Qrgano – Metallic: Co-ordination compounds of group IB

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ORGANO - METALLIC

CO-ORDINATION COMPOUNDS OF GROUP IB

by

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A thesis submitted for the Degree of
Doctor of Philosophy in the University of Durham.

PREFACE

The work described in this thesis is the original work of the author except where acknowledged by reference, has not been submitted for any other degree and has been carried out under the supervision of Professor G. E. Coates, at the Science Laboratories of the Durham Colleges in the University of Durham, between September 1959 and June 1962. It is also the subject of two papers, published with Professor Coates, entitled: (a) Ethynylcopper(I) Complexes with Tertiary Phosphines, J. Inorg. Nuclear Chem, 1961, 22, 59, (b) Gold(I) Ethynyls and their Co-ordination Complexes, J., in the press.

The author wishes to express his sincere thanks to Professor G. E. Coates for his invaluable advice and encouragement throughout the work. He is grateful to Dr. H.M.M. Shearer, and Mr. P.W.R. Corfield for their interest in the crystal structures of some of the compounds described and to Dr. F. Glockling for helpful discussions. He is also indebted to the Ethyl Corporation for a maintenance grant.

June 1962

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ABSTRACT

Ethynyl copper(I) tertiary phosphine complexes $RC{:}CCu(PR'_3)_n$ have been prepared from the familiar polymeric ethynyls $(RC{:}CCu)_x$. When n = 1 these complexes are dimeric in nitrobenzene and rather more associated in benzene. When n = 2 they are monomeric and one unstable complex with n = 3 has been isolated. A mixed ethynyl complex, $Bu^tC{:}CCu\ PhC{:}CCu{\cdot}2PMe_3$ and some diacetylene complexes, $PhC{:}C{\cdot}C{:}CCuPR'_3$ which are similarly associated and the complex $(PhC{:}C{\cdot}C{:}CCu)_2(PEt_3)_3$, monomeric in nitrobenzene, have also been isolated. One silver complex $PhC{:}CAgPMe_3$, dimeric in boiling benzene was prepared.

The first gold(I) ethynyls, other than Au_2C_2 have been prepared. Phenylethynylgold(I) resembles phenylethynylcopper in appearance and in its insolubility; t-butylethynylgold is tetrameric and can be assigned a square structure. They form isolatable complexes $RC{:}CAuL$ with a wide range of donor ligands, (L), and towards phenylethynylgold the order of donor strength

$$PPh_3 > PEt_3 > P(OR)_3 > RNC > AsEt_3 > SbEt_3 > \text{amines}$$

has been established.

With the exception of the amine complexes, which appear to be associated in some way, they are monomeric and have dipole moments in the range 4·4 -7·1 D.

Infra-red spectra show that in the gold complexes the

acetylenic stretching vibration is similar to those of ethynyl groups σ-bonded to various metals but in the tetramer $(\mathrm{Bu}^t\mathrm{C}{\vdots}\mathrm{CAu})_4$ and the polymer $(\mathrm{PhC}{\vdots}\mathrm{CAu})_x$ a reduction in frequencies of about 175 cm.$^{-1}$ indicates π bonding between ethynyl groups and gold atoms which is stronger than in the ethynylsilvers $(\mathrm{RC}{\vdots}\mathrm{CAg})_x$ in which the frequency is lowered by about 100 cm.$^{-1}$ but not as strong in the ethynylcoppers $(\mathrm{RC}{\vdots}\mathrm{CCu})_x$ in which it is lowered by 200 cm.$^{-1}$. In the case of the ethynylcopper(I) compounds, complex formation raises $\nu(\mathrm{C}{\vdots}\mathrm{C})$ by nearly 100 cm.$^{-1}$ from that in $(\mathrm{RC}{\vdots}\mathrm{CCu})_x$ and in the ethynylsilver(I) compounds by 20 cm.$^{-1}$.

Absorptions due to ethynyl-metal stretching vibrations were observed in the various compounds for the most part in the range 510-540 cm.$^{-1}$.

INTRODUCTION

INTRODUCTION

The new complexes of Group IB metals described in this thesis are of two main types: ethynyl copper(I) complexes with tertiary phosphines of general formula $(R_3P)_x(CuC\vdots CR')_y$, and ethynyl gold(I) complexes with a variety of ligands $RC\vdots CAuL$. Interest in these compounds arose from the nature of the acetylides $(R.C\vdots CM)_x$ (M = Cu,Ag) whose structures are still unknown, and from recent work in this department[1] in which a preliminary study had shown that they could be depolymerised by some donor molecules containing Group V elements.

The general picture of the co-ordination chemistry of the coinage metals when univalent is considered in this introduction, complexes with halogens, nitrogen, oxygen and sulphur as donors being mentioned briefly, those with phosphorus (and arsenic) and with carbon-metal bonds are described more fully as they are more relevant to the present work. Finally transition metal acetylene complexes are discussed as during the last ten years compounds with several types of acetylene-metal bonding have been prepared.

CO-ORDINATION CHEMISTRY OF COPPER(I), SILVER(I) AND GOLD(I)

The first ionization potentials (shown in the table below) of the coinage metals are much larger than those of the alkali metals, which they scarcely resemble.

First Ionization Potential (electron-volts)	Li	Na	K	Rb	Cs	Cu	Ag	Au
	5.39	5.14	4.34	4.18	3.90	7.72	7.57	9.22

It is not surprising therefore that they tend to form mostly covalent compounds and the tendency is in the sense Au $>$ Cu $>$ Ag.

The co-ordination numbers exhibited by a metal atom, in a particular valency state, depend on the nature of the ligand and the type of bonding it produces and to a lesser extent on steric effects. In the case of copper(I), silver(I) and gold(I) the preferred co-ordination numbers are usually considered to be: for copper 2 and 4, silver 2 and 3, and gold 2, though compounds have been isolated in which each metal exhibits any one of the states 2, 3 or 4. Examples are described later. Although silver has been thought to have a preferred co-ordination number of 2 and sometimes 3, Arhland and Chatt and co-workers[2] have found from studies of stability constants of a variety of water-soluble ligands to silver(I) ion that 4 is found for more types of atoms than any other co-ordination number. In particular they clearly demonstrated that silver(I) changes its co-ordination number according to the nature of the ligand. With ligands which afford little or no π-bonding such as ammonia, chloride, bromide and cyanide, considerable stability is shown by the linear 2 co-ordinated state, though further molecules are taken up in solution to give co-ordination numbers of 3 and 4. With sulphides and selenides, ligands with a slightly greater π-bonding capacity, complex formation in solution passes smoothly to give 4 co-ordinated silver, and with ligands which form strong π-bonds, in particular phosphorus and also to a lesser extent arsenic and iodide ion, co-ordination of 1 and 3 ligands seems to produce the most stable complexes, the stability being increased relative to AgL_2. The tendencies of co-ordinated atoms to form d_π bonds with silver increases in the order amines $<$ selenides $\simeq$ sulphides $<$ arsines $<$ phosphines and for the halogens in the sense Cl $<$ Br $<$ I.

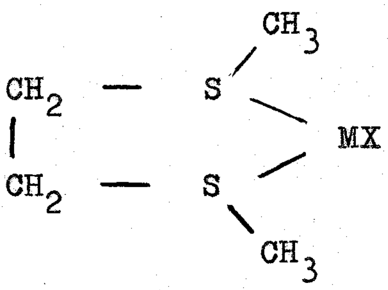
In the 4 covalent state *sp*^{3} tetrahedral hybrid orbitals of the metal are used to accommodate the electrons from the ligand, in the 3 covalent state *sp*^{2} trigonal hybrid orbitals. The 2 covalent state which on the molecular orbital theory is considered to involve *sp* hybridisation of the metal, has recently been discussed by Nyholm[4] and Orgel[3]. In a recent lecture Nyholm[4] considers the energy of separation of the *ns* and *np* orbitals of copper, silver, and gold, which are 3.79, 3.66 and 4.63 ev. respectively, and shows that the formation of *sp*^{3} tetrahedral hybrid bonds is more difficult for gold(I) than for copper(I) or silver(I). Digonal *sp* hybridisation is consistent with a large energy difference between the *ns* and *np* orbitals, but in fact the *s* - *p* separations in Cu^+, Ag^+, Au^+ and Hg^{2+} are not much greater than in related ions (e.g. Cd^{2+}, Zn^{2+}) which do not form *sp* bonds. For this reason and because the energy difference between the nd^9 and nd^{10} $(n + 1)s$ configuration is small (for Cu^+ 2.7, Ag^+ 4.8, Au^+ 1.9; cf. Zn^{2+} 9.7 ev.) Orgel[3] suggests that hybridisation between the $\underline{nd}_{z^2}$ and ($\underline{n}$ + 1)$\underline{s}$ orbitals takes places. This leads to strong electronegativity along the z axis and therefore strong 2-covalent bonding occurs along this axis. Nyholm[4] has suggested that the residual charge on the metal determines which is the better explanation of 2-co-ordination. If the charge is small, then the larger $\underline{s}$ - $\underline{p}$ separation seems the determining factor and $\underline{sp}$ hybridisation is a reasonable assumption; on the other hand, if the charge is appreciable the smaller $\underline{d}$ - $\underline{s}$ separation and Orgel's picture is the more likely explanation.

Complexes with halogens, nitrogen, oxygen and sulphur

Halogen complexes of the type $[MX_2]^-$ and $[MX_3]^{2-}$ (X = Cl, Br, I), are the most common species in the case of copper and silver[5]. $[MX_4]^{3-}$ complexes are known but are less common. Several crystalline salts containing the $[CuI_2]^-$ anion have been described, for example, $[Cu(en)_2][CuI_2]_2$.

Ammonia forms ammines $[M(NH_3)_n]^+$ with all three elements, where n is usually 2, but can be 1 and 3. Pyridine and substituted ammonias behave similarly.[6] A variety of nitriles form complexes with copper(I)[7] and silver(I)[8] compounds forming mainly 1:1 adducts, e.g., $CH_3CNCuCl$.

Sulphur has a much greater affinity for these metals than oxygen which forms few complexes. The thioether complexes[9] of gold(I) are well known, e.g. monomeric Et_2SAuCl, and all three elements give a series of thiourea and ethylenethiourea complexes.[10] Polymeric mercaptides of unknown constitution, of copper(I)[11] and silver(I)[12] (formula R•S•M), have been prepared and their reaction with aryl halides to prepare thioethers investigated. Most of the chelated complexes of these metals are compounds with oxygen and sulphur as donor atoms. Examples are the complex thiosulphate anion[13] $[Cu(S_2O_3)_2]^{3-}$ and the copper and gold derivatives of di(methylthio)ethane,[14]



(X = Cl, Br)

Phosphorus and Arsenic Complexes

Copper-phosphine complexes of formula $CuX.nPH_3$ (X = Cl, Br, I; n = 1 or 2) have been isolated. The 2:1 complexes lose phosphine readily to give the 1:1 complexes[15]. The only silver and gold complexes with phosphine are those of silver iodide which forms $AgI.PH_3$ and $2AgI.PH_3$, and the very unstable gold compound $AuI.PH_3$.

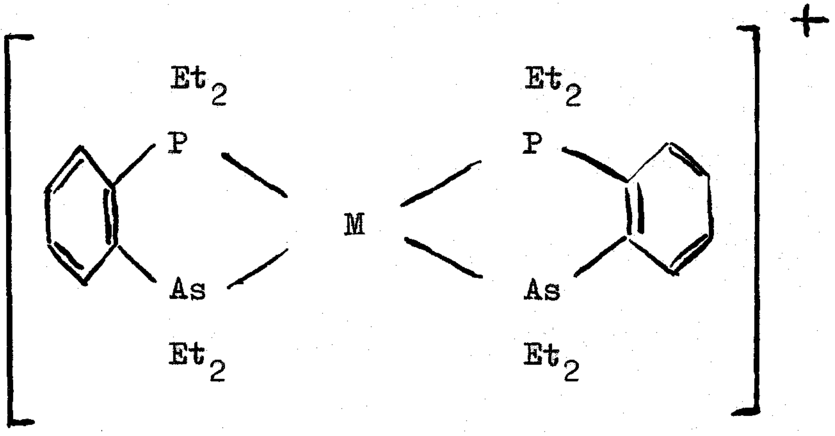
Mann, Purdie and Wells[9], examined the tetrameric tertiary phosphine (and arsine) complexes $[R_3P(As) - Cu(Ag)I]_4$ and the crystal structures of some of them have been investigated.[17] The copper and silver atoms are 4 co-valent being attached to one Group V donor atom and three iodine atoms. Gold(I) halides on the other hand form characteristic monomeric complexes R_3PAuX[9], many of which are low melting and can be purified by distillation under reduced pressure. Addition of halogens gives the corresponding gold(III) compound, R_3PAuX_3.

Some 3 covalent copper and silver iodide complexes have been isolated, e.g. $(Me_2NC_6H_4PMe_2)_2CuI$. The analagous gold complexes are ionized.[18]

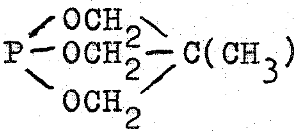
Cotton and Goodgame have recently described some triphenylphosphine complexes in which four phosphine-copper or silver bonds are present.[19] They are isolated as nitrates or perchlorates, e.g. $[Cu(PPh_3)_4]^+ ClO_4^-$. In the case of copper, attempts to isolate the corresponding nitrate yielded instead a bistriphenylphosphine complex $Cu(PPh_3)_2NO_3$, which is not a salt. The nitrate group is apparently involved in co-ordination to the copper atom, in either a monomer or a nitrate bridged dimer.

Various tertiary arsine complexes have been prepared. Copper(I) halides form complexes with one, two, three or four molecules of methyldiphenylarsine co-ordinated to the copper atom.[20] A 4 co-ordinate gold diarsine complex has also been described,[21] $[Au(diarsine)_2]^+I^-$.

Cochran, Hart and Mann[22] have prepared chelate complexes of all three metals which are stable salts.



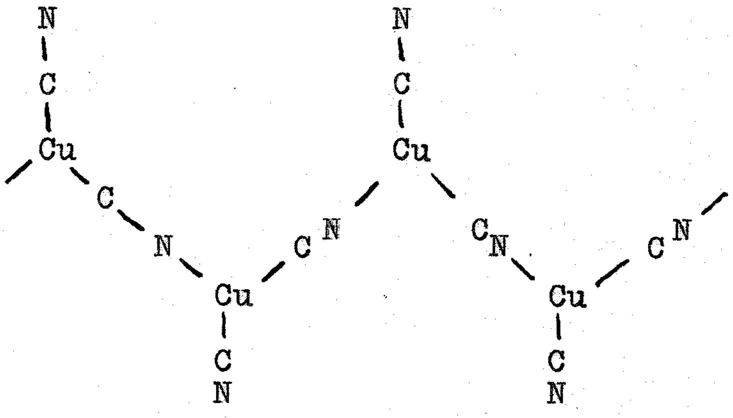
x-ray analysis shows a tetrahedral configuration of the ligands.

Tertiary phosphites also form complexes with group IB metals. The compounds $(Pr^{i}O)_3PMX$ (X = Cl, Br, I; M = Cu, Ag), are approximately trimeric in solution, and a bisphosphite complex $((PhO)_3P)_2CuX$ was found to be slightly less than monomeric.[23] The analagous gold complexes[24] $(RO)_3PAuX$ are monomeric as expected, and can be prepared from phosphorus trichloride-(trichloro)gold $AuCl_3.PCl_3$, by hydrolysis with an alcohol.[25] A~~g~~u$Cl_3.PCl_3$ itself is formed by the addition of phosphorus trichloride to an ethereal solution of gold(III) chloride. Verkade and Piper[26] have recently used the unusual ligand  $P\begin{matrix}\diagup OCH_2 \diagdown \\ - OCH_2 - \\ \diagdown OCH_2 \diagup\end{matrix}C(CH_3)$ (referred to as 'Phos', by the authors), to prepare some further examples of co-ordinatively saturated complexes. Thus gold gives the dimeric complex $[Au(Phos)_2Cl]_2$ and whereas Cotton[19] could only obtain two phosphine molecules in the co-ordination sphere in the case of the nitrate complex $Cu(PPh_3)_2$

NO_3, 'phos' affords the salt $[Cu(Phos)_4]NO_3$. This ligand has a low steric hindrance and although it is a weaker donor than trimethylphosphite,[26a] it is probably a better π acceptor.

Cyanide Complexes

The cyanide complexes of copper, silver and gold are well-defined and provide good examples of the characteristic co-ordination of the univalent metals. The salts $M[Cu(CN)_2]$, $M_2[Cu(CN)_3]$ and $M_3[Cu(CN)_4]$ have been isolated, and the main species in solution shown[27] to be $Cu(CN)_4^{3-}$. The structure of $KCu(CN)_2$ has been shown to contain spiral polymer chains $[Cu(CN)_2]^-_\infty$:



In the case of silver the $Ag(CN)_4^{3-}$ ion is unstable and only $M[Ag(CN)_2]$ and $M_2[Ag(CN)_3]$ have been isolated. The only gold complex is the linear $An(CN)_2^-$ ion which is more stable than its copper and silver analogues. $K[Ag(CN)_2]$ has also been shown[29] to contain linear ions $[NC-M-CN]^-$. With 2:2 bipyridyl $K[Au(CN)_2]$ forms a 4 covalent bipyridyl complex.[30]

Isocyanide Complexes

Isocyanide complexes have recently been reviewed by Malatesta.[31] The affinity of the group IB metals towards isocyanides increases with atomic number, though examples of the gold(I) complexes were the last to be prepared. The reaction between copper(I) cyanide and alkyl iodides was investigated by Guillemard[32] and later by Hartley.[33] Two series of complexes, with two and three molecules of isocyanide respectively are formed, e.g., $CuCN(CN\underline{p}\text{-tolyl})_3$ and $CuCN(CNR)_2$. Copper(I) chloride and p-tolylisocyanide form the complexes $CuCl(CN\ \underline{p}\text{-tolyl})n$ where n can range from 1 - 4. When n = 4 the compound is a uniunivalent electrolyte.

