6.2%). (c) A third portion, similarly treated with potassium iodide (although the preliminary boiling was unnecessary in this case), gave the *iodide* (X; $X = I$), m. p. 266° (from aqueous ethanol) (Found: C, 40.7; H, 5.9. $C_{28}H_{48}AuIP_4$ requires C, 40.4; H, 5.8%). The ethanolic chloride, treated with aqueous sodium picrate, gave the *picrate* (X; $X = O \cdot C_6H_2N_3O_6$), crystals, m. p. $136-137^\circ$ (from aqueous ethanol) (Found: C, 43.3; H, 5.5; N, 4.5. $C_{34}H_{50}AuN_3O_7P_4$ requires C, 43.6; H, 5.4; N, 4.5%).

Di-[o-phenylenebis(diethylphosphine)]gold(III) Salts (IX).—The *trichloride* (IX; $X = Cl$). In the above preparation of the gold(I) chloride, if the solution was shaken for 15 min. instead of being heated, addition of the petroleum deposited the *trichloride pentahydrate*, prisms, m. p. 162° (from ethanol-ether) (Found: C, 37.4; H, 6.3. $C_{28}H_{48}AuCl_3P_4 \cdot 5H_2O$ requires C, 37.3; H, 6.4%). The bisphosphine (2 mol.) is, however, sufficient for this preparation.

The *tribromide* (IX; $X = Br$). (a) The addition of lithium bromide to the trichloride, both in cold ethanolic solution, precipitated the *tribromide dihydrate*, pale greenish-yellow prisms, m. p. $154-155^\circ$ (from ethanol) (Found: C, 34.5; H, 5.6. $C_{28}H_{48}AuBr_3P_4 \cdot 2H_2O$ requires C, 34.3; H, 5.4%). (b) The addition of bromine (8.9 mg., 1 mol.) in carbon tetrachloride (0.21 ml.) to the gold(I) bromide (43.3 mg., 1 mol.) in chloroform (2 ml.) gave a yellow

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precipitate which, after recrystallisation from ethanol, furnished the tribromide dihydrate, m. p. and mixed m. p. 154—154.5°. The hydrated trichloride and tribromide decomposed when heated at 80°/0.1 mm. and 40°/0.1 mm., respectively.

The *tri-iodide* (IX; X = I) or (XI; X = I). (a) The trichloride treated with potassium iodide, both in aqueous ethanol, deposited the *tri-iodide*, yellow-orange prisms, m. p. 180° (decomp.) (from aqueous ethanol) (Found: C, 30.9; H, 4.8. $C_{28}H_{48}AuI_3P_4$ requires C, 30.9; H, 4.5%). (b) The gold(I) iodide, treated with iodine (1 mol.), both in chloroform, gave the *tri-iodide* (100%), m. p. and mixed m. p. 180° (decomp.). The gold(I) chloride, similarly treated, also gave the *tri-iodide*.

An ethanolic solution of the trichloride, when (a) treated with aqueous sodium picrate, deposited the *tripicrate* (IX; X = $O \cdot C_6H_2N_3O_6$), needles, m. p. 211° (from ethanol) (Found: C, 39.8; H, 4.1; N, 9.3. $C_{46}H_{54}AuN_9O_{21}P_4$ requires C, 39.8; H, 3.9; N, 9.1%). (b) treated with 60% aqueous perchloric acid, deposited the crystalline *triperchlorate* (IX; X = ClO_4), which exploded without melting at the reproducible temperature of 292° (Found: C, 34.0; H, 5.2. $C_{28}H_{48}AuCl_3O_{12}P_4$ requires C, 33.5; H, 4.8%).

Reactions of the tri-iodide. (a) A saturated (but very dilute) ethanolic solution, treated with aqueous sodium picrate, gave the *tripicrate*, m. p. and mixed m. p. 211°.

(b) The *tri-iodide* (50 mg.) in boiling water (40 ml.), treated dropwise with the above perchloric acid, rapidly deposited the yellow *iodo-perchlorate* (XI; X = ClO_4), m. p. 190—193° (Found: C, 32.8; H, 4.9. $C_{28}H_{48}AuCl_2IO_5P_4$ requires C, 32.6; H, 4.7%).

