

621. Gold(I) Alkynyls and their Co-ordination Complexes.

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The gold(I) ethynyls $(\text{Ph}\cdot\text{C}\equiv\text{CAu})_x$, $(\text{Bu}^t\cdot\text{C}\equiv\text{CAu})_4$, and their complexes with amines and various other donor molecules are described. Their infrared spectra show that in the complexes the frequency of the stretching vibration of the C:C bond is similar to those of ethynyl groups σ -bonded to various other metals, but in the tetramer $(\text{Bu}^t\cdot\text{C}\equiv\text{CAu})_4$ and the polymer $(\text{Ph}\cdot\text{C}\equiv\text{CAu})_x$ a reduction of frequency by 100—150 cm^{-1} indicates π -bonding between alkynyl groups and gold atoms.

Towards $\text{Ph}\cdot\text{C}\equiv\text{CAu}$ the order of donor strength $\text{PR}_3 > \text{P}(\text{OR})_3 > \text{RNC} > \text{AsR}_3 > \text{SbR}_3 > \text{Amines}$ has been established.

Some organogold(I) compounds RAuPR'_3 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{mesityl}$; $\text{R}' = \text{Et}, \text{Ph}$) are described.

MANY organic derivatives of gold(III) have been described, mainly by C. S. Gibson and his collaborators, and in all those compounds whose structure has been examined the metal is bound to four ligands arranged at the corners of a square.¹ In most of the organic derivatives of gold(III) two of the ligands are alkyl groups, the remaining two commonly being nitrogen, oxygen, or the halogens (but not fluorine). A few trimethyl derivatives of gold(III), stabilized by co-ordination to nitrogen, have been prepared by Gilman and Woods.²

It is possible though unlikely that an organic compound of gold(I) was present in the insoluble, apparently polymeric, intermediate observed in the thermal decomposition of the dialkylgold(III) cyanides³ (see ref. 1):



The compounds $(\text{RAuCN})_x$ are generally considered as mixed gold(I)-dialkylgold(III) complexes. Several colourless, monomeric (cryoscopically in benzene), compounds of gold(I) of the form RAuPR'_3 ($\text{R} = \text{Me}, \text{Et}, \text{Ph}, \text{C}\equiv\text{CPh}$; $\text{R}' = \text{Et}, \text{Ph}$) have recently been briefly described. They were prepared from the (tertiary phosphine)gold(I) halide and the appropriate organolithium reagent.⁴

An explosive gold(I) acetylide Au_2C_2 was described over 60 years ago,⁵ and both the analogous copper and silver compounds and the alkynyls $\text{R}\cdot\text{C}\equiv\text{CCu}(\text{Ag})$ are well-known substances, though their chemical constitution remains obscure. It is surprising that alkynylgold(I) compounds $(\text{R}\cdot\text{C}\equiv\text{CAu})_x$ have not hitherto been described.

Phenylethynylgold(I) is precipitated as a yellow powder when phenylacetylene and sodium acetate are added to a freshly reduced solution of gold(III) chloride containing sodium bromide. It resembles its copper(I) analogue in appearance, and we regard it similarly as a co-ordination polymer.⁶ It differs in being soluble in a considerably greater variety of donor solvents; presumably the co-ordination polymer is more readily depolymerized by replacement of ethynyl groups by other donor ligands. This is likely to be connected with the fact that in most of its complexes gold(I) has a co-ordination number of only two, whereas copper(I) is commonly bound to four ligands.

With triethylphosphine, phenylethynylgold(I) forms a complex, $\text{Et}_3\text{PAu}\cdot\text{C}\equiv\text{CPh}$, identical with that earlier prepared from bromotriethylphosphinegold(I) and phenylethynyl-lithium. The direct reaction between phenylethynylgold(I) and donor molecules allows the preparation of a much wider range of complexes than is feasible by the action

¹ Sidgwick, "The Chemical Elements and their Compounds," Oxford, 1950, Vol. I, pp. 181—187.

² Gilman and Woods, *J. Amer. Chem. Soc.*, 1948, **70**, 550.

³ Burawoy, Gibson, and Holt, *J.*, 1935, 1024.

⁴ Calvin, Coates, and Dixon, *Chem. and Ind.*, 1959, 1628.

⁵ Mathews and Watters, *J. Amer. Chem. Soc.*, 1900, **22**, 108.

⁶ Blake, Calvin, and Coates, *Proc. Chem. Soc.*, 1959, 396.

of an organolithium reagent on a complexed gold(I) halide; thus we have been able to obtain complexes with isocyanides, phosphites, and a variety of amines containing amino-hydrogen atoms.