The reaction between silver cyanide and methyl iodide takes place in three stages:[35]

$$2AgCN + CH_3I \xrightarrow[\text{temperature}]{\text{room}} 2AgCN.CH_3I$$

$$2AgCN.CH_3I + CH_3I \xrightarrow{40^\circ} (AgCN.CH_3I)_2 + \cancel{CH_3I}$$

$$AgCN.CH_3I + AgCN \xrightarrow{100^\circ} AgCN(CNCH_3) + AgI$$

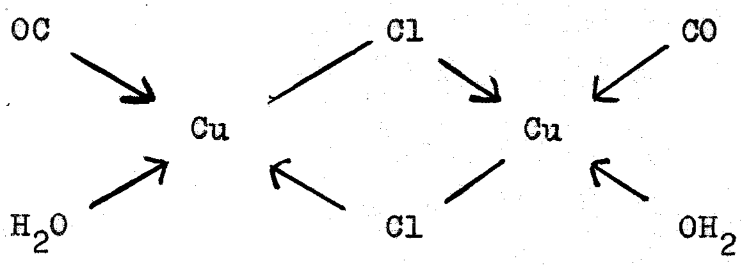
The alkyl isocyanide complexes are colourless and crystalline but the aryl analogues are rather unstable.[36] Klages and co-workers have recently prepared the salts $[Ag(CN\ \underline{p} - \text{tolyl})_4]X$, $(X = NO_3, ClO_4^-)$. The nitrate loses isocyanide in ether-chloroform solution to give a bisisocyanide complex $[Ag(CN\ \underline{p} - \text{tolyl})_2]NO_3$.

Several arylisocyanide derivatives of gold are known.[37] The reaction between excess isocyanide and chloroauric acid affords the co-ordinatively saturated gold(I) compound, $[Au(CNR)_4]Cl$, which although stable in the solid state is unstable in solution unless excess isocyanide is present. The corresponding complex with the tetraphenylborate ion $[B(C_6H_5)_4]^-$ is a stable uniunivalent electrolyte. Recrystallisation of tetrakisarylisocyanidegold(I) compounds from ethanol in the absence of excess isocyanide affords the corresponding bisisocyanide complexes $(RNC)_2AuX$ which are probably dimeric with halogen bridges.

Carbon Monoxide Complexes

Copper, silver, and gold do not appear to form stable carbonyls. A reported preparation[38] of $Cu(CO)_3$ was later withdrawn as the compound was later found to contain halogen. However small quantities of an unstable copper carbonyl were formed when chloride free carbon monoxide was passed over heated copper at 500°, since a copper mirror was deposited on a colder part of the tube.

Copper(I) halides form carbon monoxide complexes in the presence of water, or ammonia and various amines, e.g. aniline, pyridine.[40] The compound $CuCl.CO.H_2O$ can be isolated as colourless crystals which lose carbon monoxide in air. It appears to be dimeric:



The corresponding silver compound has not been isolated, though silver sulphate in fuming sulphuric acid, absorbs carbon monoxide at 0°C. and liberates it on warming.[41] Copper(I) salts prepared by the action of copper(I) oxide On ammonium salts in liquid ammonia,

$$Cu_2O + 2NH_4^+ + 2NH_3 \longrightarrow 2[Cu(NH_3)_2]^+ + H_2O$$

react with carbon monoxide in liquid ammonia, to yield unstable addition compounds $CuX.CO._xNH_3$.[42] Chloro(carbonyl)gold(I) was first prepared[43] from carbon monoxide and solid gold(I) chloride at -90°. It is more easily prepared[44] by bubbling carbon monoxide through a solution of gold(III) chloride in tetrachlorethylene at 100 - 140°.

$$AuCl_3 \xrightarrow{CO} AuCl + COCl_2 \xrightarrow{CO} ClAuCO$$

It crystallises from petroleum as colourless plates and is monomeric in benzene. It is decomposed by water and alcohols. The $C\vdots O$ stretching frequency 2152 $cm.^{-1}$ is one of the highest recorded for metal carbonyls, suggesting that $\underline{d}\pi - \underline{\pi}g$ bonding between gold and the carbonyl group is relatively weak.[45]

Alkyls and Aryls

Group IB alkyls and aryls are unstable, the aryls being slightly more stable than the alkyls.

Copper

Methylcopper can be prepared as an unstable yellow solid by the reaction between copper(I) iodide and methyl-lithium at -15°. It decomposes in boiling ether with the formation of copper methane and ethane. In the presence of excess methyl-lithium (1 mole), it dissolves to an almost colourless solution which probably contains the salt $Li^{+}[CuMe_2]^{-}$.[46] Methylcopper has also been prepared from copper(II) nitrate and tetramethyl-lead and can also be detected in the reaction between methyl-chloride and copper at 350°. At 250°, its half life is 0.002 seconds.[47]

Ethylcopper[48] is less stable, and a solution in ether decomposes above -50°. The kinetics of the decomposition of methyl and ethyl copper have been studied.[49]

Phenylcopper separates as a greyish brown powder when copper(I) iodide is added to phenyl-lithium. It decomposes at 80° to copper and diphenyl. It is insoluble in most organic solvents but dissolves in pyridine and benzonitrile, and is hydrolysed by water to benzene and copper(I) oxide. Phenylcopper undergoes 1:4 addition to the conjugated system C:C.C:O, in contrast to the 1:2 addition of phenyl-lithium. The action of copper powder on diazonium borofluorides at 80° has been reported to yield phenyl, p-tolyl, and o-and p-nitrophenylcopper, though they were isolated only in the form of alleged pyridine complexes, $ArCupy_4$[50].

Triethylphosphinecyclopentadienylcopper,[51] $C_5H_5CuPEt_3$

This phosphine - stabilized compound is obtained from the reaction between cyclopentadiene, copper(I) oxide and triethylphosphine. It is the most stable organocopper compound, other than some of the ethynyl complexes, decomposing slowly in air. It is stable to water, but hydrolysed by dilute acids to cyclopentadiene. With iron(II) chloride in tetrahydrofuran it gives ferrocene and it seems to be a sigma bonded cyclopentadienyl complex.

Silver

Methylsilver is precipitated[52] when alcoholic silver nitrate is added to alcoholic tetramethyllead at -10° to -60°.

$$AgNO_3 + Me_4Pb \quad = \quad Me_3PbNO_3 + MeAg$$

It decomposes by the formation of ethyl radicals[49]. A more recent study shows the precipitated material to have the composition $(MeAg)_2AgNO_3$, but with a deficiency of silver nitrate the product is methylsilver.

Isobutenylsilver is obtained from isobutenyltriethyllead and ethanolic silver nitrate, as an orange solid which affords[53] isobutenyl radicals on decomposition above 30°. Similar reactions between Et_3PbR where R is an aryl or alkyl radical afforded RAg though the latter was usually unstable. Its stability is apparently determined by that of the free radical R· the stability of the silver compound increasing as the stability of R decreases. Thus phenylsilver is relatively stable but benzylsilver is only stable below -100°.

Impure phenylsilver has been isolated as a grey powder by addition of silver chloride or silver bromide to phenyl magnesium bromide at low temperatures. It decomposes at -18° to silver and diphenyl, is explosive when dry; and is insoluble in most organic solvents.[48,54]

The action of alcoholic silver nitrate on ethyltriphenyllead, ethyltriphenyltin or triphenylbismuth affords a double compound $(PhAg)_2AgNO_3$ which slowly decomposes at room temperature.[55]

Attempts to isolate phosphine stabilized silver alkyls and aryls by the reaction between a phosphine silver halide complex with a Grignard or organo-lithium reagent have been unsuccessful.[56]

Gold

Gold(I) alkyls or aryls have not been isolated. Evidence for an intermediate gold(I) aryl was obtained by Kharasch and Isbell[44] who showed that an ethereal solution of chloro(carbonyl)-

gold(I) reacts with a Grignard reagent according to the equation:

$$2RMgBr + 2ClAuCO \quad = \quad 2Au + R_2 + 2MgClBr + 2CO$$

the more electronegative the radical R, the slower is the formation of gold.

The only organogold(I) complexes prepared before those described in this thesis, were the co-ordination stabilized complexes of the type R_3PAuR' (R = Et, Ph; R' = Me, Et, Ph, $PhC\vdots C\cdot$, mesityl).[57] They are isolated as crystalline solids (or occasionally as oils) from the reaction between the phosphine gold halide R_3PAuX and the appropriate organo-lithium reagent. They are monomeric in benzene, with dipole moments between 5.5 and 6.5 D.

Gold(III) alkyls and their co-ordination compounds with donors of the oxygen and nitrogen type, have been reviewed.[58,59]

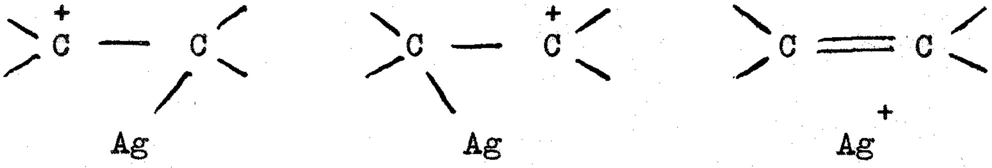
Ethylene complexes

The stability of the ethylene complexes of group IB metals decreases in the series Cu > Ag > Au, and in fact no ethylene complexes of gold are known.

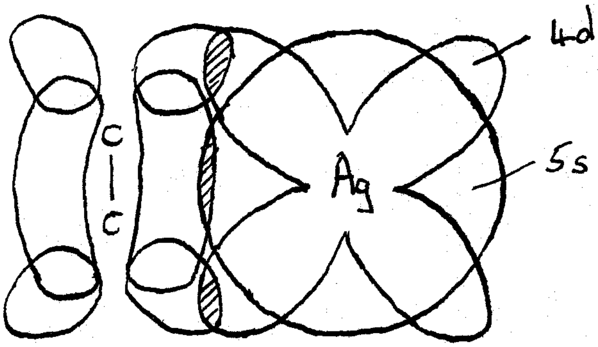
Copper(I) chloride[60] absorbs ethylene under pressure and the compound C_2H_4CuCl has been isolated[61]. Reaction between butadiene and copper(I) halides affords the pale yellow complex C_4H_6CuX (X = Cl, Br), which can be stored at -78° for several days but decomposes at room temperature or on exposure to air.[62] Studies on the chemistry of copper[63] and silver[64] - olefin complexes in solution have shown that only 1:1 complexes are formed.

Cyclo-octa 1:3 diene and 1:4 diene form unstable addition compounds with silver nitrate, $C_8H_{12}(AgNO_3)_2$. The chelating 1:5 diene gives a more stable 1:1 complex $C_8H_{12}AgNO_3$, m.p., 135-136.[65]

H. J. Lucas and co-workers suggested that the structure of silver-olefin complexes can be represented as a resonance hybrid of the forms:[66]



The bonding has more recently[67] been regarded as similar to that in palladium and platinum[68] complexes. The silver 5*s* orbital interacts with the olefin πu bonding orbital and back co-ordination occurs from the silver *d* or hybridised *dp* orbital to the olefin $\overset{*}{\pi} g$ antibonding orbital.



Several complexes between silver perchlorate and olefins are described[69] and are generally of the type $(\text{olefin})_2\ AgClO_4$. Many are explosive, and are decomposed by water.

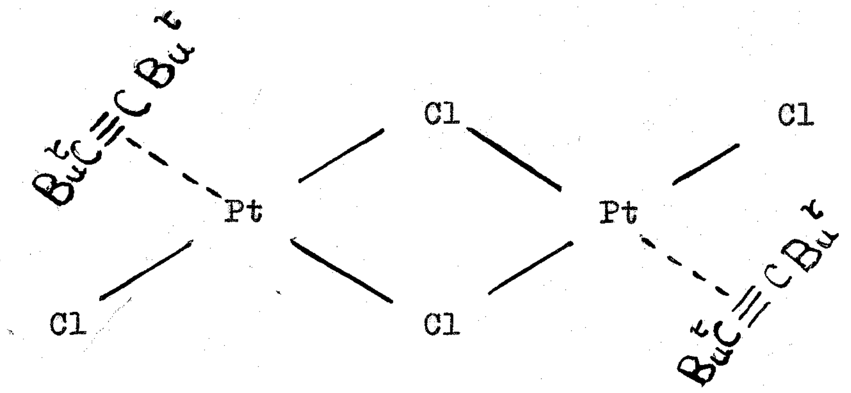
TRANSITION METAL ETHYNYL COMPLEXES

Reactions of ethynylic molecules with transition metal complexes have provided complexes in which various types of acetylene-metal bonding occur. Many reactions have recently been studied between metal carbonyls and various acetylenes[70] and a range of rather unusual molecular configurations have resulted. They are not considered here since group IB carbonyl complexes are so few and unstable.

The most common type of ethynyl complexes are those in which there is sigma bonding between the ethynyl group and the metal and also substantial back co-ordination between the occupied metal d orbitals and the acetylene unoccupied antibonding orbitals. Firstly other types of ethynyl complexes will be considered.

'Olefin-type' complexes with disubstituted acetylenes

Ditertiary butyl acetylene reacts with sodium tetrachloroplatinate(II) in ethanol to give the fairly stable compound:



A series of disubstituted acetylene complexes of this type[71] have been prepared but to obtain compounds sufficiently stable to be isolated it seems that there must be at least one tertiary carbon atom adjacent to the triple bond. The acetylene stretching frequency in these complexes is lowered by about 200 $cm.^{-1}$ (in comparison with 150 $cm.^{-1}$ in the corresponding olefin complexes) with which the bonding seems to be similar.

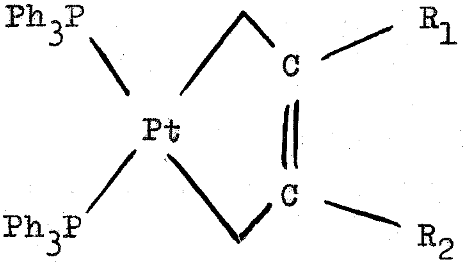
The copper complex MeC⋮CMe,CuCl, which is formed between but-2-yne, and copper(I) chloride has been studied crystographically.[72] The copper atom lies on the perpendicular bisector of the triple bond. The corresponding silver nitrate complexes with but-2-yne and pent-2-yne have also been isolated[73] but are unstable.

<u>Complexes with an acetylene acting as a bidentate ligand</u>

A series of stable ethynyl complexes have been prepared by reducing *cis*-bistriphenylphosphine(dichloro)platinum(II) with hydrazine in the presence of both mono- and di-substituted acetylenes.[74]

$$\underline{cis}(PPh_3)_2PtCl_2 + N_2H_4 + 2C_2R.R' = 2(Ph_3P)_2PtC_2RR' + N_2 + 4HCl$$

The stability of these complexes increases with the electron attracting power of the acetylene, and di*para*nitrophenylacetylene will replace *o*-phenylene*bis*dimethylarsine from its complex $Pt(PPh_3)_2C_6H_4(AsMe_2)_2$. The structure of these complexes can be formulated:



This is concluded from x-ray studies of the di*p*-bromophenylacetylene complex which suggests a *dsp*^{2} square planar configuration of the platinum, and from the I.R. absorption band at 1700 cm.$^{-1}$ which is consistent with an olefinic rather than an acetylenic stretching frequency. The large dipole moments of the compounds in which R_1 and R_2 are both *para*substituted phenylgroups are further evidence that the aryl groups are not co-linear.

Complexes with σ-bonding between the metal and the acetylene

Sigma bonded ethynyl groups are present in some compounds of nickel, palladium and platinum of the type[75] $(R_3P)_2M(C\vdots CR')_2$ (M = Ni, Pd, Pt, R = H, Me, Ph). Their marked stability is attributed to interaction between the metal d_{xy} orbital and the acetylene antibonding π-orbitals giving the metal carbon bonds appreciable double bond character. Addition of diethylphenylphosphine to the complex with this phosphine gives the 5 co-ordinate complex $(PhEt_2P)_3Ni(C{:}CPh)_2$ which is probably monomeric.

Nast and his colleagues have prepared complex anionic ethynyl derivatives of copper[76,77], chromium[78], manganese[79], iron[80], cobalt[81] and nickel[82] by the reaction in liquid ammonia between an alkali metal acetylide and the soluble thiocyanate or nitrate of the transition metal. For example Iron(II) and cobalt(II) form two series of complexes $M_2[Fe(C{:}CR)_6]$ and $M_3[Fe(C{:}CR)_6]$ ($R = H, Me; M = K, Na$), chromium(III) forms an explosive complex $K_3[Cr(C{:}CH)_6]$. They are generally similar to the iso-electronic cyanide complexes except that they are less thermally and hydrolytically stable. Nickel(II) salts analogous to $Ni(CN)_4{}^{2-}$ are those of the type $M_2[Ni(C{:}CR)_4]$ ($R = H, Me, Ph$), the phenylethynylcomplexes being the most stable. Various other nickel complexes have been prepared including a binuclear complex $K_6[Ni_2(C{:}CR)_8]$ Electron flow from the *d* orbitals of the transition metal to the πg antibonding orbitals of the ethynyl groups will oppose the charge transfer to the nickel atom due to the sigma carbon to metal bond, and so decreases the charge on the metal atom and increases the metal carbon order.