(c) The *tri-iodide* (50 mg.) in dimethylformamide (2 ml.), treated with saturated ethanolic sodium picrate (2 ml.), deposited yellow plates, which on recrystallisation from ethanol-dimethylformamide, furnished the *dimethylformamido-iodo-dipicrate* (XIII), m. p. 141° (decomp.) unaffected by heating at 70°/0.1 mm. for 6 hr. (Found, for the heated material: C, 38.1; H, 4.7; N, 7.3. $C_{40}H_{52}AuIN_6O_{14}P_4 \cdot C_3H_7NO$ requires C, 37.9; H, 4.4; N, 7.2%). A solution of the *tri-iodide* (6.2 mg., 1 mol.) and the *tripicrate* (15.9 mg., 2 mol.) in dimethylformamide (1.5 ml.), when diluted with ethanol (2 ml.), deposited the compound (XIII), m. p. and mixed m. p. 141° (decomp.).

The *dipicrate* (XIII), when recrystallised from methyl ethyl ketone containing ca. 1% of water, gave the *iodo-dipicrate trihydrate*, also of m. p. 141° (decomp.) and unaffected by heating at 65°/0.1 mm. for 6 hr. (Found, for the heated material: C, 35.6; H, 4.5; N, 6.5. $C_{40}H_{52}AuIN_6O_{14}P_4 \cdot 3H_2O$ requires C, 35.7; H, 4.4; N, 6.3%).

If, in the preparation of the compound (XIII), the ethanol-dimethylformamide contained more than a trace of water, the *tripicrate* (IX; X = $O \cdot C_6H_2N_3O_6$) was deposited.

Di-[4-methyl-o-phenylenebis(diethylphosphine)]gold(III) Tri-iodide.—The addition of iodine (1 mol.) to the gold(I) chloride (III; R = Me, X = Cl), each in chloroform, gave an immediate precipitate of the gold(III) *tri-iodide*, m. p. 110—111° (Found: C, 32.4; H, 4.7. $C_{30}H_{52}AuI_3P_4$ requires C, 32.3; H, 4.7%); recrystallisation from aqueous ethanol gave the *dihydrate*, of unchanged m. p. (Found: C, 31.1; H, 5.1. $C_{30}H_{52}AuI_3P_4 \cdot 2H_2O$ requires C, 31.3; H, 4.9%). The anhydrous *tri-iodide*, treated in dimethylformamide with ethanolic sodium picrate, deposited the *dimethylformamido-iodo-dipicrate* (as XIII), m. p. 152—154° (decomp.) (from ethanol-dimethylformamide) (Found: C, 39.2; H, 5.2; N, 6.9. $C_{42}H_{56}AuIN_6O_{14}P_4 \cdot C_3H_7NO$ requires C, 38.9; H, 4.6; N, 7.0%).

Di-[4-methyl-o-phenylenebis(diethylphosphine)]silver(I) Salts (XIV).—Silver nitrate (1.5 g., 1 mol.) was added to potassium iodide (5 g.), each in water (15 ml.), and ethanol (15 ml.), and the bisphosphine (4.5 g., 2 mol.) added in turn to the clear solution. The mixture was shaken for 2 hr., giving a deposit (4 g.) which slowly crystallised. The deposit was extracted with hot ethanol; evaporation of the extract gave a residue which on recrystallisation from ethanol-ether afforded the *iodide* (XIV; X = I), m. p. 201—203° (Found: C, 46.6; H, 6.9. $C_{30}H_{52}AgIP_4$ requires C, 46.7; H, 6.7%). It gave a *picrate*, m. p. 141—143° (from ethanol) (Found: C, 49.7; H, 6.2; N, 5.1. $C_{36}H_{54}AgN_3O_7P_4$ requires C, 49.6; H, 6.2; N, 4.8%).

The insoluble residue from the ethanol extraction, recrystallised from dimethylformamide, gave the *di-iodoargentite* (XIV; X = AgI_2), prisms (1.5 g.), m. p. 255—260° (decomp.) (Found: C, 35.2; H, 5.2. $C_{30}H_{52}Ag_2I_2P_4$ requires C, 35.8; H, 5.2%).

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