Like the organogold(I) complexes reported earlier,⁴ the complexes formed from phenylethynylgold(I) and tertiary phosphines and arsines, phosphites, and isocyanides are mostly monomeric in benzene solution; however, (triethylphosphine)phenylethynylgold is slightly associated ($n \approx 1.3$) in benzene, less so ($n = 1.1-1.2$) in nitrobenzene. (Triethylstibine)-phenylethynylgold(I), though it was isolated, was insufficiently stable to permit reliable molecular-weight measurements. It resembled the triethylarsine complex in appearance and solubility properties, and we would guess it is monomeric too. The diphosphine $\text{Ph}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2$ combines with two mol. of phenylethynylgold(I), giving the compound $\text{PhC}\equiv\text{CAu}\leftarrow\text{PPh}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PPh}_2\rightarrow\text{AuC}\equiv\text{CPh}$.

The dipole moments (Table 1) of some gold(I) complexes are, with the exception of the triphenyl phosphite complex, in the range 5.4—7.1 D. These moments are rather larger

TABLE 1.

Complex	Dipole moment (D)	Complex	Dipole moment (D)	Complex	Dipole moment (D)
Et_3PAuMe	5.5	$\text{Et}_3\text{PAu}\cdot\text{C}\equiv\text{CPh}\dots\dots$	6.5 ₅	$\text{Et}_3\text{AsAu}\cdot\text{C}\equiv\text{CPh}\dots\dots\dots$	6.2
Et_3PAuEt	5.4	$\text{Ph}_3\text{PAu}\cdot\text{C}\equiv\text{CPh}\dots\dots$	6.7	$(\text{Bu}^n\text{NC})\text{Au}\cdot\text{C}\equiv\text{CPh}\dots\dots\dots$	6.9
Et_3PAuPh	6.2	$(\text{PhO})_3\text{PAu}\cdot\text{C}\equiv\text{CPh}$	4.4	$(o\text{-C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{NC})\text{Au}\cdot\text{C}\equiv\text{CPh}$	7.0 ₅

than might be expected in relation to those of the *cis*-dialkyl or -diaryl bis(tertiary phosphine) derivatives of platinum(II).⁷ For example, the moment of *cis*-(Et_3P)₂PtEt₂ is 5.5 D, which is very close to that of Et_3PAuEt (5.4 D), whereas on the simplest basis one could expect the gold compounds to have moments $(\sqrt{2})^{-1}$ times those of the analogous *cis*-platinum compounds. Possibly some saturation effect reduces the R-Pt and Pt-P moments. Though infrared intensities are more related to rate of change of moment with bond length, it is significant that the infrared band associated with Au-CH₃ stretching (532 cm.⁻¹ in $\text{Et}_3\text{P}\cdot\text{Au}\cdot\text{CH}_3$) is much stronger than corresponding bands in methyl-platinum (or -palladium) compounds.

Phenylethynylcopper(I) is soluble in liquid ammonia, and a colourless ammine has been isolated. However, this is so unstable that it reverts to the yellow starting material when dried in a current of nitrogen.⁸ Phenylethynylcopper(I) is slightly soluble in some primary and secondary amines, but evaporation of such solutions yields $(\text{Ph}\cdot\text{C}\equiv\text{CCu})_x$ containing no amine. Phenylethynylsilver forms an unstable complex with isopropylamine⁶ from which the amine is easily removed by pumping at room temperature. In contrast, phenylethynylgold(I) forms colourless crystalline complexes with one mol. of a variety of amines. Complexes with amines of low molecular weight are surprisingly sparingly soluble in all solvents investigated. The ammine $(\text{Ph}\cdot\text{C}\equiv\text{C}\cdot\text{AuNH}_3)_x$ is formed directly from aqueous ammonia and a suspension of $(\text{Ph}\cdot\text{C}\equiv\text{CAu})_x$, but the conversion of one insoluble suspension into another is rarely a good preparative method and the ammine is better obtained by the displacement of *n*-octylamine from a solution of $\text{Ph}\cdot\text{C}\equiv\text{C}\cdot\text{Au}(\text{NH}_2\cdot\text{C}_8\text{H}_{17})$ by addition of ammonia.