Copper(I) and silver(I) ethynyl complexes

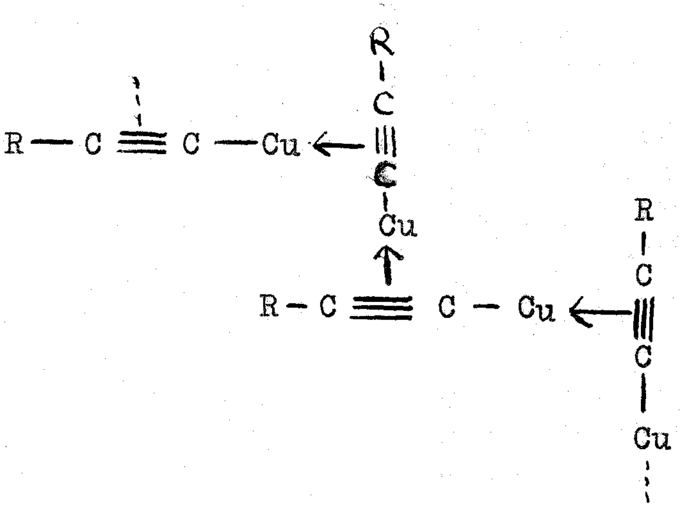
Several anionic ethynyl complexes of copper have been isolated by reactions in liquid ammonia, similar to those described above. Copper(I) iodide and propynyl- or phenylethynylsodium afford salts of the type $M_2[Cu(C\vdots CR)_3]$ and $M[Cu(C\vdots CR)_2]$ (M = Na, K; R = Me, Ph)[76]. These anions are comparable with the $[Cu(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ ions, but no analogue of $[Cu(CN)_4]^{3-}$ has been reported. The reaction between $KC\vdots CH$ and copper(I) iodide at -78° in liquid ammonia gives the orange coloured copper derivative, $CuC\vdots CH$.[77] Above -45° it decomposes into a black crystalline copper acetylide. The anionic complexes are not explosive or pyropheric, but are suseptible to hydrolysis by water or acids:

$$[Cu(C\vdots CR)_3]^{2-} + 2H_2O \longrightarrow CuC\vdots CR + 2RC\vdots CH + 2OH'$$

$$[Cu(C\vdots CR)_3]^{2-} + 3HCl \longrightarrow CuCl_3'' + 3RC\vdots CH$$

Conductivity measurements in nitrobenzene show them to be moderately strong electrolytes. Some will crystallise from ammonia as ammines, e.g. $Na[Cu(C\vdots CPh)_2]2NH_3$ which are only stable at room temperature in an atmosphere of ammonia.

Copper(I) and silver(I) carbide and the acetylides $RC\vdots CCu(Ag)$ were familiar compounds in the last century but their structures are still unknown. All the copper derivatives are obtained as bright yellow or red powders, generally insoluble in all solvents with which they do not react, and are apparently polymeric. An interpretation of their structure has been suggested[1] in which the metal atom forms two sigma sp hybrid bonds, an acetylene group acting as a donor to provide an extra electron.



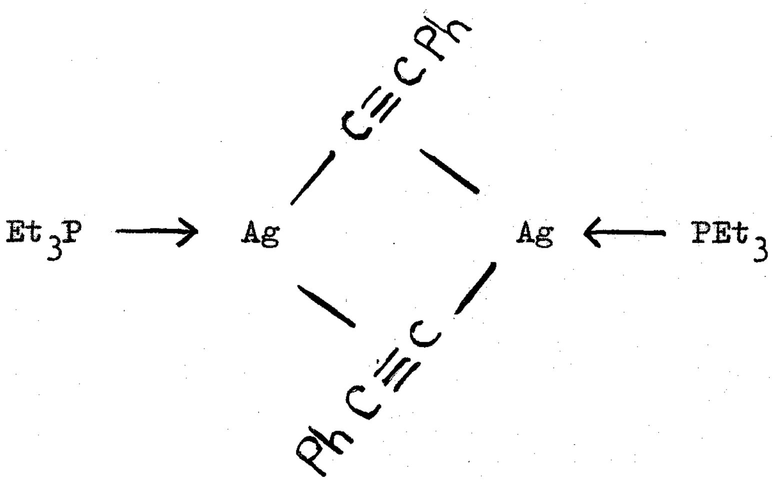
Back co-ordination is expected from the filled metal d orbitals to the π_g antibonding orbitals of at least two acetylene groups. Additional bonding between layers should be possible if the polymer chains are arranged so that acetylene groups lie above and below the copper atoms. The corresponding colourless silver derivatives presumably could have a similar structure. In many cases where R is an alkyl group the silver compounds are moderately soluble in several organic solvents, in particular in chloroform, carbon tetrachloride and acetone.[83] R. Vestin and E. Ralf[84] have reviewed the earlier silver acetylide chemistry.

A few silver complexes with disubstituted acetylenes are known[69,85]. Silver nitrate forms a crystalline complex with diethylacetylene, $C_6H_{10}AgNO_3$ and silver perchlorate is soluble in diethyl and methylethylacetylene, the solid complexes $C_5H_8(AgClO_4)_3$ and $C_6H_{10}(AgClO_4)_3$ having been isolated. A 5% solution of silver nitrate in 95% ethanol gives a quantitative precipitate of even traces of 1-alkynes as the silver acetylide-silver nitrate complex $RC{\vdots}CAg, AgNO_3$. Treatment with aqueous sodium cyanide regenerates the acetylene.[86] The insolubility of the copper acetylides has long been used to detect and purify monoacetylenes. Both the copper and silver compounds readily yield the acetylene with dilute mineral acids or sodium cyanide solution[87].

Copper(I) ethynyl complexes, $RC{\vdots}CCu$, are oxidised to diacetylenes $RC{\vdots}C{\cdot}C{\vdots}CR$ in aqueous copper(I) chloride - ammonium chloride solution. This coupling reaction is also catalysed by copper(II) chloride, hydrogen peroxide and potassium ferricyanide.[88] The oxidation is best carried out in the presence of a base[89]. The copper catalysed reaction of mono-substituted acetylenes in aqueous pyridine has been studied kinectically which suggests the formation of intermediate ethynyl anions.[90]

Phenylethynylcopper(I) forms a colourless unstable ammine $PhC{\vdots}CCuNH_3$ which loses ammonia readily in air or in a stream of nitrogen[76]. It is sparingly soluble in liquid ammonia but dissolves as a soluble adduct with carbon monoxide which is too unstable to isolate.[42] An isocyanide complex $PhC{\vdots}CCu$-

(p-tolyl NC)$_3$ has been isolated[34] as white crystals which decompose above 100°. The first co-ordination compound with phosphorus as a donor was prepared by G. Calvin[91] and G. E. Coates of this department who obtained PhC⋮CCuPEt$_3$ as yellow needles, soluble in hexane and many organic solvents. Subsequent work[1,92] showed the donor strength of group V elements to R·C⋮CCu to be in the order N ≪ P ≫ As and that arylethynyl complexes are stabler than alkynyl complexes. Thus propynylcopper was found to be unaffected by a variety of amines and to form a weak complex with triethylphosphine, which decomposed immediately in air, whereas phenylethynylcopper dissolves in pipendine and isopropylamine and the triethylphosphine complex decomposed only slowly. The latter complex was found to be dimeric in nitrobenzene and slightly more associated in benzene. The analogous silver complex PhC⋮CAgPEt$_3$ was found to be similarly associated in solution and the structure



was suggested.

Phenylethynylsilver(I) in contrast to methylethynylsilver dissolves in various amines and an unstable isopropylamine complex which loses amine on exposure to air, and a slightly more stable triethylarsine complex were isolated. It appears that the silver complexes are slightly more stable than their copper analogues.

A more comprehensive further study of ethynylcopper complexes has been carried out (and is now described) with a view to (a) obtaining more extensive molecular weight data on various ethynylcomplexes, (b) finding out whether more than one molecule of tertiary phosphine would co-ordinate to each copper atom, (c) investigating the infra-red absorption frequencies of the ethynyl groups in these compounds.

Gold(I) ethynyl complexes

Gold(I) acetylide, Au_2C_2, was known sixty years ago, having been obtained as an explosive powder.[93] It is surprising that no other gold acetylides have previously been described.

The only gold ethynyl complex reported[57] is $PhC{\vdots}CAuPEt_3$ prepared in a series of experiments mentioned earlier. It is monomeric, in contrast to the analogous silver and copper compounds, gold(I) showing its characteristic tendency not to raise its co-ordination number above two.

EXPERIMENTAL

CHAPTER I

PREPARATION AND PURIFICATION OF REAGENTS

The attempted preparation of trialkylphosphines from trialkylaluminiums

The reaction

$$AlR_3 + PCl_3 \longrightarrow RPCl_2 + R_2PCl + R_3P$$

has been reported[94] to give alkyldichlorphosphines in satisfactory yields, and using excess triethylaluminium a 30% yield of triethylphosphine has been obtained.

Attempts were made to prepare trimethyl and triethylphosphine using aphosphite instead of phosphorus trichloride. A reaction of this type, if successful, would obviate the use of large amounts of ether necessary in Grignard or alkyl lithium methods of preparing tertiary phosphines. Unfortunately the most successful reactions afforded no more than a 9% yield of trimethyl or triethylphosphine. One of these is described.

Since this work was carried out, M. Sander[95] has shown that on heating the adduct formed between an alkyl phosphite and a trialkylaluminium, the phosphite rearranges to a phosphonate (in 70% yield), in a similar way to the Arbuzov reaction.

Preparation of trimethylaluminium[96,97]

$$6MeI + 4Al = Me_4Al_2I_2 + Me_2Al_2I_4$$

$$3Me_4Al_2I_2 + 6Na = 6NaI + 2Al + Me_6Al_2$$

Aluminium turnings (80g., 3 mole) were added to dimethylaluminium iodide (60g.) from a previous reaction, followed by methyl iodide (568g., 249 cc., 4 mole) over 3 hours, the reaction being kept at 80° with an oil-bath. The mixture was then fractionated, using an electrically heated and well-lagged glass helices column, 50 cm. long, and a take-off head. The fraction boiling 62-63°/75-76 mm., pure trimethylaluminium (20 cc.) which froze in the receiver, and a second fraction 110°/50 mm., mostly dimethylaluminium iodide (297g.) were collected.

The dimethylaluminium iodide was transferred to a dropping funnel and cautiously added, with stirring, to excess sodium (56g.) keeping the reaction at 130° with an oil-bath. An unbreakable mass was obtained, which on distillation gave trimethylaluminium (58g., 0.805 mole, 40%), b.p. 126°.

Attempted preparation of trimethylphosphine

Trimethylaluminium (40g., 53 cc., 0.55 mole) in methylcyclohexane (100 cc.) and triphenylphosphite (redistilled, b.p. 178-180°/$<$ 0.5 mm) (171g., 140.5 cc., 0.55 mole) in methylcyclohexane (260 cc.) were added dropwise with stirring

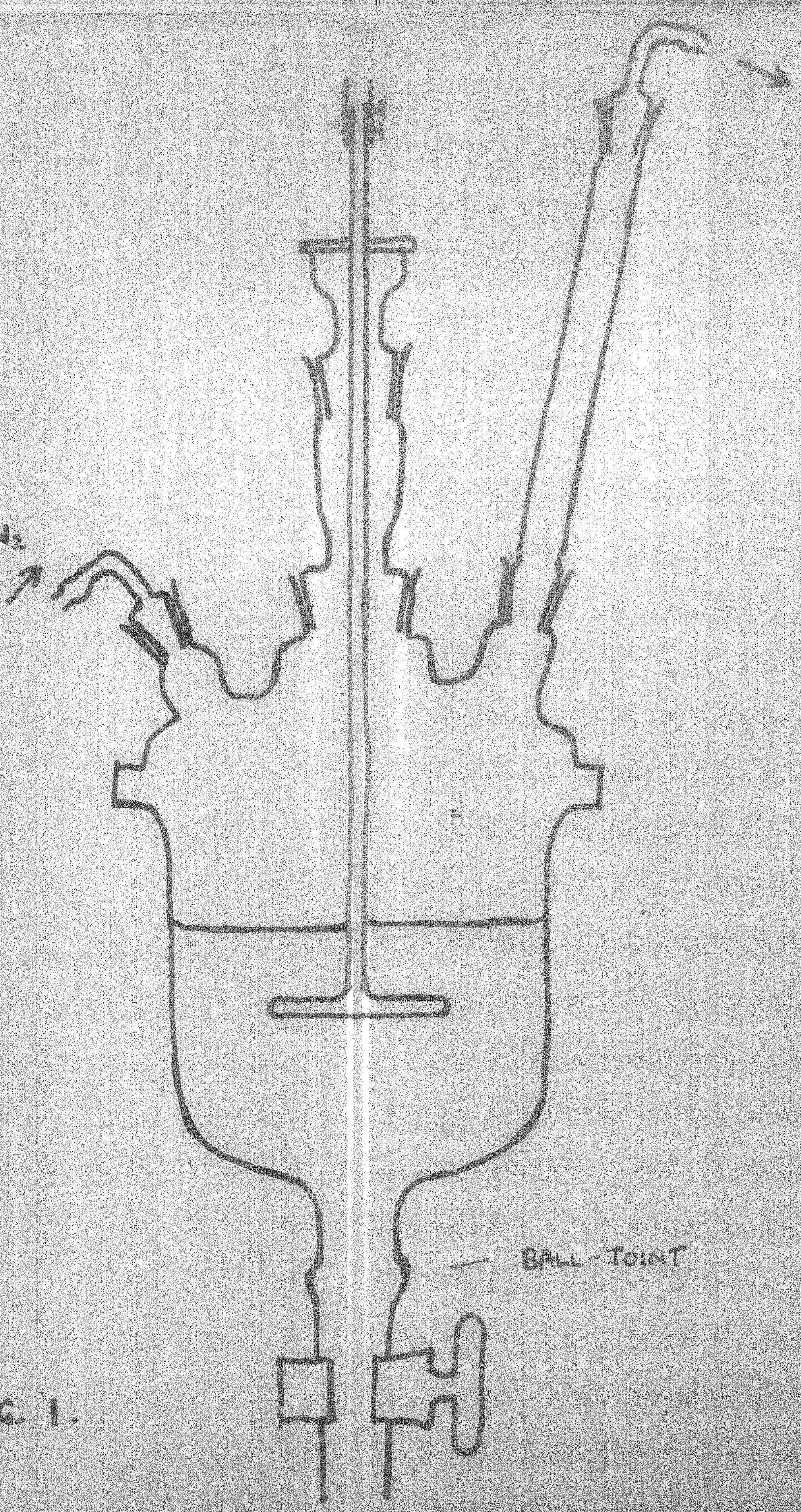


FIG. 1.

into a 1 litre 3 necked flask containing methylcyclohexane (30 cc.). The flask was connected to a trap cooled to -78°. A slightly exothermic reaction warmed the flask to 60°, and the solution turned cloudy. Attempts to distil out any phosphine were unsuccessful. After cautious hydrolysis with caustic sodasolution, the mixture was steam distilled, and the organic layer treated with silver iodide in aqueous conc. potassium iodide. The silver iodide complex obtained (15g.) corresponded to a 9% yield of trimethylphosphine.

Preparation of trimethylphosphine from methyl-lithium

$$2Li + CH_3Cl = LiCl + MeLi$$

$$3MeLi + PCl_3 = Me_3P + 3LiCl$$

$$4Me_3P + 4AgI = [Me_3P\ AgI]_4$$

(a) Preparation of the silver iodide complex

Lithium shot (70g., 10 mole) was prepared in the apparatus shown (Fig.1.). The petroleum oil (b.p. 210/230) was heated to boiling and the lithium then stirred vigorously with the 'vibromixer' stirrer. The shot was washed through the wide-bore tap with ether (1200 cc.) into a 5 litre 3 necked flask. Methylchloride was passed through the solution cooled to -5°, the required amount being measured with a previously calibrated flowmeter. The methyl-lithium (4 mole) solution was transferred to two 1 litre dropping funnels and added to phosphorus(III) chloride (173.5g., 110 cc., 1.26 mole) in ether (500 cc.), at -78°C, allowing 5% excess methyl-lithium. After hydrolysis with deoxygenated water, the organic layer was separated and added with good stirring to silver iodide in concentrated potassium iodide solution. The precipitated silver iodide complex[98] was filtered, washed with conc. potassium iodide solution and methanol and dried in vacuo. Yield 224g., 0.72 mole, 57%, m.p. dec.> 100°.

(b) Decomposition of the silver iodide complex

Tetrakistrimethylphosphineiodosilver(I) (224g.) was placed in a long-necked flask surrounded by an air-bath. A sintered disc was placed between the flask and a cold trap which in turn was connected to a vacuum line with ampoules for collecting and storing the phosphine. After obtaining a good vacuum, the air bath was heated to 200°, and the phosphine collected in the ampoules cooled to -78°. Yield of trimethylphosphine 45g., 82%. The unchanged complex was recovered and added to that for further decompositions.

In more recent preparations by Mr. R. Coult of this department, the trimethylphosphine has been isolated and stored in 4N sulphuric acid as its air-insensitive salt $Me_3HP^+ HSO_4^-$. The phosphine was released as required, by addition of caustic soda solution, into an organic solvent which was convenient for the reaction being studied. The phosphine solution is dried over magnesium sulphate, and standardised by weighing the meth-iodide formed from a known aliquot.

Preparation of triethylphosphite[99]

$$3EtOH + PCl_3 + PhNEt_2 = 3PhNEt_2HCl + (EtO)_3P$$

To pure dry ethyl alcohol (143.5g., 182 cc., 3.1 mole) and diethyla~~m~~niline (445g., 482 cc., 3.05 mole; redistilled 215-216°) in dry pentane (2 litres), phosphorus(III) chloride (137.4g., 88.6 cc., 1 mole) was added, over 1 hour, with good stirring at 10-15°. The white precipitate was filtered in air, and the filtrate gave, on distillation, triethylphosphite (129g., 82.4%, b.p. 155-160°).

Preparation of triethylstibine

Antimony(III) chloride (79.5g., 0.348 mole; redistilled b.p. 158-159°) in ether (250 cc.) was added to ethylmagnesium-bromide (from magnesium 38g.) in ether (500 cc.) at -20°. After most of the antimony(III) chloride had been added, a black colour (finely divided antimony) developed. At this point it would probably have been advantageous to stop, instead of adding the remainder. Hydrolysis with oxygen-free ammonium chloride solution, and separation of the ether layer which was dried and finally distilled gave triethylstibine (40g., 0.192 mole, 58%, b.p. 161-162°).

Preparation of prop-1-yne(methylacetylene) and its copper and silver derivatives.

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$

$$CH_3CHBr{\cdot}CH_2Br + 3NaNH_2 = CH_3C{\vdots}CNa + 2NaBr + 3NH_3$$

$$CH_3C{\vdots}CNa + H_2O = CH_3C{\vdots}CH + NaOH$$

Methylacetylene released by hydrolysis of propynyl sodium was passed directly into ammoniacal copper(I)chloride or silver nitrate to isolate the required copper(I) and silver(I) derivatives.[100]

A 2 litre 3 necked flask was filled with liquid ammonia (1200 cc.) and cooled to -40°. Sodium was catalytically decomposed to sodamide[101] by adding powdered hydrated iron(III) nitrate (c. 1g.) to the liquid ammonia followed by sodium (2g.). The deep blue colour was replaced by the black colour of finely divided iron. Sodium (76g., 3.3 mole) was added in 10g. quantities allowing time for it to react before adding further portions. When no further blue colour remained, 1,2-dibromopropane (202g., 1 mole) was added cautiously to the fine grey suspension of sodamide, a vigorous reaction ensueing. The mixture was stirred for a further hour and the ammonia allowed to evaporate. Two preparations were carried out to this stage.

In the first preparation, the methylacetylene which was now liberated by addition of brine (1000 cc.) was bubbled into ammoniacal copper(I)chloride solution (copper(I)chloride (80g., 0.8 mole) was suspended in water (500 cc.) and ammonia added till the solid dissolved). This solution was stirred well, a carbon dioxide reflux condenser being attached to the exit neck of the flask to condense any unreacted methylacetylene. When addition of brine was complete the contents of the reaction flask were heated to drive over any methylacetylene that remained. The yellow precipitated propynylcopper was filtered off, washed with ammonia (4N), ammoniacal ethanol, acetone and ether and dried in vacuo. Yield 50g., 0.485 mole, 48.5%. The relatively low yield was due to loss of some material during the vigorous reaction which took place on addition of the 1,2-dibromopropane.

In the second preparation, the methylacetylene was bubbled through ammoniacal silver nitrate (from silver nitrate 153g., 0.9 mole) which afforded after filtration, washing with water, ethanol, acetone and ether and drying, propynylsilver 112.5g., 76%.

Preparation of 3:3 dimethyl-1-butyne (t-butylacetylene)

$$(CH_3)_3C\cdot CCl_2CH_3 + 3NaNH_2 = (CH_3)_3C\cdot C\vdots CNa + 2NaCl + NH_3$$

$$(CH_3)_3C\cdot C\vdots CNa + H_2O = (CH_3)_3C\cdot C\vdots CH + NaOH$$

2,2-dichloro3,3-dimethylbutane was dissolved in toluene and dried by adding anhydrous magnesium sulphate. The solution was filtered. Sodium (76g., 3.3 mole) was converted to sodamide using ferric nitrate as described above.

2,2-dichloro3,3-dimethylbutane (143g., 1 mole) in toluene (250 cc.) was added over 1½ hours with stirring, and the ammonia was then allowed to evaporate overnight. The residue was hydrolysed with brine (500 cc.) followed by water (500 cc.) the volatile products being passed through, (a) an empty 2 litre flask as safety trap, (b) a 2 litre flask containing water and phenolphthalein, to which hydrochloric acid was added from a dropping funnel to neutralise the ammonia, (c) a calcium chloride drying tower, (d) two traps cooled to -78° to condense the t-butylacetylene. The liquid which had collected in the empty flask and on the surface of the water was separated, dried over magnesium sulphate, andcombined with that from the traps and the trap washings with dry toluene. The whole was distilled up a short helices column. The fraction b.p. 37.2-38°, t-butylacetylene, was collected. Yield 40.7g., 0.495 mole, 49.5%.

Preparation of p-bromophenylacetylene

1. $C_6H_5Br + (CH_3CO)_2O \xrightarrow{AlCl_3} BrC_6H_4COCH_3$
2. $BrC_6H_4COCH_3 + PCl_5 \longrightarrow BrC_6H_4CCl_2CH_3 + POCl_3$
3. $BrC_6H_4CCl_2CH_3 + 2KOH \longrightarrow BrC_6H_4C\vdots CH + 2KCl + 2H_2O$

1. Preparation of p-bromacetophenone[102]

Bromobenzene (157g., 105 cc., 1 mole) was added to aluminium(III)chloride (294g., 2.2 mole) in carbon disulphide (500 cc.). Acetic anhydride (102.1g., 94.4 cc., 1 mole) was added with good stirring, and the contents of the flask refluxed for 30 minutes. The mixture was poured on to ice-water, extracted with ether, and the ether layer dried over magnesium sulphate and distilled. Two fractions were collected: (a) 36.7g., 60-114°/7 mm., (b) 136.7g., 114-116°/ 6.75 mm., p-bromacetophenone, m.p. 48-50°, 69%.

2. Preparation of p-bromophenyl2,2-dichlorethane[103]

Parabromacetophenone (130g., 0.65 mole) and phosphorus(V) chloride (146g., 0.70 mole) were mixed in a 500 cc. 3 necked flask. On warming, when the mixture melted a vigorous reaction took place which was complete in 15 minutes. Distillation gave two fractions: (a) 45-55°/18 mm., mostly phosphorus oxychloride, (b) 128-134°/18 mm., p-bromphenyl-2:2dichlorethane, 117.6g., 0.47 mole, 72%.

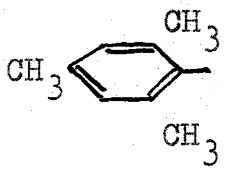
3. Preparation of p-bromphenylacetylene[103]

Parabromphenyl2,2-dichlorethane (115g., 0.46 mole) was added to ethanolic potassium hydroxide (129g., in 610 cc. ethanol, 25% solution) and refluxed for three hours. The resulting liquid was poured on to ice, and the oil produced was separated. The aqueous ethanolic layer was extracted with ether, and the extracts combined with the oil and dried over potassium hydroxide. Removal of the ether and distillation afforded p-bromophenylacetylene (22g., 0.12 mole, 26%), which was recrystallised from methylated spirits, m.p. 59-61° (literature gives[9] m.p. 64-65°).

Preparation of mesitylacetylene

1. $MesH + (CH_3CO)_2O \xrightarrow{AlCl_3} MesCOCH_3$
2. $MesCOCH_3 + PCl_5 \longrightarrow MesCCl{:}CH_2$
3. $MesCCl{:}CH_2 + NaNH_2 \longrightarrow MesC\vdots CH + NaCl + NH_3$

Mes =



1. Preparation of 2,4,6-trimethylacetophenone[102]

Mesitylene (51.1g., 47.5 cc., 0.50 mole) was added to aluminium(III)chloride (147g., 1.1 mole) in carbon disulphide (200 cc.). Acetic anhydride (51.05g., 47.2 cc., 0.50 mole) was added with good stirring. The mixture was refluxed for 30 minutes, poured on to ice, extracted with ether and the ether layer dried. Removal of the ether and distillation afforded 2,4,6-trimethylacetophenone, 66.4g., b.p. 86-87°/2.75 mm., 82%.

2. Preparation of 2,4,6-trimethylachlorostyrene[104]

2:4:6 trimethylacetophenone (60g., 0.37 mole) was added to phosphorus(V)chloride (90g., 0.43 mole) in a 500 cc. 3 necked flask. The mixture was heated on a boiling water bath for 4 hours, and then poured on to ice. The dark green oily layer was separated, neutralised with 10% caustic soda, and combined with the ether extracts of the neutralised aqueous layer. The ethereal solution was dried over magnesium sulphate and distilled. Two fractions were collected: (a) 124-130°/25 mm. 2,4,6-trimethyl*α*chlorostyrene, 43.1g., 0.239 mole, 65%; (b) 132-136°/12 mm., 5.4g., - probably the dichlorocompound.

3. Preparation of mesitylacetylene[104]

2,4,6-trimethyl*α*chlorostyrene (42g., 0.233 mole) was added to a suspension of sodamide (11g., 0.275 mole) in petroleum oil (fraction 210-240°) and the mixture heated, with an oil-bath at 150° for 3 hours. After cooling, it was poured on to ice, acidified with dilute hydrochloric acid and extracted with ether. The ether layer was dried over magnesium sulphate. After removal of the oil, distillation afforded two fractions: (a) 85-110°/23 mm. (c. 60 cc.), petroleum oil and mesitylacetylene which could not easily be fractionated, (b) 110-114°/23 mm., (c. 50 cc.), almost entirely petroleum oil. The mesitylacetylene was therefore used as a solution in petroleum oil to prepare the required copper(I), silver(I) and mercury(II) derivatives in the usual way (see page 63). By preparing mesitylethynylcopper from a known aliquot of the petroleum solution the yield of mesitylacetylene was calculated to be

14.4g., 0.076 mole, 33%.

Further reactions should be carried out in a higher boiling oil, e.g. heavy white oil.

Preparation of 1-phenylbutadiyne

$$\mathrm{PhCH{:}CHCHO} \xrightarrow[\text{2. } \mathrm{KHSO_4}]{\text{1. } \mathrm{MeMgBr}} \mathrm{PhCH{:}CH{\cdot}CH{:}CH_2}$$

$$\mathrm{PhCH{:}CH{\cdot}CH{:}CH_2} \xrightarrow[\text{4. } \mathrm{NaNH_2}]{\text{3. } \mathrm{Br_2}} \mathrm{PhC{:}C{\cdot}C{:}CH}_{\cancel{2}}$$

1. + 2. Preparation of phenylbutadiene[105]

Cinnamaldehyde (redistilled b.p. 84-86°/1 mm., 80g., 0.67 mole) in ether (500 cc.) was added to methylmagnesiumbromide (c. 0.73 mole, from magnesium (18.5g.)). After hydrolysis with excess ammonium chloride, a further 200 cc. of ether was added and the layers separated. Ether was removed and the residue distilled in the presence of potassium hydrogen sulphate (8g.). Fractionation gave pure phenylbutadiene (55.5g., 70%, b.p. 44-47°/0.5 mm.), which solidified on cooling to 0°.

3. Preparation of phenylbutadienetetrabromide[106]

Bromine (106g., 34 cc., 0.66 mole) in carbon tetrachloride (200 cc.) was added to 1-phenylbutadiene (41.5g., 0.319 mole) in carbon tetrachloride (100 cc.). The bromine was decolourised rapidly at first, but then more slowly with formation of the only moderately soluble white tetrabromide. The reaction was stirred for 3 hours before filtering. The filtrate was shaken with 2N sodium carbonate to remove excess bromine, the carbon tetrachloride evaporated, and the solids combined and recrystallised from petroleum ether (60-80°). Yield of recrystallised tetrabromide, 116g., 81%, m.p. 123-124°. A similar preparation afforded a further 145g., 85%.

4. Preparation of 1-phenylbutadiyne[106]

Discussion. As reaction of phenylbutadienetetrabromide with sodamide has been reported[13] to give yields of the unstable diyne from only 8-20%, attempts were made to isolate the required copper derivative by adding the ether extract, obtained after evaporation of the ammonia, to ammoniacal copper(I) chloride and so avoid isolating the diyne itself. However, instead of yellow-orange acetylide, the solid which was obtained was brown and contaminated with the polymeric solid always present in large amounts as a biproduct in this reaction. The preparation is best carried out by using a small amount of the tetrabromide (say 30g.) in any one reaction, and working up the product as quickly as possible. The most successful preparation is described below. Several yields of only 20% were obtained.

Preparation The tetrabromide (30g., and 25.5g.) in two concurrent experiments was added, in small portions and with good stirring~~s~~, to sodamide (from sodium 8g. and 7g.) in two 1 litre neck flasks. Ether was then added which encouraged rapid evolution of the ammonia, followed by brine (2 x 100 cc.). The mixture was filtered to remove the brown insoluble material which was washed well with ether. The ether layers from each experiment were combined and the ether removed, at the pump, to leave a brown oily liquid which on distillation, collecting the distillate in a cold trap, afforded phenylbutadiyne (6.2g., 0.049 mole 40%), b.p. 45°/0.05 mm. which agrees with that given by Schlubach and Franzen[107]. Polymerisation to a dark brown mass took place rapidly above 45°. Phenylbutadiyne may be kept at -78°, but above 0° it melts and darkens rapidly. It was converted immediately to the required copper(I) silver(I) and mercury(II) derivatives.

Preparation of copper(I) chloride[108]

A filtered solution of sodium sulphi~~d~~te ($Na_2SO_3 \cdot 7H_2O$, 267g., 1.1 mole) in water (750 cc.) was added slowly to a filtered solution of copper(II) chloride ($CuCl_2 \cdot 2H_2O$, 170.5g., 1 mole) in water (150 cc.). The mixture was poured into a large volume of water(5 litres) containing sodium sulphite (26.7g., 0.1 mole) and conc. hydrochloric acid (20 cc.). The pale blue solution was decanted and the copper(I) chloride filtered, washed with glacial acetic acid, ethanol and ether and dried at 80° for 20 minutes. Yield 94g., 93%. It was stored under nitrogen, in the dark.

The author would like to thank the following for samples of the compounds listed:

Dr. D. Blake	ethylacetylene
Mr. J. M. Braddock	dimethylphenylphosphine
Mr. R. Coult	triethylarsine, 2:2 dichloro 3:3-dimethylbutane *p*-nitrophenylacetylene triethylphosphine tri-n-propylphosphine
Mr. M. Jewitt	diethylphenylphosphine
Mr. J. Lloyd	n-butyl isocyanide *o*-ethylphenylisocyanide *p*-tolylisocyanide

Purification of solvents

Benzene

(a) For Molecular Weight and Infra Red Measurements.

'Analar' benzene was dried over sodium wire

(b) For Dipole Moment Measurements

'Analar' benzene (10 litres) was fractionally crystallised, shaking the freezing solution at half-hourly intervals, and discarding about one sixth. This was repeated three times. It was then distilled from potassium and stored in a flask attached to a column containing molecular sieve (Linde 4A), so that about 400 cc. was in contact with the sieve immediately before use.

Ether

"Ether Anhydrous Methylated" (J. Macfarlan & Co., Ltd.) was dried over sodium wire for 24 hours.

Methanol and ethanol[109]

Magnesium (usually 1 mole) was placed in a 2 litre flask under nitrogen and the alcohol (200 cc.) added. Stirring with gentle warming at first initiated the reaction, and when it had subsided the remainder of the alcohol (1 litre) was added. After refluxing for two hours, the dried alcohol was distilled leaving behind the residue of magnesium hydroxide and alkoxide.

Nitrobenzene

For molecular weight determinations, 'A~~a~~nalar' nitrobenzene (2½ litres) was fractionally crystallised three times (as for benzene). It was then stood overnight over phosphorus pentoxide and distilled from phosphorus pentoxide under reduced pressure.

Tetrachlorethylene[110]

Tetrachlorethylene (2½ litres) was stood over calcium chloride for several days and then fractionally distilled, collecting the fraction with b.p. 119.5°. Thymol (5 p.p.m.) was added as a stabilizer[111] to avoid oxidation to phosgene and trichloracetic acid, and it was stored under nitrogen in the dark.

Petroleum Fraction, 200-230°.

Petroleum (200-230°; 2 litres) was shaken with concentrated sulphuric acid (100 ml. portions) until the acid was only slightly discoloured red. It was then washed with water, sodium carbonate and more water until the washings were neutral. After standing over magnesium sulphate the fraction distilling 210-230° was collected.