The sparing solubility of the amine complexes suggests that they might be associated in some way. The *n*-octylamine and *n*-nonylamine complexes were sufficiently soluble in benzene to permit cryoscopic molecular-weight measurements, and the apparent degrees of association, which increased with concentration, were in the range 2.6—4.1. Ebullioscopic methods are less satisfactory since many of the amine complexes decompose fairly quickly in solution during boiling, and darken slowly even at room temperature. They are less soluble in nitrobenzene than in benzene. Since benzene solutions of the amine complexes evidently contain two or more molecular species, we were unable to measure

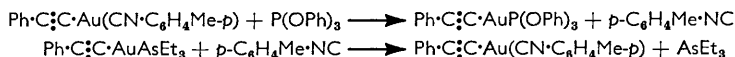
⁷ Chatt and Shaw, *J.*, 1959, 705, 4020.

⁸ Nast and Pfab, *Chem. Ber.*, 1956, 89, 415.

their dipole moments. However, the dielectric constants of their benzene solutions indicated the presence of species which are much less polar than the phosphine complexes.

We cannot satisfactorily account for these differences between nitrogen and heavier ligands in their phenylethynylgold complexes. Evidently the co-ordination number of the metal is greater than two in the amine complexes, and a preliminary X-ray study of the isopropylamine complex by Mr. P. W. R. Corfield and Dr. H. M. M. Shearer of this department indicates that gold atoms occur in pairs in an infinite chain.* On account of π -bonding the metal-ligand bond would be a little greater in bond order in complexes with phosphorus, arsenic, and similar ligands than in the amine complexes, but this scarcely seems an adequate explanation for the association of the last.

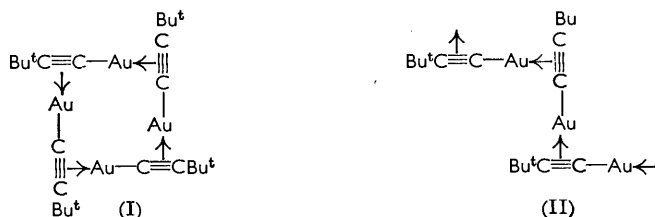
The relative donor character of various ligands towards phenylethynylgold was established by a series of displacement reactions, *e.g.*:



The resulting order is: $\text{PEt}_3 > \text{P}(\text{OPh})_3 > p\text{-C}_6\text{H}_4\cdot\text{NC} > \text{AsEt}_3 > \text{SbEt}_3 > \text{ammonia}$, primary and secondary amines $>$ tertiary amines. Pyridine was the only tertiary amine which yielded a complex. Bipyridyl in benzene solution did not dissolve phenylethynylgold, but some aliphatic tertiary amines (NEt_3 , NBu^n_3) gave solutions which gradually darkened and deposited metallic gold.

No complex appeared to be formed by diethyl sulphide, phosphorus(III) chloride, diphenylacetylene, methyl or phenyl cyanide, or carbon monoxide at atmospheric pressure. Phenylethynylgold was slowly dissolved by dimethyl sulphide (in a Soxhlet extractor), but the resulting solution continuously deposited gold. Trimethyl and triethyl phosphite yielded complexes which were liquid at room temperature.

3,3-Dimethylbut-1-ynylgold(I).—This resembles its copper(I) analogue in being soluble in inert non-polar solvents. Whereas $\text{Bu}^t\text{C}\equiv\text{C}\text{Cu}$ is octameric in boiling benzene solution,^{9,10} the pale yellow gold compound is tetrameric. If the co-ordination number of the metal is two, the gold compound is likely to have the structure (I). An insoluble form of this compound was also obtained, generally as a pale purplish-white powder, the colour almost



certainly being due to a trace of metallic gold. Both forms yielded identical complexes, $\text{Bu}^t\text{C}\equiv\text{C}\cdot\text{AuPMe}_3$, with trimethylphosphine. It is probable that the insoluble form is a polymer (II). The polymer and the tetramer had almost identical infrared spectra; differences in the acetylenic stretching region are recorded in Table 3.

Infrared Spectra.—All the phenylethynylgold complexes, except those formed by triphenyl phosphite, *p*-tolyl isocyanide and *o*-ethylphenyl isocyanide, absorbed in the region where acetylenic stretching bands would be expected (Table 2). There is no apparent relation between $\nu(\text{C}\equiv\text{C})$ and the nature of the ligand, and it is remarkable that

* Individual molecules of $\text{PhC}\equiv\text{C}\cdot\text{Au}(\text{NH}_2\cdot\text{Pr}^i)$ can be distinguished in the crystal structure. The amino-hydrogen atoms, whose positions can be inferred from those of the gold atom and the isopropyl group, are not directed towards gold atoms but one hydrogen is apparently directed towards an acetylenic group.

⁹ Favorski and Morev, *J. Russ. Phys. Chem. Soc.*, 1920, **50**, 571.