CHAPTER II

EXPERIMENTAL METHODS

A. MOLECULAR WEIGHT DETERMINATIONS

Cryoscopically

Molecular weight determinations, in benzene and nitrobenzene (the solvents being purified as described on page 40) were carried out in an apparatus of standard design[112], which consisted of the solution tube, with nitrogen inlet and Beckmann Thermometer, surrounded by a second tube as an air jacket, the whole being immersed in a cooling bath at four to five degrees below the freezing point of the solvent. A known volume of solvent was placed in the inner tube containing 4 pellets of molecular sieve (Linde Grade 5A) and varying amounts of solid were added and the depressions measured. Alternatively solvent (10.00 cc.) was placed in the tube initially, and 5 cc. aliquots of a solution of known strength of the compound added, the latter method being favoured when the compound was very soluble, and large amounts were available. A slow nitrogen stream was passed over the solution to avoid decomposition of air-sensitive compounds and to prevent condensation of water-vapour. The nitrogen flow rate appeared to be critical: if it was too fast evaporation of the solvent occurred, and if too slow condensation of water vapour. Diphenyl was used to

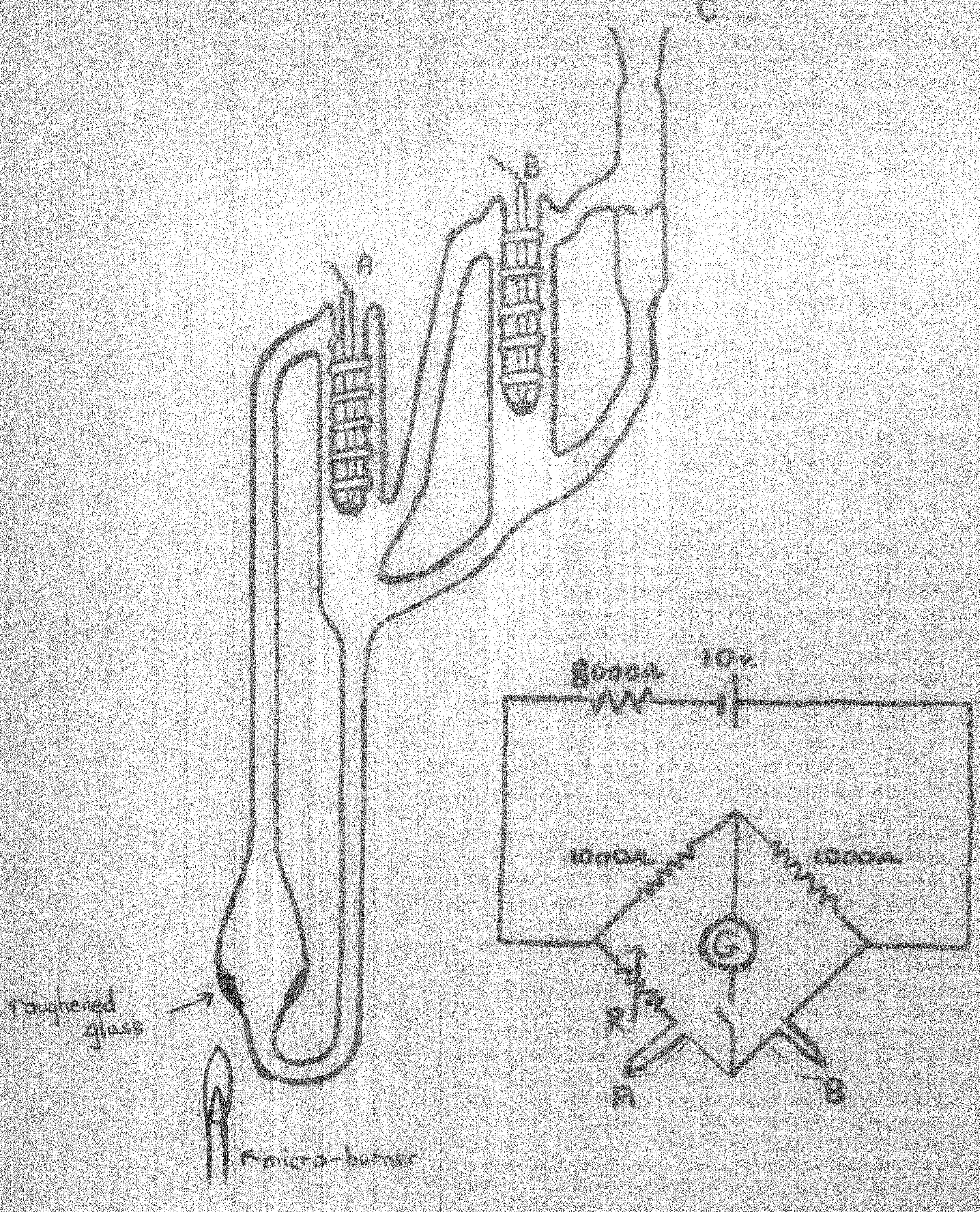

C
B
A
roughened glass
micro-burner
8000Ω
10v.
1000Ω
1000Ω
G
R
A
B

FIG. 2.

determine the cryoscopic constant for benzene (found to vary between 51.2 and 53.5 for various purifications of benzene) and <u>para</u>nitrotoluene in the case of nitrobenzene (k = 69.6 - 70.9).

<u>Ebullioscopically</u>

A Swietoslawsky ebulliometer, shown in Fig. 2, was placed in a large cardboard box to exclude draughts. Solvent (25.00 cc.) was boiled steadily with a microburner so that the pure solvent flowed over the well containing thermistor A, and pure vapour refluxed over well B, and then from a water condenser attached at C. A few drops of heavy white oil were used to ensure good contact between the thermistors and the wells. The matched thermistors formed two arms of a Wheatstone Bridge circuit, a variable resistance R, being in series with thermistor A. The ratio arms were each of 1000 ohms, and a 10 volt D.C. transistor supply was used to drive the circuit together with an 8000 ohm resistance so that the heat dispersion of the thermistors was well below the maximum (10 m watts). A relatively large voltage was chosen, as it could be reproduced satisfactorily, because it is important that the characteristics of the circuit are the same for both the compound whose molecular weight is required and the standard, as the change in resistance per millimole of solute varies slightly with the small current through the thermistors. Equilibrium was attained after boiling for

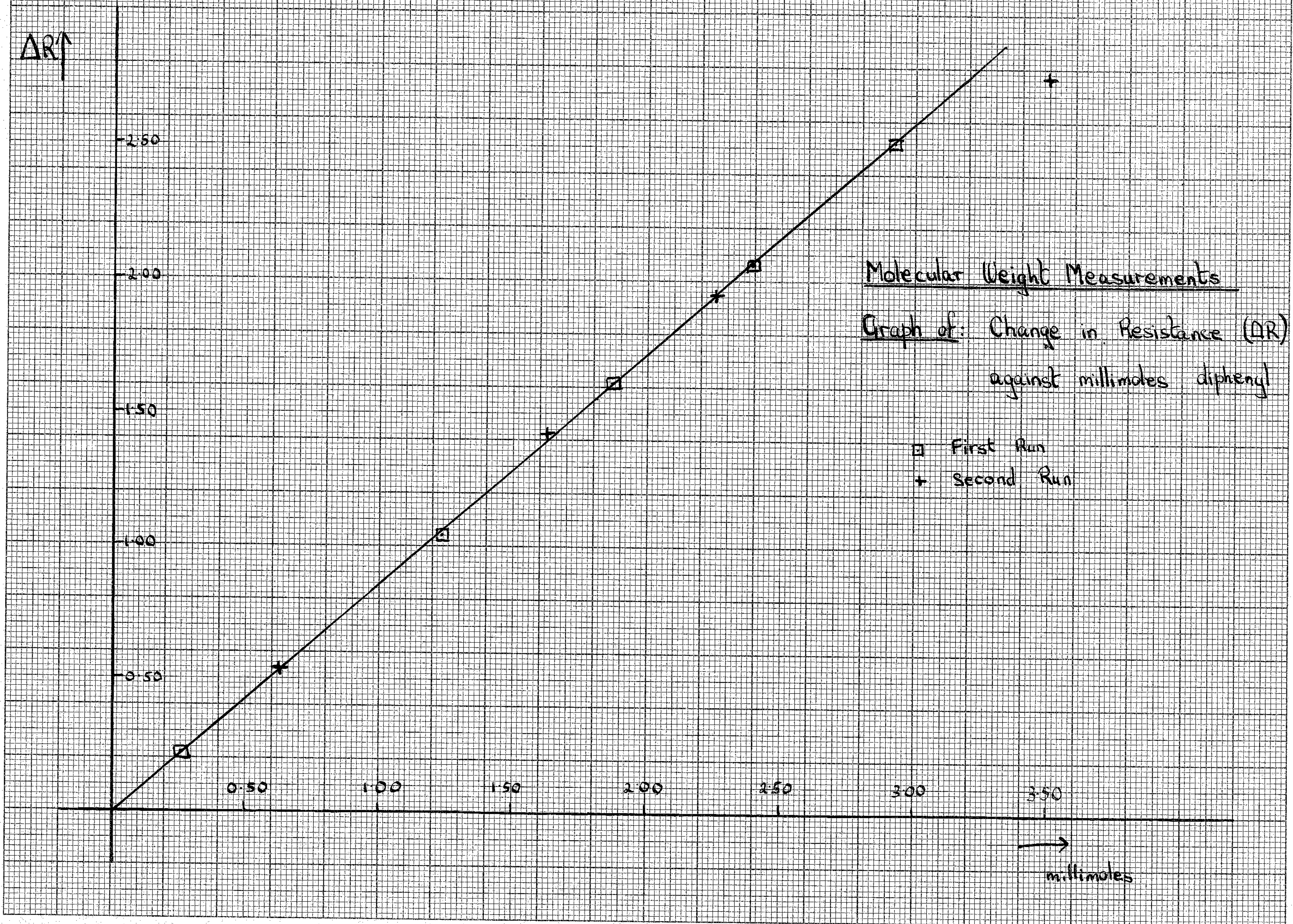
45 minutes, and a weighed amount of the compound was then added down the top of the condenser. A second condenser was placed above this, and the water withdrawn from the latter, so that the solvent climbed up the condenser and washed the compound into the apparatus. Water was again passed through the lower condenser and the solution left for 10 minutes to attain equilibrium. The change required in the variable resistance to rebalance the circuit was measured. This increase in resistance is proportional to the elevation of the boiling point which is proportional to the number of moles of solute. Diphenyl was used as a standard and the standard was repeated to ensure reproducibility. A graph (see overleaf) relating the change in resistance per millimole of diphenyl was plotted. Hence by finding the resistance change for weighed amounts of a compound, the number of millimoles present, and therefore its molecular weight can be calculated.

Benzene and acetone were found to be the most suitable solvents though frothing of the solution over both wells occurred at greater concentrations (usually c. 4%). Steady conditions were not achieved with diethylether. Results are collected in Table 2a, page 106.

B. DIPOLE MOMENT MEASUREMENTS

Theoretical

Faraday[113] showed that the molecules of a dielectric



Molecular Weight Measurements

Graph of: Change in Resistance (ΔR) against millimoles diphenyl when placed in an electric field become polarised. Clausius[114] and Moscotti[115] interpretated this mathematically and derived the relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{1}{d} = p$$

where ε is the dielectric constant, d the density, and p the specific polarisation. Multiplying this equation by the molecular weight M, gives the molecular polarisation P

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = P \qquad (1)$$

The polarisation is constant for many materials of small dielectric, independent of temperature and pressure and varies little between the solid and liquid states. For these materials, the relation between the dielectric constant and the refractive index n, is that developed by Maxwell[116], namely $n^2 = \varepsilon \phi$, where ϕ is the magnetic permeability of the material and is almost unity for ferromagnetic substances. If the values of the refractive index obtained in the visible region are extrapolated to infinite wavelength, which is virtually the wavelength at which ε is measured, then

$$\varepsilon = n^2_{\infty} \qquad (2)$$

In practice in the case of materials of high dielectric constant $\varepsilon > n^2_\infty$. From (1) and (2):

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = r$$

Lorenz[117] and Lorentz[118] showed this relation to hold, where r is the specific refraction and multiplied by M gives the molecular refraction R.

$$\therefore \qquad R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \qquad (3)$$

Molecular refractions are additive within certain limits and can be calculated by allowing appropriate values to the various atoms and bonds comprising the molecule. On the other hand the molecular polarisation P, is only additive for compounds of low dielectric constant (where $\varepsilon = n^2_\infty$).

This difference in behaviour was explained by Debye[119] who suggested that although a molecule as a whole may be neutral there was no reason why the distribution of charges should not be unsymmetrical in some molecules in the absence of an externally applied field, giving a permanent charge separation or dipole which would orientate itself in an electric field of relatively low frequency (i.e. radiofrequency).

The Total Polarisation = Orientation Polarisation (Po) + Distortion or Induced Polarisation.

$$T.P. = P_o + P_E + P_A \qquad (4)$$

where P_E and P_A are the electron and atom polarisations respectively. The atom polarisation arises since if a molecule contains polar bonds, the atoms carry different effective charges and so the nuclei are displaced with respect to one another thus contributing to the induced dipole.

The refractive index is ordinarily measured for visible light, the refraction being due primarily to the displacement of electrons and so equation (3) gives only the electron polarisation.

$$P_E = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

The refractive index may be extrapolated to infinite wavelength, but values of R obtained in this way are only slightly different from those at visible frequencies and often no correction is made in calculating dipole moments.

Measurement of the dielectric constant gives the total polarisation, since in the slowly alternating field there is time for molecules to 'line up' and atoms to undergo displacement. P_A cannot be measured except in the case of simple molecules by studying their infrared spectra in which atom polarisations are additive functions of various absorptions,[120] or in the case of symmetrical molecules for which P_O is zero. P_A is small and can often be ignored in the case of highly polar compounds, or assumed to be between

5-15% of P_E.

From the Debye Theory in which a molecule with permanent dipole, μ is inclined to an electric field, F the expression

$$P_0 = \frac{4}{3} \pi \frac{N\mu^2}{3kT} \quad \text{is obtained.}$$

(k = Boltzman's constant, T = absolute temperature, N = avogadro number)

$$\therefore \mu = \sqrt{\frac{9kT}{4\pi N} \cdot P_0}$$

As all measurements were made at 25°C,

$$\mu = 0.2212 \sqrt{P_0}$$

And since from equation (4):

$$P_0 = (T.P.) - (P_E + P_A)$$

the dipole moment can be evaluated.

Dipole moments of most molecules lie between 0 and 9×10^{-18} e.s.u. (0-9 Debye), since the magnitude of the electronic charge is 4.0×10^{-10} e.s.u. and the distance between small atoms is 1 to $2 \times 10^{-\cancel{1}8}$ cm.

The polarisation of a solution may be expressed in terms of the polarisation (p_1 and p_2) and the mole fractions (f_1 and f_2) of the solvent and solute respectively as given by Debye[119]:

$$P = p_1f_1 + p_2f_2 = \frac{\varepsilon - 1}{\varepsilon + 2} \quad \frac{M_1f_1 + M_2f_2}{d}$$

Halverstadt and Kumler[121] used specific volumes instead of densities and weight fractions instead of mole fractions. By assuming that the specific volume and dielectric constant of the solution are linear functions of the weight fraction (i.e. $\varepsilon = a + \alpha\omega_2$ and $V = b + \beta\omega_2$) where a and b are the dielectric constant and specific colume of the solvent respectively, and ω_2 is the weight fraction of the solute, they derived an expression for the specific total polarisation of the solute at infinite dilution:

$$T.P._2 = \frac{3\alpha V_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}(V_1 + \beta) \qquad (6)$$

(V_1 = volume of the solvent; ε_1 = dielectric constant of the solvent)

Similarly the electron polarisation may be expressed as:

$$P_{E_2} = \frac{6\gamma n_1 V_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2}(V_1 + \beta) \qquad (7)$$

(where $n = n_1 + \gamma\omega_2$; n_1 = refractive index of the solvent)

By plotting ε, v and n against ω_2; α, β and γ may be obtained and by substituting these values into (6) and (7) the total polarisation, and electron polarisation may be evaluated.

At low concentrations ($\omega_2 \leqslant 0.02$) the graphs are linear[121] and linear plots of n against ω_2 may be obtained at even greater concentrations.

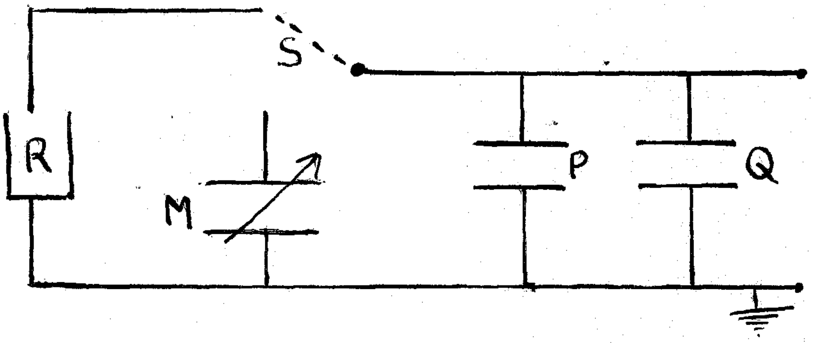
Apparatus and Experimental Details

The apparatus used is that previously described and used by P. Dixon[122] and J. G. Livingstone[123] with several minor modifications, and therefore is described somewhat briefly. All measurements were made at 25°C in benzene.

1. Dielectric Constant Measurements

The change in capacitance which occurred when the dielectric of a capacitor (the dielectric cell) was changed was measured. The cell of the Sayce-Briscoe type[124] with plates of platinum burnt on to the glass, could be filled with benzene or the benzene solution of the compound and solutions changed easily by blowing out with nitrogen, washing with pure benzene and replacing with the required liquid. It was immersed in a thermostat filled with transformer oil to reduce stray capacitances.

A heterodyne beat capacitance meter of the type described by Hill and Sutton[125] was used to measure the capacitance change in the cell. The X plates of a cathode ray tube carried the output from a beat frequency generator which consisted of two oscillators, one of fixed frequency, f_o (C.10^5 c.p.s.), and the other of variable frequency, f_1 incorporating the measuring system. The circuits of the oscillators were as nearly identical as possible. The Y plates carried the output from an audiofrequency oscillator, f_2 (C. 1000 c.p.s.). The measuring system, shown below, consisted of the cell C, two air-spaced uncalibrated variable capacitors P and Q, and a calibrated concentric cylinder variable capacitor, M, with a micrometer screw, having a capacitance change of 3.38 pf. per cm. length. The cell and the calibrated capacitor could be interchanged by the switch, S.



P is adjusted until the output of the beat frequency generator gave a figure of eight on the cathode ray tube corresponding to $f_1 - f_o = f_2/2$ which was used as a balance point throughout all the measurements. After filling the cell and allowing it to reach thermal equilibrium (about 10 minutes) P was adjusted. M was then switched in, to replace the cell, and adjusted in order to reobtain the figure of eight. After adjusting each circuit several times, and when a steady figure of eight was obtained on both sides of the switch, the value of M was noted (arranging that for pure benzene the balance occurred with the calibrated capacitor reading about 2.4 cm., since its range was 0-25 cm.) After blowing out the benzene, the cell was washed out (twice with benzene) and then filled with a solution of the compound and the balance point again obtained. The difference in M, gave the difference in capacitance between the solution and pure benzene. Readings of M, with pure benzene in the cell, were taken after each solution, and an average value taken if a slight drift occurred.