¹⁰ Coates and Parkin, *J. Inorg. Nuclear Chem.*, 1961, **22**, 59.

the observed frequencies fall within such a narrow range (2107—2135 cm.⁻¹), close to those of phenylethynyl-nickel,¹¹ -palladium,¹² and -platinum(II)¹³ complexes with triethylphosphine (2100—2108 cm.⁻¹). Polymeric phenylethynylgold has a very weak band at 1973 cm.⁻¹, about 150 cm.⁻¹ less than $\nu(\text{C}\equiv\text{C})$ observed in the complexes listed in Table 2. The acetylenic stretching frequencies observed in bisphenylethynylmercury are at 2149

TABLE 2.

C \equiv C, N \equiv C, and NH stretching frequencies (cm.⁻¹) in complexes Ph·C \equiv C·AuL.

L	$\nu(\text{C}\equiv\text{C})$	$\nu(\text{NH})$	L	$\nu(\text{C}\equiv\text{C})$	$\nu(\text{N}\equiv\text{C})$
NH ₃	2120,* 2121 ¶	3328,* 3247 *	PEt ₃	2109 *	—
Pr ⁱ ·NH ₂	2122 *	3254,* 3208 *	PPh ₃	2123 * vw, 2129 † vw	—
n-C ₆ H ₁₁ ·NH ₂	2126,* 2127 †	3287,¶ 3232 ¶	$\frac{1}{2}(\text{Ph}_2\text{P}\cdot\text{CH}_2)_2$	2125 §	—
n-C ₈ H ₁₇ ·NH ₂	2122 *	3283,* 3226 *	AsEt ₃	2113,* 2128 †	—
n-C ₉ H ₁₉ ·NH ₂	2125 *	3264,* 3224 *	SbEt ₃	2107 *	—
Bu ⁿ ·NH.....	2131 *	3167 *	Bu ⁿ ·NC	2130,* 2134 ‡	2249,* 2253 ‡
Piperidine ...	2130 *	3179 *	<i>p</i> -C ₆ H ₄ Me·NC	abs.*	2232 *
Pyridine	2134 *	—	<i>o</i> -C ₂ H ₅ ·C ₆ H ₄ ·NC	abs.* †	2218,* 2211 †

* KBr disc. † In benzene. ‡ In carbon tetrachloride. § Nujol mull. ¶ In hexachlorobutadiene.

cm.⁻¹ and a weaker band at 2117 cm.⁻¹ (in a KBr disc). In the alkyl compounds (Alkyl·C \equiv C)₂Hg, $\nu(\text{C}\equiv\text{C})$ is slightly greater, 2156—2165 cm.⁻¹. Since the acetylenic frequencies in the gold complexes are only very slightly less than those of (Ph·C \equiv C)₂Hg, one may conclude that π -bonding between metal *d*-orbitals and the acetylenic π_g -orbital is not significantly greater in the gold complexes. In (Ph·C \equiv C·Au)_{*x*} itself such bonding is evidently quite strong, as in the copper(I) compounds (R·C \equiv C·Cu)_{*x*}.¹⁰ It is significant in this connection that the C \equiv O stretching frequency (2152 cm.⁻¹) in ClAuCO is one of the highest recorded for metal carbonyls, suggesting that *d* _{π} - π_g -bonding between gold and the carbonyl group is relatively weak.¹⁴

The stretching frequencies of the isocyanide groups bonded to phenylethynylgold are about 100 cm.⁻¹ greater than those of the free isocyanides, the differences $\nu(\text{bonded}) - \nu(\text{free})$ being 103, 98, and 81 cm.⁻¹ for *n*-butyl, *p*-tolyl, and *o*-ethylphenyl isocyanide. These are substantially larger increases than those recently reported for isocyanide complexes of silver(I) and manganese(II), and are ascribed partly to the kinematic effect of

TABLE 3.

Acetylenic stretching frequencies (cm.⁻¹) in (Bu^t·C \equiv C·Au)₄ and its complexes.

	$\nu(\text{C}\equiv\text{C})$ (in KBr)		
(Bu ^t ·C \equiv C·Au) ₄	2027,	2002,	1982
(Bu ^t ·C \equiv C·Au) ₂	2000sh,	1972sh,	1956w
Bu ^t ·C \equiv C·AuNH ₃	2110w,	2004vw,	1968vw
Bu ^t ·C \equiv C·AuPMe ₃	2150vw,	2122m,	2041vw, 1980vw

coupling the CN oscillator to the MC oscillator, but mainly to the effect of the positive charge on the metal ion.¹⁵ Since the gold atom in complexes R·C \equiv C·Au(C \equiv N·R') is likely to carry a fractional negative charge, we prefer to ascribe the increase of $\nu(\text{N}\equiv\text{C})$ on co-ordination to a rise in the bond order of the isocyanide group from less than three in the free isocyanide to three in the co-ordinated isocyanide. In fact the frequencies we observed

¹¹ Chatt and Shaw, *J.*, 1960, 1718.