If ε_3 is the dielectric constant of the solution and C_1, C_2 and C_3 are the capacitances of the cell filled with benzene, air and solution respectively, then

$$\frac{C_3 - C_2}{C_1 - C_2} = \frac{\varepsilon_3 - \varepsilon_2}{\varepsilon_1 - \varepsilon_2}$$

$$\therefore \; \varepsilon_3 = \left(\frac{C_3 - C_1}{C_1 - C_2} + 1 \right)(\varepsilon_1 - \varepsilon_2) + \varepsilon_1$$

The dielectric constants of air (ε_2) and benzene[126] (ε_1) were taken as 1.0006 and 2.2727 respectively; $C_1 - C_2$ was taken as 69.05 pfs., as previously found[122]. $C_3 - C_1$ corresponds to the change in capacitance (ΔC) measured with M.

$$\therefore \quad \varepsilon_3 = \left(\frac{\Delta C}{69.05} + 1\right) 1.2721 + 1.0006$$

If ℓ is the reading on the condenser in cm., as the capacitance change per cm. is 3.38 pfs., then,

$$\varepsilon_3 = \left(\frac{3.38\,\Delta\ell}{69.05} + 1\right) 1.2721 + 1.0006$$

$$\therefore \quad \delta\varepsilon_3 = \left(\frac{3.38\,\delta\ell}{69.05}\right) 1.2721$$

$$\therefore \quad \frac{d\varepsilon}{dw} = \frac{1.2721\ .\ 3.38}{69.05} \cdot \frac{d\ell}{dw}$$

$$= 0.06227 \cdot \frac{d\ell}{dw}$$

$\frac{d\ell}{dw}$ is the slope of the graph of (change in length on the calibrated condenser) against weight fraction and $\frac{d\varepsilon}{dw}$ corresponds to α in equation (6).

2. Measurement of Refractive Index

A Pulfrich refractometer with a divided cell, attached to the prism with silicone rubber, was used. The cell could be washed out with bromine in sodium bromide solution to remove any gold which was deposited as a purple film by some of the less stable compounds. The refractometer was enclosed in a box fitted with a glove and window which could be lifted on a hinge. When closed it rested on polyurethane foam, to ensure a good fit and so avoid draughts. The temperature was kept at 25 ± 0.2°C, throughout the box, by means of a fan, and heater in circuit with a thermostatted thermometer. A sodium lamp was generally used as a light source, but occasionally a projection lamp together with a red Jena Interference Filter ($\lambda_{max} = 6620°A$) was used. Pure benzene was placed in one side of the cell and a solution in the other, a polythene cap being placed over the cell to prevent evaporation. The window was closed and the solutions left for 15 minutes to attain equilibrium. The difference in extinction angles between the solution and pure solvent was measured.

The relationship between extinction angle and refractive index is given by $n = \sin A \sqrt{N^2 - \sin^2 B} + \cos A \sin B$ where, A is the refractive angle of the prism, B is the angle of emergence, and N is the refractive index of the prism. A graph of extinction angle against refractive index is linear and shows that 1 minute of arc = 1087×10^{-7} ($\lambda = 7090 - 5893A°$). A graph of Δn against ω_2 gives $\frac{dn}{dw} = \gamma$ in equation (7).

3. Measurement of Specific Volume

The Sprengel type pyknometer used previously[122,123] was replaced by a similar one of larger capacity, as the accuracy of this measurement contributes appreciably to the final accuracy of the dipole moments. It was fitted with ground glass caps to prevent evaporation, and calibrated with distilled water. (Volume = 12.1208 cc.). Density measurements on pure benzene gave a value of 0.87376 gm./cc. (Literature gives 0.87368 gm/cc.[127]). A solution in the pyknometer was placed in a water bath at 25° for 30 minutes and then on the balance for 10 minutes, to allow thermal equilibrium to be attained in each case.

$$\text{Specific volume of solution} = \frac{12.1208}{\text{weight of solution in the pyknometer}}$$

$$V = b + \beta\omega_2 = \frac{12.1208}{w_s}$$

$$\therefore \qquad \beta = \frac{\frac{12.1208}{w_s}}{w_2}$$

β is the slope of the graph of specific volume against weight fraction.

<u>Example of Dipole Moment calculation from experimental results</u>

Compound: $C_6H_5C{\equiv}CAuCNC_6H_4\underline{o}\text{-}C_2H_5$ (phenylethynyl $\underline{o}$-ethylphenylisocyanidegold) M = 429.3

	(1)	(2)	(3)	(4)
Wt. flask	43.9142	39.3344	49.6747	44.5370
Wt. flask and compound	43.9760	39.5549	50.0120	44.7668
Wt. flask and cpd. and benzene	60.7450	67.9070	79.7700	60.5920
Wt. compound	0.0618	0.2205	0.3373	0.2298
Wt. compound and benzene	16.7690	28.3521	29.7580	15.8252
Weight fraction $\omega \times 10^6$	3685	7777	11355	14521

Dielectric measurements

	(1)	(2)	(3)	(4)
Reading for pure benzene	2.489	2.485	2.485	
Reading for solution	1.626	0.825	0.100	
Δc(cm.)	0.863	1.660	2.385	

Refractivity measurements

	(1)	(2)	(3)	(4)
Δn (λ = 5893Å)		9'.00"	12'.40"	16'.10"
$10^7 . \Delta n$		9783	13769	17573

Density measurements (wt. pyknometer = 20.6429)

	(1)	(2)	(3)	(4)
Wt. pyknometer + sol^n.		31.2776	31.2975	31.3144
∴ wt. sol^n.		10.6347	10.6546	10.6715
Specific Volume V $\left(= \frac{12.1208}{\text{wt. sol}^n.}\right)$		1.13974	1.13761	1.13581

Graphs of Δc, $10^6 \Delta n$, and V against ω give:

$$
\begin{aligned}
\alpha &= 0.06227 \times \frac{d\Delta c}{dw} \\
&= 0.06227 \times 209.8 \\
&= 13.0642
\end{aligned}
$$

$$\beta = -0.5850$$

$$\gamma = 0.1205$$

From equation (6):

$$\underline{\text{Total Polarisation}} = \frac{3\alpha V_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} (V_1 + \beta)$$

V_1 = specific volume of benzene = 1.1445 $\varepsilon_1 = 2.2727$

$$\therefore \quad \text{T.P.} = [0.1881\,\alpha + 0.2979\,(1.1445 + \beta)]M$$

$$\therefore \quad \text{T.P.} = [2.4574 + 0.1667]429.3$$

$$= 1126.5 \text{ cc.}$$

From equation (7):

$$\underline{\text{Electron Polarisation}} = \frac{6n_1\gamma V_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2} (V_1 + \beta)$$

$V_1 = 1.1445$, $n_1 = 1.4979$ (for sodium D line)

$$\therefore \quad P_E = [0.5712\gamma + 0.2931(1.1445 + \beta)]M$$

$$\therefore \quad P_E = [0.6883 + 0.16399]429.3$$

$$= 99.9 \text{ cc.}$$

$$P_o = \text{T.P.} - (P_E + P_A)$$

Assuming the atom polarisation to be 10 cc.

$$P_o = 1126.5 - 99.9 - 10$$

$$= 1016.6 \text{ cc.}$$

$$\therefore \quad \text{Dipole moment, } \mu = 0.2212\sqrt{P_o}$$

$$= 0.2212\sqrt{1016.6}$$

$$\therefore \quad \underline{\mu = 7.05 \text{ D}}$$

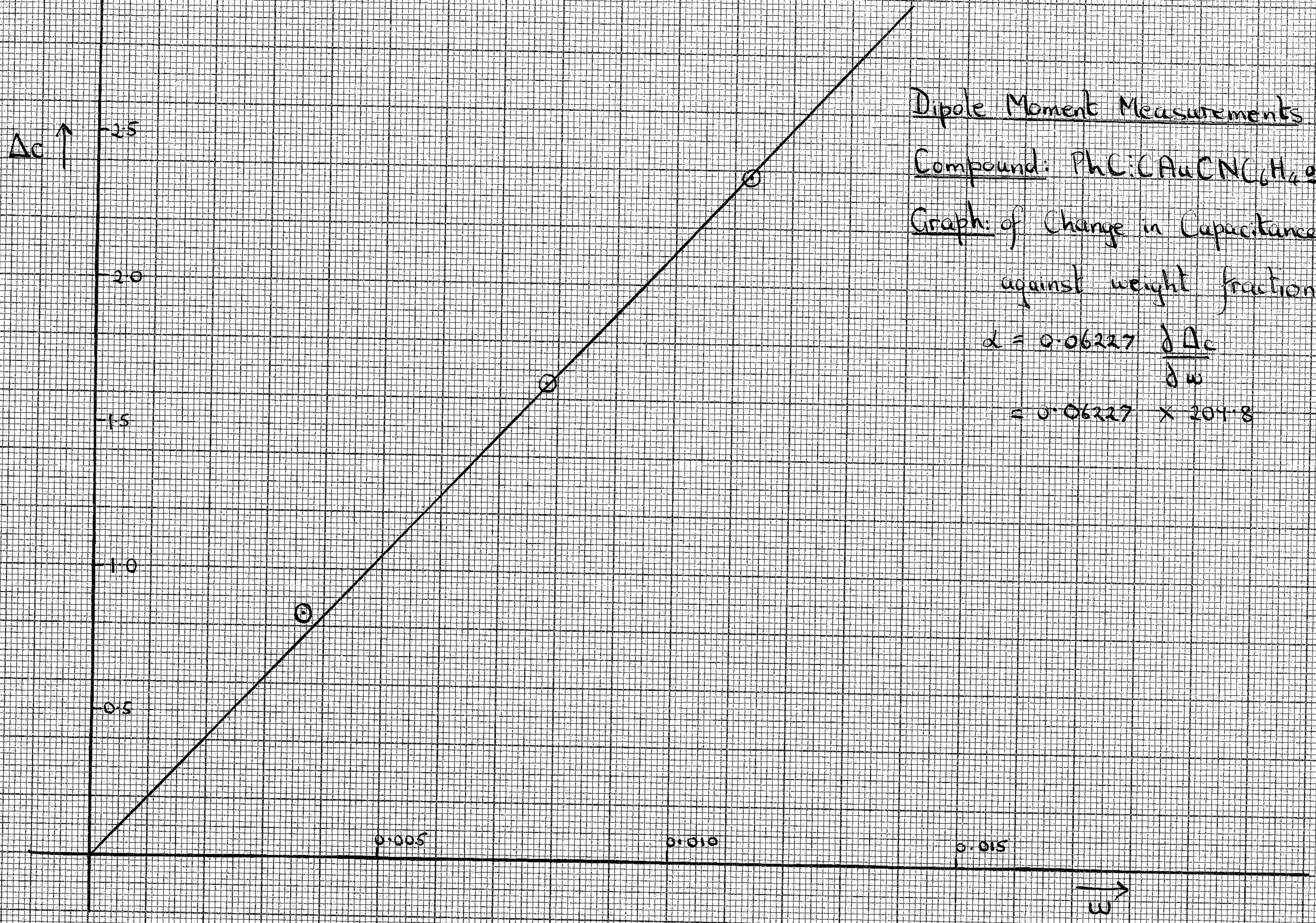
Dipole Moment Measurements

Compound: $PhC{:}CAuCNC_6H_4$-o-C_2H_5

Graph: of Change in Capacitance (Δc) against weight fraction (ω).

$$\alpha = 0{\cdot}06227 \frac{\partial \Delta c}{\partial \omega}$$

$$= 0{\cdot}06227 \times 204{\cdot}8$$

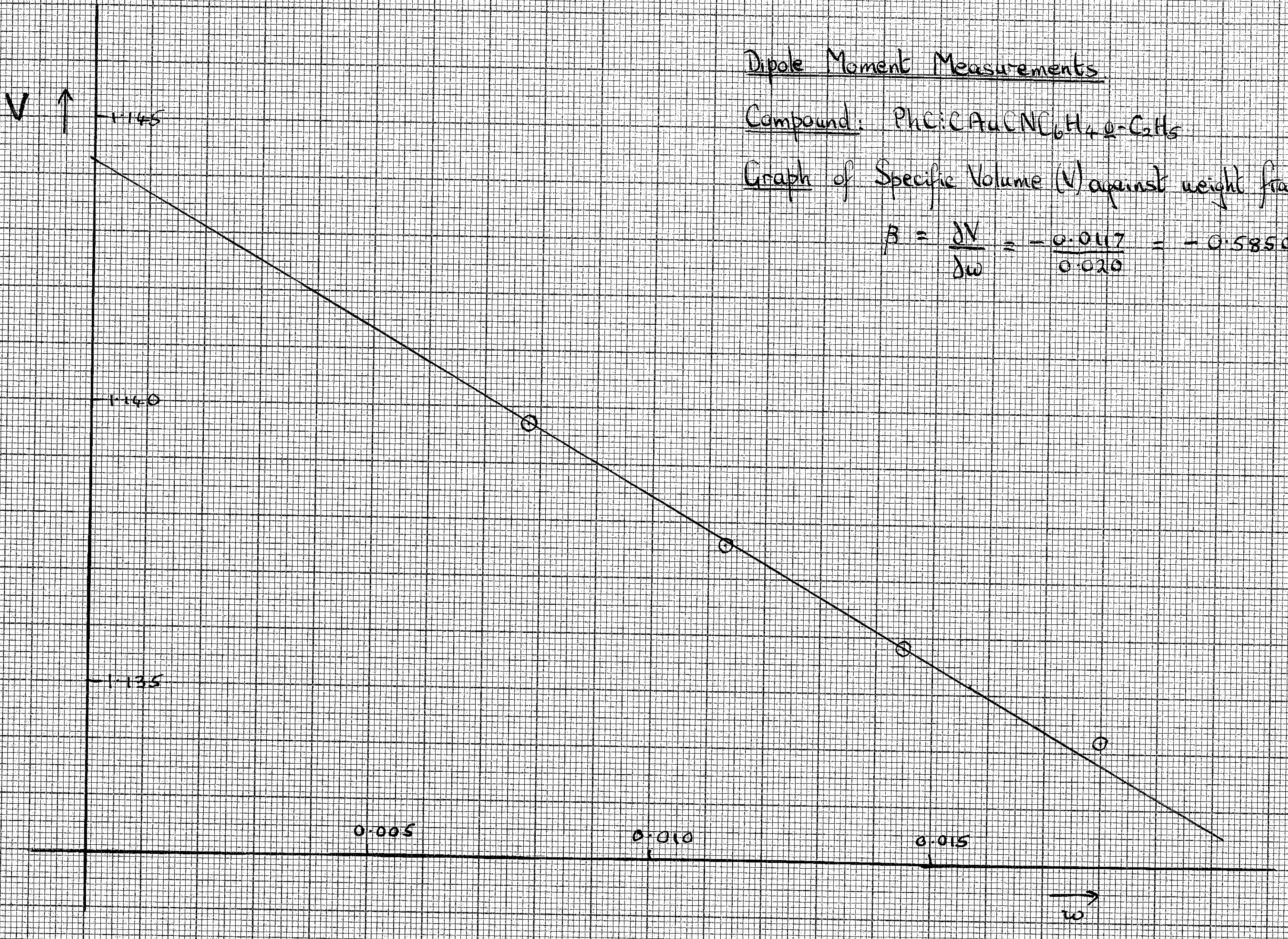


Dipole Moment Measurements.