¹² Calvin and Coates, *J.*, 1960, 2008.

¹³ Chatt and Shaw, *J.*, 1959, 4020.

¹⁴ Nyholm, *Proc. Chem. Soc.*, 1961, 284.

¹⁵ Cotton and Zingales, *J. Amer. Chem. Soc.*, 1961, **83**, 351.

in the isocyanide gold complexes are about the same as those of normal cyanide groups (2220—2260 cm^{-1}).

The spectra of the 3,3-dimethylbut-1-ynyl compounds are peculiar in that three (and in one case four) weak bands are found in the acetylenic stretching region (Table 3).

In nearly all complexes a band at 520—560 cm^{-1} was observed; this band was absent or very weak indeed in the isopropylamine complex, and was obscured by ligand bands in the case of arylphosphine or aryl phosphite complexes. By analogy with the Au-CH₃ stretching frequency (532 cm^{-1}) in Et₃PAuCH₃,⁴ and with the range of Pt-C¹⁶ and Hg-C¹⁷ stretching frequencies, we consider that the 520—560 cm^{-1} band in the gold complexes is due to a gold-alkynyl stretching vibration. The band is strongest (560 cm^{-1}) in (Bu^t:C:C·Au)₄ and in (Bu^t:C:C·Au)_x; it is weaker (524 cm^{-1}) in (Ph·C:C·Au)_x and lies in the rather narrow range 520—529 cm^{-1} in phenylethynylgold complexes. The bands at 539 cm^{-1} in (Bu^t:C:C·Cu)₈ and at 542 and 464 cm^{-1} in (Bu^t:C:C)₂Hg are very likely to be due to metal-alkynyl stretching.

The interpretation of the infrared spectra of amine complexes can be considerably complicated by hydrogen bonding to the solvent or intermolecularly. For example, the spectrum of the complex (PPRⁿ₃,NH₃PtCl₂) has six N-H stretching bands even in carbon tetrachloride solution.¹⁸ We found, however, that the spectra of the gold-amine complexes are relatively simple, even in the solid state, and observed no more than three bands (at 3183m, 3252m, and 3313s for Bu^t:C:C·AuNH₃). The single bands due to secondary amines were relatively sharp (sharper than those due to C-H vibrations in the same complexes). Bands due to primary amines were a little broader, but the N-H bands even of the ammonia complexes, in which hydrogen bonding effects would be greatest, were not very much broader than aliphatic C-H stretching bands. In both ammonia complexes bands were observed at 1241m cm^{-1} for Ph·C:C·AuNH₃, and at 1253s cm^{-1} for Bu^t:C:C·AuNH₃, which were absent from the spectrum of the uncomplexed ethynyl and could be due to a rocking mode. For the t-butyl complex, NH₃ deformation bands were observed at 1613 and 1623 cm^{-1} .

EXPERIMENTAL

Microanalyses (carbon and hydrogen) were by Miss V. Conway and Mr. T. Caygill of this Department. M. p.s are corrected. Infrared spectra were measured with a Grubb-Parsons GS2A spectrometer with a 1200 line per inch grating.

Phenylethynylgold.—A solution of gold(III) chloride (10 g. of hydrate containing 5.1 g. of gold) and potassium bromide (14 g.) in water (50 c.c.) was diluted with 1:1 acetone-water until the total volume was about 200 c.c. Sulphur dioxide was bubbled in to the reaction mixture, which was agitated with a vibro-mixer, until the colour was pale red. The flow of sulphur dioxide was then stopped, agitation continued for a few minutes, and then addition of sulphur dioxide was cautiously resumed until the colour was pale yellow. It is important to avoid an excess of sulphur dioxide, and to prevent the mixture's becoming warmed above 15—20°.

Phenylacetylene (2.6 g.) in acetone (10 c.c.) was then added, followed by hydrated sodium acetate (20 g.). The initial pale yellow precipitate gradually increased in amount, and after agitation for ½ hr. was collected, washed with acetone and ether, and dried. The bright yellow *product* (7.0 g., 91%) darkens rapidly above 105° (Found: C, 32.0; H, 1.8; Au, 65.2, 65.7. C₈H₅Au requires C, 32.2; H, 1.7; Au, 66.1%); we have been unable to make it explode. It should be stored in the dark.

Isopropylamine(phenylethynyl)gold.—An excess of isopropylamine was added to phenylethynylgold (1.1 g.) suspended in benzene (10 c.c.). After removal of solvent and the excess of amine from the resulting white suspension, the *complex* was crystallized from acetone, forming white needles (1 g.) (Found: C, 36.7; H, 4.1; Au, 54.8, 55.1. C₁₁H₁₄AuN requires C, 37.0;

¹⁶ Adams, Chatt, and Shaw, *J.*, 1960, 2047.

¹⁷ Boyd, Thompson, and Williams, *Discuss. Faraday Soc.*, 1950, 9, 154; Gutowsky, *J. Chem. Phys.*, 1949, 17, 128.

¹⁸ Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; 1956, 2712.

H, 3.95; Au, 55.2%). The complex darkens rapidly above 115°, and is soluble in hot acetone and benzene, and insoluble in carbon tetrachloride, chloroform, ether, and methylcyclohexane. *n*-Pentylamine(phenylethynyl)gold.—Similarly prepared, this complex crystallized as white needles on cooling to -20° of its solution in 1,2-dimethoxyethane (Found: C, 40.9; H, 4.8; Au, 51.1, 51.0. C₁₂H₁₆AuN requires C, 40.5; H, 4.7; Au, 51.1%). It darkens above 115° and melts at 124—125° (decomp.). It is moderately soluble in benzene at 25°, soluble in warm acetone, chloroform, and carbon tetrachloride, but insoluble in ether and in hexane.

Similarly prepared were: *n*-octylamine(phenylethynyl)gold, colourless needles (from 1,2-dimethoxyethane), decomp. >120° (Found: C, 45.0; H, 5.6; Au, 45.7, 45.8. C₁₆H₂₄AuN requires C, 44.9; H, 5.7; Au, 46.1%. Degree of association 3.08, 3.40, 3.79, 3.54, 4.12 cryoscopically in 1.34, 2.87, 3.39, 4.22, 5.73 wt. % benzene); *n*-nonylamine(phenylethynyl)gold, colourless needles (from 1,2-dimethoxyethane), m. p. 117—118° (decomp., darkening from 105°) (Found: C, 46.6; H, 5.9; Au, 44.6, 44.4. C₁₇H₂₆AuN requires C, 46.2; H, 5.9; Au, 44.7%. Degree of association 2.58, 3.12, 3.30, 3.62, 4.06 cryoscopically in 0.73, 1.56, 2.62, 3.62, 5.15 wt. % benzene); *di*-*n*-butylamine(phenylethynyl)gold, colourless needles (from acetone), m. p. 91—92° (decomp.) (Found: C, 45.5; H, 5.7; Au, 46.2, 46.3. C₁₆H₂₄AuN requires C, 44.9; H, 5.7; Au, 46.1%); *piperidine*(phenylethynyl)gold, colourless needles (from 1,2-dimethoxyethane), m. p. 111.5—112°, sparingly soluble in most solvents (Found: C, 40.9; H, 4.1; Au, 51.2, 51.4. C₁₃H₁₆AuN requires C, 40.7; H, 4.2; Au, 51.4%); *pyridine*(phenylethynyl)gold, colourless needles (from 1,2-dimethoxyethane) containing free pyridine, decomp. >80° (Found: C, 42.0; H, 2.6; Au, 52.1, 52.3. C₁₃H₁₀AuN requires C, 41.4; H, 2.7; Au, 52.25%).

Ammine(phenylethynyl)gold, [Ph·C:C·AuNH₃].—This *ammine* was obtained as a colourless crystalline precipitate when ammonia was added to a solution of *n*-octylamine(phenylethynyl)gold in acetone; it is insoluble in all solvents which do not cause decomposition, and decomposes above 120° without melting (Found: Au, 62.5, 62.3. C₈H₈AuN requires Au, 62.5%).