Compound: $PhC{:}CAuCNC_6H_4$-o-C_2H_5

Graph of Specific Volume (V) against weight fraction (ω).

$$\beta = \frac{\delta V}{\delta \omega} = -\frac{0.0117}{0.020} = -0.5850$$

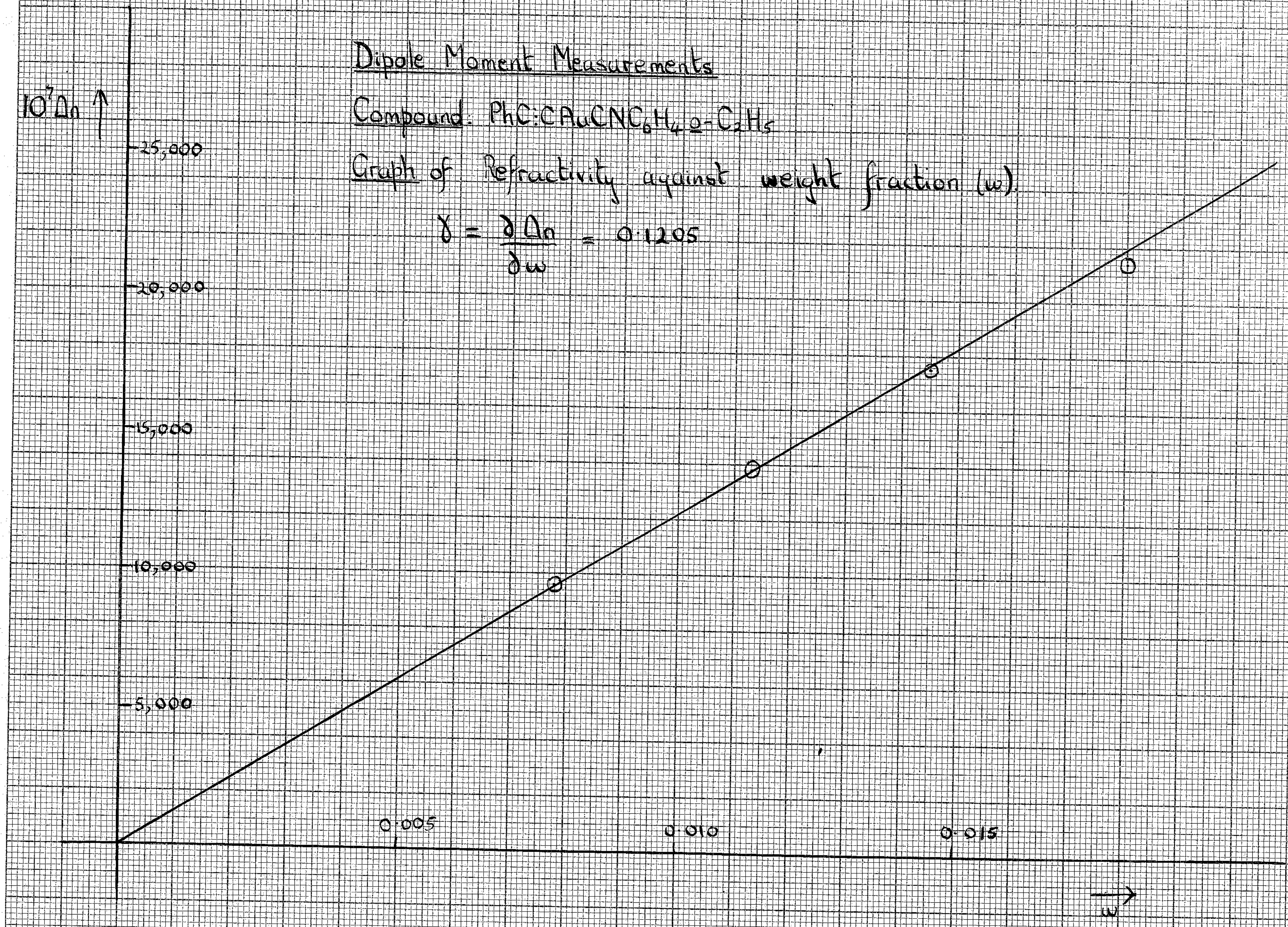


Dipole Moment Measurements

Compound. $PhC:CAuCNC_6H_4$-o-C_2H_5

Graph of Refractivity against weight fraction (w).

$$\gamma = \frac{\partial \Delta n}{\partial w} = 0.1205$$



DETERMINATION OF ACCURATE -C≡C- FREQUENCIES

COMPOUND: $PhC{:}CCu \cdot Bu^tC{:}CCu \cdot 2PMe_3$

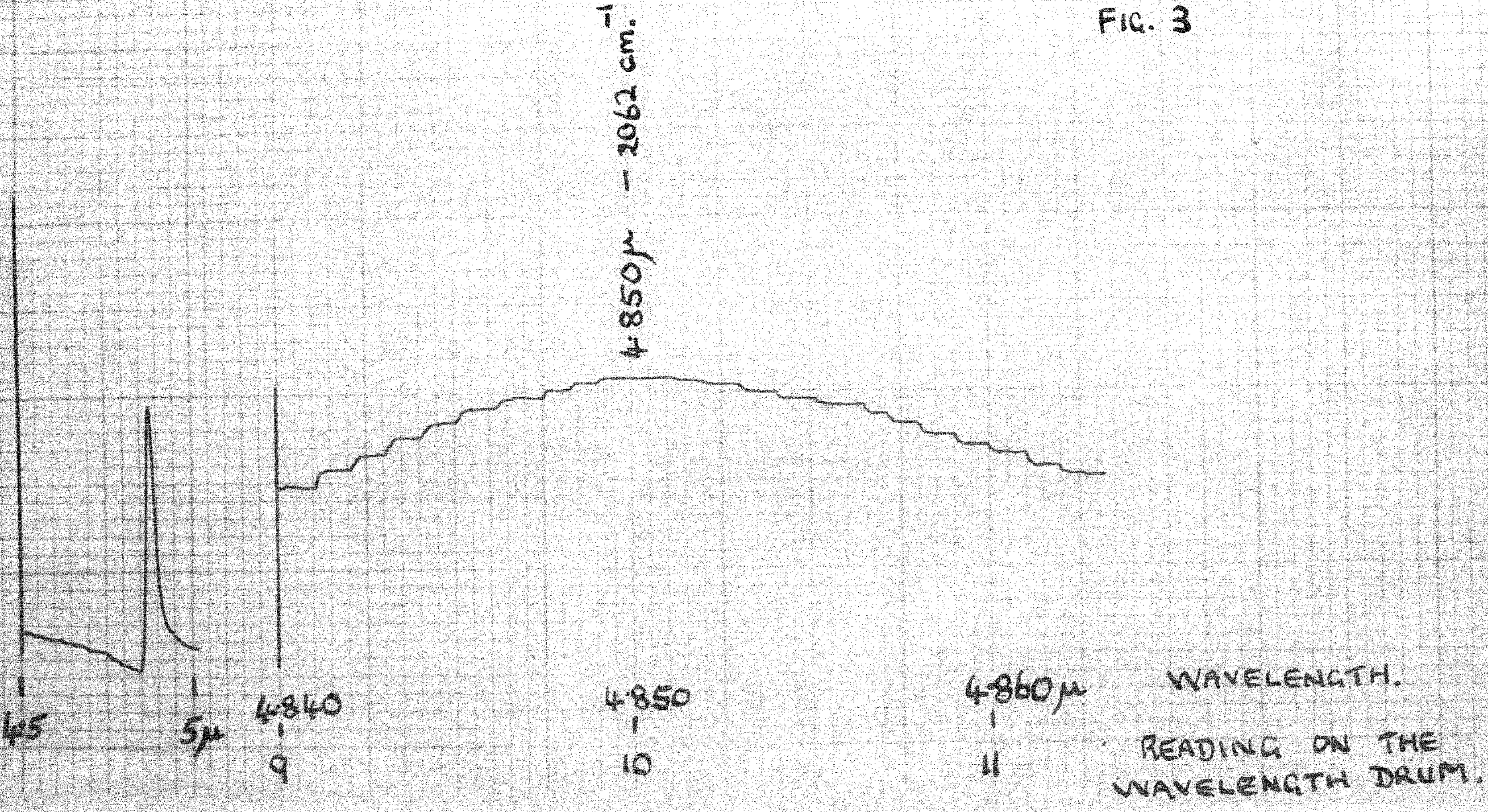


FIG. 3

Accuracy of the measurements

For moments greater than 3.5D, the error is not greater than 0.1D. Moments of 1D have an error not greater than 20% (i.e. 0.2D), the error increasing rapidly as the moment approaches zero.

C. INFRA RED SPECTRA

Infra red spectra of solid compounds were generally taken in KBr at a concentration of 2-3mg. A Grubb Parsons GS2A spectrometer was used. The acetylenic frequencies given throughout this thesis are measured accurately and are correct to 1 cm.$^{-1}$ for frequencies above 2000 cm^{-1}, and to 2 cm^{-1} for frequencies less than 2000 cm^{-1}. To measure an absorption frequency accurately, the approximate position was noted in the course of a run through the spectrum. The wavelength drum of the spectrometer was then adjusted to about 0.02 microns before the wavelength being measured. The recording chart was run 2 squares (i.e. 0.2" on the paper) at that wavelength. Then the wavelength drum was turned manually by one small division (corresponding to 0.001μ in the second order) and the chart run a further two squares. The wavelength drum was now moved a further division, and the chart run two more squares, and this process repeated until about 0.2μ after the peak which had now been traced out as a broader curve as shown in Figure 3. The maximum point on this curve corresponds to the accurate acetylenic stretching frequency.

The acetylenic frequencies are collected in tables in the Discussion.

D. QUANTITATIVE ANALYSES

Micro carbon and hydrogen analyses are by Miss V. Conway and Mr. T. Caygill of this department. Other analyses were performed, in duplicate, as described.

Copper

(a) Gravimetrically as copper(I) thiocyanate.[128]

About 0.1g., of the compound was decomposed by adding 5N nitric acid (2 cc.), warming gently and then adding conc. nitric acid (5 cc.) and boiling until the solution was pale blue. Concentrated hydrochloric acid (10 cc.) was added and boiling continued until no more oxides of nitrogen were evolved. The solution was cooled, diluted to 150 cc., and if a precipitate formed it was filtered off. A saturated solution of sulphur dioxide (about 20 cc.) was added to the filtrate and the solution boiled for 30 minutes. If the smell of sulphur dioxide persisted the solution was allowed to cool, if not more sulphur dioxide was added and boiling continued. The solution was made just acid and 2% ammonium thiocyanate solution (saturated with SO_2) added (10ml. for every 50mg of copper present). The precipitate was allowed to settle overnight, filtered through a sintered glass crucible (porosity 4) and dried at 110 - 120° for 3 hours.

(b) Volumetrically[129]

When several copper analyses on compounds of uncertain constitution or purity were required, the more rapid volumetric estimation was carried out, decomposing the compound as described above, and estimating the iodine released on addition of potassium iodide to the copper solution, with standard sodium thiosulphate solution.

Gold

(a) Compounds easily combusted to gold (i.e. compounds containing only, C, H, N, Au, and sometimes P).

50-80mg. of the compound was weighed in a silica crucible with lid, which had previously been heated, cooled in a desiccator and weighed. The crucible and contents were heated with a Méker ~~mecca~~ burner, very gently at first until the compound had decomposed, and then strongly until all organic matter had been combusted and the crucible containing only the gold residue had reached constant weight.

(b) Other compounds

About 0.1g. of the compound, was heated in a silica crucible until all organic matter had combusted. The crucible was allowed to cool, placed in a beaker (400 cc.) and the gold dissolved by addition of conc. nitric acid (5 cc.) and conc. hydrochloric acid (15cc.). The contents of the beaker were heated to remove oxides of nitrogen. The crucible was washed with water and removed from the beaker, and the solution was diluted to 200cc.. Any precipitate at this stage was filtered off. A solution of hydrazinehydrochloride was added to precipitate metallic gold, and the solution was boiled to coagulate the precipitate as much as possible. It was then filtered and the gold collected on a sintered disc (porosity 4) and dried at 150-170° to constant weight.

It is often difficult to transfer the last traces of gold from the beaker to the sintered disc, as when it is finely divided it sticks to the glass and policeman; analyses by this method, therefore, are usually slightly lower than the required value. (e.g. If 50% Au, is required; a value of about 49.5% would be acceptable).

Nitrogen was determined by the Kjeldahl method.[132]

Mercury was estimated gravimetrically as mercur~~ous~~y(II) sulphide.[130]

Silver was estimated gravimetrically as silver chloride.[131]

CHAPTER III

COPPER, SILVER AND MERCURY ACETYLIDES

The copper, silver and mercury derivatives of various acetylenes were prepared by the well-known methods, and have all been reported previously. The preparations of the phenylacetylene derivatives are described in each case, and any interesting or unusual behaviour of other acetylenes is added.

Preparation and solubility properties of copper acetylides $(RC\vdots CCu)_x$

All yields are quantitative with the exception of t-butylethynylcopper. All the copper derivatives described, except t-butylethynylcopper, are insoluble in common organic solvents. They are all yellow, excepting p-nitrophenylethynylcopper and t-butylethynylcopper which are red, (though the latter is yellow if isolated by cooling a solution in ether).[92]

Phenylethynylcopper

Copper(I) chloride (23g., 0.23 mole) was placed, in a nitrogen atmosphere, in a 500 cc., 3 necked flask equipped with stirrer and dropping funnel. Water (200cc.) was added, and sufficient concentrated ammonia to give a pale blue solution. Phenylacetylene (23g., 24.8cc., 0.2 mole) in ethanol (100cc.) was added with good stirring, an immediate bright yellow precipitate being formed. After addition was complete the solution was stirred for a further 30 minutes and the precipitate filtered. It was washed with 4N ammonia and water until the washings were colourless, and then with alcohol, acetone and ether and dried in vacuo (3 hours) with a sintered disc placed between the solid and the pump, so that the dry fine powder was not sucked into the vacuum system. Yield of phenylethynylcopper, 37g., 97%.

Prop-1-ynyl, *but-1-ynyl*, *pent-1-ynyl*, and *isopropenylethynyl copper* were prepared similarly with a condenser (acetone/CO_2, or water cooled) above the flask to avoid any loss of the acetylene. They were insoluble in amines as well as organic solvents.

The solid aromatic acetylenes were added as solutions in 1:2 dimethoxyethane.

t-Butylethynylcopper. On addition of t-butylacetylene to ammoniacal copper(I) chloride, a red granular precipitate was formed. After filtration, and washing with 4N ammonia and water, the red solid was dissolved in benzene. Any insoluble material was separated, the benzene removed and the t-butylethynylcopper recrystallised from hexane. (m.p. 148-150° dec.). The best yield obtained was only 55%. Ebullioscopic molecular weight measurements in benzene showed t-butylethynylcopper to be octameric. Found: M, 1140, 1161, 1177 in 0.73, 1.48, 2.95% benzene solution. $(C_6H_9Cu)_8$ requires M, 1157.

The attempted preparation of "crystalline" phenylethynylcopper.

1. From copper(II)phenylpropiolate $(PhC{\vdots}CCO_2)_2Cu$

Preparation of the copper salt. Phenylpropiolic acid (10g., 68.4 m.mole) was dissolved in ethanol (20cc.) and added to sodium acetate (9.4g., 70 m.mole) in water (20cc.). A solution of copper(II) chloride (9.4g., 70 m.mole) in water (20cc.) was then added. On standing blue leaflets separated which were filtered off, washed with water and pumped dry. Yield 11.9g., 95%. An I.R spectrum showed $\nu C{\vdots}C$ at 2232 cm^{-1}.

Decomposition to phenylethynylcopper. Attempts were made to repeat the observation made by F. Straus[133] that on gently warming copper phenylpropiolate with various amines fine yellow needles of phenylethynylcopper are formed.

$$2(PhC{\vdots}CCO_2)_2Cu \longrightarrow PhC{\vdots}C\cdot C{\vdots}CPh + 2PhC{\vdots}CCu + 4CO_2$$

Samples of the copper salt (1g.) were added to pyridine, quinoline, and isopropylamine (10cc.) forming deep blue solutions. Slight warming caused evolution of CO_2 and the solutions turned greenish yellow with deposition of phenylethynylcopper. Even with very slow warming, or on keeping the solutions for a week at 25°C., the best specimen of phenylethynylcopper was only obtained as very fine feathery needles and was that from the pyridine solution.

2. Extraction of phenylethynylcopper with amines

Samples of phenylethynylcopper (2 - 3g.) were placed in Soxhlet extraction thimbles and extracted with various amines, (N_2 atmosphere). From the isopropylamine and diethylamine extractions, microcrystalline phenylethynylcopper was obtained. Solutions containing a suspension of a few milligrams of the microcrystalline material in their respective solvents were kept in sealed tubes for several months, but no larger crystals grew.

Phenylethynylcopper could not be extracted by triethylamine and it is unaffected by 2,2-bipyridyl.

Preparation and solubility properties of silver acetylides $(RC{\equiv}CAg)_x$

All yieldsof silver acetylides were quantitative.

Phenylethynylsilver. Silver nitrate (37.5g., 0.22 mole) was dissolved in a mixture of water (100cc.) and methanol (100cc.) in a 500cc. 3 necked flask. Concentrated ammonia was added until the precipitated silver oxide just redissolved. Phenylacetylene (20g., 0.20 mole) in methanol (30cc.) was added with good stirring. The white precipitate was washed thoroughly with water and then with methanol, acetone and ether, and dried in vacuo (2 hours). Yield 40g., 0.202 mole, 100%. An infra-red spectrum of the solid was identical with that of phenylethynylcopper except for the $\nu C{\equiv}C$ stretching, indicating that no appreciable amount of silver nitrate was present.

p-nitrophenylethynylsilver, which was pale yellow, *p-bromethynylsilver* and *mesitylethynylsilver* were prepared similarly, adding the acetylene in 1,2-dimethoxyethane solution, and they are insoluble in common organic solvents. p-nitrophenylethynylsilver could not be caused to explode as suggested in Beilstein.[134]

But-1-ynyl, *pent-1-ynyl* and *isopropenyl*ethynyl silver, prepared similarly, are soluble in cold chloroform, carbon tetrachloride, acetone and warm benzene with discolouration, and are insoluble in hexane and ether. Pentynylsilver is soluble in cold pyridine and in hot isopropylamine.

t-Butylethynylsilver is slightly soluble in boiling carbon tetrachloride, benzene and chloroform. Soxhlet extraction with benzene and cyclohexane afforded greyish feathery needles. It is insoluble in ammonia and triethylamine but soluble in cold pyridine and isopropylamine, extraction with the latter solvent giving colourless feathery needles.

Alkyl and Aryl ethynyl mercury(II)compounds $(RC{:}C)_2\,Hg$

These were all prepared by adding the acetylene in alcohol or 1,2-dimethoxyethane in the case of VI and VII (see table I) to alkaline potassium mercuri-iodide e.g. *bisphenylethynylmercury*.

Phenylacetylene (4g., 0.04 mole) in alcohol (10cc.), was added to alkaline potassium mercuri-iodide [mercuric chloride (11.1g., 0.041 mole), potassium iodide (27.5g., 0.165 mole), sodium hydroxide (5g.) in water (200cc.)]. After stirring well for 30 minutes, the white precipitate was filtered, washed with alcohol, and pumped dry. Recrystallisation from methanol afforded bisphenylethynylmercury 5.5g., 92%.

Table 1 lists the mercury derivatives prepared, their solvents of recrystallisation and their melting points. The melting points were compared with those previously reported.