The following complexes with 1 mol. of the named ligands were prepared directly from phenylethynylgold and the ligand, with exclusion of air since several of the ligands are readily oxidized: *triphenylphosphine*, very pale cream plates (from benzene-methylcyclohexane), m. p. 163—164° (decomp.) (Found: C, 56.1; H, 3.8; Au, 35.1%; *M*, cryoscopic in benzene 533, 482, 482. C₂₆H₂₀AuP requires C, 55.7; H, 3.6; Au, 35.2%; *M*, 561); *triphenyl phosphite*, colourless needles (from ethanol), m. p. 113—114° (Found: C, 50.8; H, 3.2; Au, 32.3, 32.0%; *M*, cryoscopic in benzene, 548, 596, 578, 596. C₂₆H₂₀AuO₃P requires C, 51.3; H, 3.3; Au, 32.4%; *M*, 609); *triethylarsine*, colourless needles (from ether), m. p. 67—68° (Found: C, 35.9; H, 4.7; Au, 42.7%; *M*, cryoscopic in 0.46, 0.66, 1.01 wt. % benzene, 474, 484, 460. C₁₄H₂₀AsAu requires C, 36.5; H, 4.6; Au, 42.8%; *M*, 460); [also 1,2-*diphenylphosphinoethane*(*bisphenylethynyl*)digold, (Ph·C:C·Au)₂Ph₂P·CH₂·CH₂·PPh₂, colourless needles (from chloroform-ethanol), decomp. >200° (Found: C, 49.9; H, 3.7; Au, 39.7. C₄₂H₃₄Au₂P₂ requires C, 50.6; H, 3.4; Au, 39.6%) (this was also prepared by displacement of *n*-octylamine from its complex; it differs from the other phosphine and similar complexes in its insolubility in cold benzene)]; *n*-butyl isocyanide, colourless needles (from ether), m. p. 40.5—41.5° (Found: C, 41.0; H, 3.8; Au, 51.5, 51.5%; *M*, cryoscopic in 1.00, 1.50, 1.79, 1.99 wt. % benzene, 386, 409, 417, 412. C₁₃H₁₄AuN requires C, 40.9; H, 3.7; Au, 51.7%; *M*, 382); *p*-tolyl isocyanide, colourless leaflets (from benzene, in which it is only sparingly soluble in the cold), m. p. 176—177° (decomp.) (Found: C, 46.2; H, 2.8; Au, 47.7. C₁₆H₁₂AuN requires C, 46.3; H, 2.9; Au, 47.5%); *o*-ethylphenyl isocyanide, colourless needles (from 1,2-dimethoxyethane), m. p. 107—108° (Found: C, 47.5; H, 3.4; Au, 45.7, 45.7%; *M*, cryoscopic in 0.95, 1.43, 1.72, 1.91 wt. % benzene, 439, 400, 446, 427. C₁₇H₁₄AuN requires C, 47.55; H, 3.3; Au, 45.9%; *M*, 429); triethylstibine, very pale yellow needles (from propan-1-ol), m. p. 96—97°, very unstable and darkening rapidly in air though more slowly under nitrogen (we were unable to purify it satisfactorily) (Found: C, 32.7; H, 3.2. Calc. for C₁₄H₂₀AuSb: C, 33.1; H, 4.0%) [a product with identical infrared spectrum was obtained by displacement of *n*-octylamine from Ph·C:C·Au(NH₂·C₈H₁₇) by triethylstibine]. The above complexes, with the exception of that formed by 1,2-diphenylphosphinoethane, were much more soluble than those formed by amines; they dissolved freely in most organic solvents except saturated hydrocarbons.

3,3-Dimethylbut-1-ynylgold, [Bu^t·C:C·Au]₄.—This was prepared in 77% yield by the method used for phenylethynylgold. The pale yellow product crystallized from hexane, and also from propan-1-ol; it decomposed above 150° (Found: C, 26.2; H, 3.3; Au, 70.5, 70.6%; *M*, ebullioscopic in 1.48, 2.46, 2.93, 3.47, 4.47 wt. % benzene, 1166, 1192, 1154, 1118, 1112.

$C_{24}H_{36}Au_4$ requires C, 25.9; H, 3.3; Au, 70.9%; *M*, 1113). The tetramer is soluble in benzene (only sparingly at the f. p.), ethyl methyl ketone, chloroform, and hexane, very slightly soluble in cold acetone, and insoluble in methanol and ethanol. An insoluble pale purplish-white product was also obtained as by-product from crystallization of the tetramer.

Ammine-3,3-dimethylbut-1-ynylgold, $Bu^tC\equiv C\cdot AuNH_3$.—Addition of ammonia to $(Bu^tC\equiv C\cdot Au)_4$ (2 g.), suspended in acetone (20 c.c.), yielded a white precipitate which dissolved when the mixture was warmed. The hot filtered solution deposited colourless needles (1.0 g.) of the complex, decomp. above 155°, and a further 0.5 g. was recovered after concentration of mother liquor (Found: C, 25.4; H, 4.2; Au, 66.5, 66.6; N, 4.7. $C_6H_{12}AuN$ requires C, 26.4; H, 4.1; Au, 66.8; N, 4.7%).

Trimethylphosphine-3,3-dimethylbut-1-ynylgold, $Bu^tC\equiv C\cdot AuPMe_3$.—Addition of trimethylphosphine (3.65 mmoles in 5 c.c. of ether) to a solution of $(Bu^tC\equiv C\cdot Au)_4$ (1 g., 0.9 mmole) in benzene (10 c.c.) discharged the pale yellow colour. Removal of benzene and recrystallization from 1,2-dimethoxyethane–hexane gave colourless cubes, m. p. 194–196° (decomp.) (Found: C, 30.4; H, 5.1; Au, 55.7, 55.8. $C_9H_{18}AuP$ requires C, 30.5; H, 5.1; Au, 55.6%). An identical product (mixed m. p. and infrared spectrum) was obtained by dissolving the polymeric $(Bu^tC\equiv C\cdot Au)_x$ in an ether solution of trimethylphosphine.

Organogold(I) Complexes from (Tertiary Phosphine)gold(I) Halide and an Organolithium Reagent (Preparations by G. CALVIN, P. S. DIXON, and J. GRAHAM).—Triethylphosphinemethylgold, $MeAuPET_3$. The monochloride, Et_3PAuCl (7 g., 0.02 mole), was allowed to react with methyl-lithium (0.025 mole) in ether. After hydrolysis the ether layer yielded a colourless product (5.3 g., 80%), m. p. 62° (after crystallization from ether) (Found: C, 25.4; H, 5.4. $C_7H_{18}AuP$ requires C, 25.4; H, 5.5%). In this and other similar preparations metallic gold was gradually deposited from the aqueous layer. This was probably due to the formation of water-soluble unstable salts $[R_2AuPR'_3]Li$, and it was observed that the use of a considerable excess of organolithium reagent gave low yields of neutral product $RAuPR'_3$. Similarly prepared were *triethylphosphinephenylgold*, colourless plates (70%) (from ether or methanol), m. p. 68° (Found: Au, 50.4%; *M*, cryoscopic in 1.26, 2.93, 4.75 wt. % nitrobenzene, 395, 404, 402. $C_{12}H_{20}AuP$ requires 50.2%; *M*, 392). Unlike the methyl compound, which was converted into the chloride, the phenyl compound appeared unaffected by alcoholic hydrogen chloride at room temperature. *Triethylphosphine(phenylethynyl)gold* formed colourless needles, m. p. 83–85°, from acetone, (Found: C, 40.3; H, 4.8%; *M*, cryoscopic in 4.61, 5.91 wt. % benzene, 542, 552, cryoscopically in 1.08, 2.42, 3.26 wt. % nitrobenzene, 486, 495, 484. $C_{14}H_{20}AuP$ requires C, 40.1; H, 4.8%; *M*, 417). *Triethylphosphine-ethylgold*, crystallized from ether and then from n-hexane, had m. p. 51° (with slight decomp.); it effervesced slowly with ethanol and vigorously with ethanolic hydrogen chloride (Found: C, 28.0; H, 6.1. $C_8H_{20}AuP$ requires C, 27.9; H, 5.9%). *Triphenylphosphinemethylgold* formed colourless plates (from acetone), m. p. 175° (decomp.) (in this preparation deposition of a small amount of gold from the aqueous phase took place very rapidly) (Found: C, 48.0; H, 3.7; Au, 41.9. $C_{19}H_{18}AuP$ requires C, 48.1; H, 3.8; Au, 41.5%). *Triphenylphosphine-ethylgold* formed colourless plates (from ether), m. p. ca. 130° (decomp.) (Found: C, 49.5; H, 4.4. $C_{20}H_{20}AuP$ requires C, 49.2; H, 4.1%). *Triphenylphosphinephenylgold* required three crystallizations from ether and a treatment with a little charcoal before a colourless product resulted [m. p. 164° (darkening from 130°)] (Found: C, 52.8; H, 3.9; Au, 37.2. $C_{24}H_{20}AuP$ requires C, 53.8; H, 3.7; Au, 36.8%). *Triphenylphosphinemesitylgold* formed a light brown oil which gradually solidified on prolonged pumping in vacuum (8 hr.). Crystallization from ether yielded a colourless product, decomp. >100° (Found: C, 55.7; H, 4.7. $C_{27}H_{26}AuP$ requires C, 56.0; H, 4.5%).

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