Table 1

Melting Points and Solvents of Recrystallisation for the compounds $(\mathrm{RC{\vdots}C})_2\mathrm{Hg}$

	R·	Solvent of Recrystallisation	Observed m.p.(°C)	Previously reported m.p.
I	Me	benzene	203-204	203-204 [135]
II	Et	ethanol	162-163	162-163 [135]
III	Pr^n	ethanol	119-120	117.9-118.3 [136]
IV	Bu^t	ethanol	92-93	91-92 [135]
V	Ph	ethanol	125-126	124.5-125 [135]
VI	p $\mathrm{NO_2C_6H_4}$	extraction with acetone	dec. $>$260	272-274 [137]
VII	p $\mathrm{BrC_6H_4}$	benzene	255-256(dec.)	256-256.5 [138]
VIII	mesityl- $\mathrm{Me_3C_6H_3}$	propanol	241-242(dec.)	238-239 [136]
IX	PhC:C-	propanol	194-195(dec.)	188-189 [139]

Bisphenylbutadiynylmercury. A complete analysis was made on this compound as it was at first thought that it was a new compound, and also to characterise the rather unstable parent acetylene. (Found: C, 52.3; H, 2.5; Hg; 44.3, 44.8. Calc. for $C_{18}H_{20}Hg$, C, 53.3; H, 2.2; Hg, 44.5%).

CHAPTER IV

COPPER ETHYNYL COMPLEXES WITH TERTIARY PHOSPHINES

Apparatus and Techniques

Preparations of copper (and silver) ethynyl complexes were carried out in a nitrogen atmosphere, with the exception of the triphenylphosphine complexes. Reactions were generally carried out in a double Schlenk tube[140] (Fig. 4 - lower half) with a sintered disc of porosity 3, placed between the two limbs. The reactants were added to and mixed in one limb, any impurities were then filtered off and the compound recrystallised in the other limb, collecting the product on the disc. Occasionally the disc would become blocked with insoluble particles. In such a case, or when it was necessary to transfer a solution to another Schlenk, this could be carried out easily using a Schlenk adapter placed above one limb of the Schlenk as shown in the upper half of the diagram. The solution or suspension was poured through a polythene tube on to the sintered disc ~~B~~ A and filtered into the clean Schlenk. In this way a second filtration could be carried out under nitrogen simultaneous with the transference from one Schlenk to another. Crystallisations were often carried out below room temperature by clamping the limb of the Schlenk containing the solution inside the upper half of a dewar half filled with acetone/CO_2

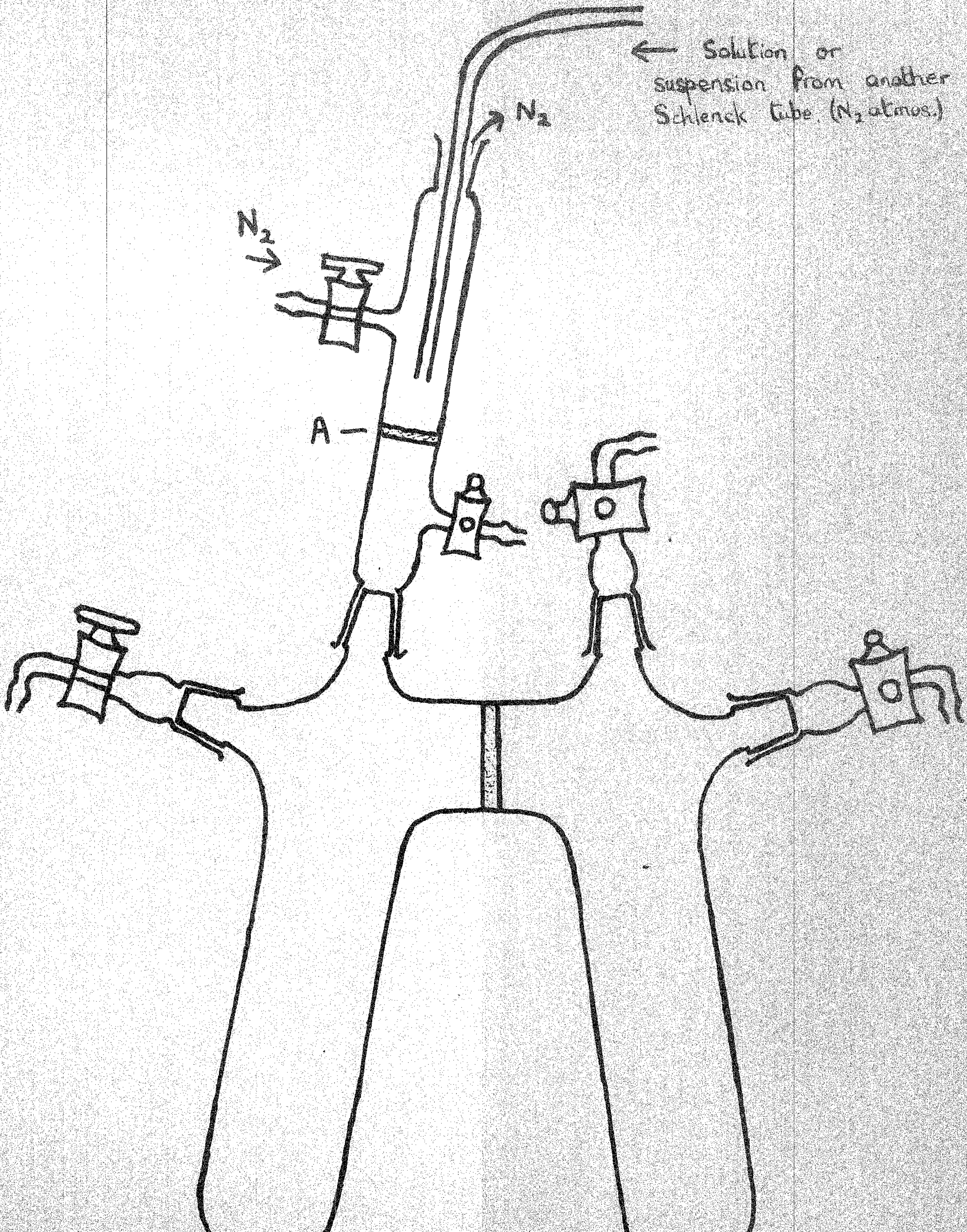

← Solution or suspension from another Schlenck tube. (N_2 atmos.)
N_2
N_2
A

Fig. 4.

at -50° to -78°. The solutions were filtered through the disc while still cold, in order to separate the crystallised product.

Good yields were sometimes sacrificed to ensure a compound was as pure as possible, and so yields are not always given, though they were seldom less than 50%. Melting points are corrected.

Monophosphine-ethynylcopper complexes

Isopropenylethynyl(trimethylphosphine)copper $CH_2{:}CMeC{\equiv}CCuPMe_3$

Isopropenylethynylcopper (4g., 0.031 mole) was suspended in benzene (20cc.) and trimethylphosphine (2.5g., 3cc., 0.034 mole) added. Removal of the benzene, and addition of hexane produced a yellow solution with some brown insoluble oily material which was filtered off. The clear filtrate was cooled to -50°C over acetone/CO_2, affording the crystalline complex (3.5g., 55%), m.p. 82-82.5, (Found: C, 46.8, H 6.9; Cu, 30.8, 30.9. $C_8H_{14}CuP$ requires C, 47.0; H, 6.9; Cu, 31.0%).

t-Butylethynyl(trimethylphosphine)copper $Bu^tC{\equiv}CCuPMe_3$

t-Butylethynylcopper (5g., 0.035 mole) was suspended in benzene (30cc.). Addition of trimethylphosphine (2.8g., 3.5cc., 0.037 mole) changed the colour of the solution from red to yellow-orange. Removal of benzene and recrystallisation from hexane gave a pale yellow-green solid, m.p. 105-106°. (Found: C, 48.9; H 8.45; Cu 28.8. $C_9H_{18}CuP$ requires C, 49.0; H 8.2; Cu 28.8%).

Phenylethynyl(trimethylphosphine)copper PhC⁝CCuPMe$_3$

Phenylethynylcopper (10g., 0.061 mole) was suspended in benzene (30cc.) and trimethylphosphine (4.8g., 6cc., 0.063 mole) was added, shaking well until all the acetylide had dissolved. Removal of the benzene and recrystallising the yellow solid from hot toluene gave yellow needle clusters, with a greenish fluorescence, (12g., 69%), m.p. 116-117° (Found: C, 54.8; H, 6.1; Cu, 261. $C_{11}H_{14}CuP$ requires C, 54.9; H, 5.9; Cu 26.4%). Phenylethynyl(trimethylphosphine)copper is soluble in carbon tetrachloride, benzene and acetone, and is insoluble in hexane.

Phenylethynyl(triethylphosphine)copper PhC⁝CCuPEt$_3$

This complex, reported previously[91,92] was prepared as above and crystallised from hexane as yellow needles. (Found: C, 59.6; H, 7.3. Calc. for $C_{14}H_{20}CuP$ C, 59.5; H, 7.1%).

Phenylethynyl(triphenylphosphine)copper PhC⁝CCuPPh$_3$

Phenylethynylcopper (4.8g., 0.03 mole) was suspended in benzene (20cc.) and triphenylphosphine (8.0g., 0.031 mole) added. The suspension was kept at 70° for 30 minutes, and unreacted phenylethynylcopper (2g.) filtered off. On cooling, the solution deposited a very pale yellow-green solid (7g.). This solid became paler on standing, and on dissolving in hot benzene and leaving the solution to cool, a bright lemon coloured amorphous solid was deposited m.p. 212-214 (decomp.), which would not redissolve in hot benzene, and was almost completely insoluble in all organic solvents. (Found: C, 73.2; H, 6.8; Cu, 14.4, 14.8. $C_{26}H_{20}CuP$ requires C, 73.2; H, 4.7; Cu, 14.9%). I.R. spectra of this complex, and the pale coloured solid were identical.

p-nitrophenylethynyl(triphenylphosphine)copper $p\text{-}NO_2C_6H_4C{\vdots}CCuPPh_3$

p-nitrophenylethynylcopper (2g., 0.01 mole) was added to triphenylphosphine (5.2g., 0.02 mole) in benzene (20cc.). On warming and shaking, all the copper acetylide dissolved. Addition of hexane precipitated orange crystalline needles (3g.), m.p. 222-224°, which were filtered off and dried. (Found: C, 66.0; H, 4.3; Cu, 13.7. $C_{29}H_{19}CuNO_2P$ requires C, 66.2; H, 4.1; Cu, 13.5%). When these crystals were stood in contact with ethanol, in which they were insoluble, they turned into a bright red powdery material which had the same analysis and m.p., (Found: C, 66.2; H, 4.5; Cu, 13.7%), as the orange crystals. This red form dissolved in benzene to give an orange solution from which the orange crystalline form was recovered. Similarly the orange form gave a red solution in nitrobenzene.

The attempted preparations of some other monophosphine complexes

Propynyl(trimethylphosphine)copper

Trimethylphosphine (3.2g., 4cc., 0.04 mole) was added to propynylcopper (4g., 0.038 mole) suspended in benzene (20cc.). Warming of the solution was avoided as decomposition was encouraged.

After shaking for 10 minutes, the solution was filtered and benzene removed from the filtrate. The resulting solid was dissolved in hexane, and on cooling to -50°, a white powder was precipitated. This white solid is the very unstable propynyl(trimethylphosphine)copper. It decomposed immediately on exposure to air, and more slowly in a nitrogen atmosphere.

Addition of dimethylphenylphosphine to propynylcopper in benzene, afforded a red viscous oil, which solidified at low temperatures and was soluble in hexane. On exposure to air it turned black.

Propynylcopper and triphenylphosphine did not react on boiling a suspension in benzene solution.

Reaction between isopropenylethynylcopper and dimethylphenylphosphine.

Dimethylphenylphosphine (4.25g., 4.4cc., 0.024 mole) was added to a benzene (20cc.) suspension of isopropenylethynylcopper (3g., 0.023 mole). Removal of the benzene afforded a red oil containing fine red crystals. Some of the oil dissolved on addition of acetone, the rest (0.5g.) remaining as a red powder, m.p. 135-138° (decomp.). Attempts to recrystallise this solid from various solvents were unsuccessful.

Reaction between t-butylethynylcopper and triphenylphosphine

On addition of triphenylphosphine (3g., 0.0115 mole) in benzene (25cc.) to t-butylethynylcopper (1.5g., 0.0104 mole) in benzene (20cc.) the solution immediately changed from red to yellow. The benzene was pumped off until about 8cc. remained, and the solid which had been precipitated was filtered (4g., m.p. 115-118°). On recrystallising from hexane it had m.p. 145-148°, (Found: C, 70.4; H, 6.6; Cu, 13.3, 14.3. T-butylethynyl(triphenylphosphine) copper, $C_{24}H_{24}CuP$, requires C, 70.8; H, 5.95; Cu, 15.6%). Complexes with triphenylphosphine are difficult to separate from excess triphenylphosphine, because of similar solubility properties. The required complex was probably obtained, but was contaminated with a little triphenylphosphine, which would account for the observed m.p. and analysis.

Reaction between phenylethynylcopper and tri*m*-tolylphosphine

Phenylethynylcopper (1.5g., 9 m mole) was suspended in benzene (25cc.) containing tri*m*totylphosphine (2.6g., 8.6 m mole). The suspension was warmed, shaking vigorously, and after 1 hour phenylethynylcopper (1.2g.) was filtered off. Evaporation of the filtrate gave a brown oil which afforded a pale yellow solid (0.4g., m.p. 125-127), on addition of ethanol. This solid dissolved in hot propanol, and on cooling a bright yellow precipitate, which was soluble in benzene, was formed. An I.R. spectra of this yellow solid indicated that reaction had taken place to a slight extent, forming some phenylethynyl-(tri*m*-tolylphosphine) copper.

Reaction between mesitylethynylcopper and triethylphosphine afforded a yellow complex, recrystallised from hexane, but no satisfactory analysis was obtained though it seemed certain that a 1:1 complex was formed as one equivalent of the phosphine was sufficient to dissolve an equivalent of mesitylethynylcopper suspended in benzene.

Reaction between p-bromophenylethynylcopper and triethylphosphine

p-bromophenylethynylcopper (5g., 0.0204 mole) was suspended in benzene (30cc.) and triethylphosphine (2.49g., 3.12cc., 0.0210 mole) added. Only part of the acetylide dissolved. After filtration, the benzene was removed from the filtrate leaving a yellow solid (m.p. decomp. > 180°). Further triethylphosphine (0.0210 mole) was added to the unreacted acetylide which then afforded more of the yellow solid. These materials were combined in hot hexane, and on cooling the solution to 15° some small yellow crystals separated and were collected (0.8g.). Found Cu, 14.95, 15.2). Further cooling to -50° gave a yellow powder (4.1g.). (Found: Cu, 16.3, 16.4. $BrC_6H_4C{:}CCuPEt_3$ requires Cu, 17.6. $BrC_6H_4C{:}CCu.2PEt_3$ requires Cu, 13.2%.). This investigation was left at this stage to carry out other work. More than one complex was apparently obtained, and the predominate one contained P:Cu ratio > 1.

Reaction between phenylethynylcopper and 1,2-diphenylphosphinoethane.

Phenylethynylcopper (4.1g., 0.025 mole) was suspended in benzene (20cc.), and did not dissolve on addition of 1,2-diphenylphosphinoethane (5.0g., 0.0126 mole) in benzene (20cc.). The benzene was pumped off and replaced by chloroform and the suspension of phenylethynylcopper refluxed for 2 hours. The hot suspension was filtered and on allowing the filtrate to cool a pale cream powder, 2.8g., m.p. 300-304°, was deposited. This material on analysis gave: C, 52.4; H, 4.8; Cu, 8.95, 9.16%. A compound of formula $(PhC\vdots CCu)_2(Ph_2PCH_2CH_2PPh_2)$ requires a larger percentage of these elements. Its infra-red spectrum showed no absorption due to acetylenic stretching. Unreacted phenylethynylcopper (2.8g.) was also recovered from the reaction.

Complexes with P:Cu ratio > 1

t-Butylethynyl(bistrimethylphosphine)copper $Bu^tC\vdots CCu.(PMe_3)_2$

t-Butylethynylcopper (3g., 0.0208 mole) was suspended in benzene (25cc.). On addition of trimethylphosphine (3.36g., 4.2cc., 0.0432 mole) the solution became very pale green. Removal of benzene left a white solid contaminated with some brown impurity. The white solid was readily soluble in hexane, and was recrystallised (3 times) by cooling the hexane solution to -50°. Yield 3g., 48.5%, m.p. 95-98° (sealed tube) (Found: C, 46.4, 46.3; H, 9.1, 9.3; Cu, 21.2. $C_{12}H_{27}CuP_2$ requires C, 48.55; H, 9.2; Cu, 21.4%). The carbon analysis was not improved with further recrystallisations. The complex was more soluble than the monophosphine compound in similar solvents, and much more air-sensitive.

<u>Phenylethynyl(bistrimethylphosphine)copper</u> $PhC{:}CCu(PMe_3)_2$

Trimethylphosphine (3.8g., 4.8cc., 0.050 mole) was added to phenylethynylcopper (4g., 0.024 mole) suspended in benzene (25cc.). The solid obtained on removing the benzene, was crystallised from cyclohexane as pale yellow-green fine crystals (2.5g.) which deepened to a yellow-green solid (m.p. 94-96°) on pumping (45 minutes). (Found: C, 52.9; H, 7.0; Cu, 20.1, 20.0. $C_{14}H_{23}CuP_2$ requires C, 53.1; H, 7.3; Cu, 20.05%).

<u>Phenylethynyl(tristrimethylphosphine)copper</u> $PhC{:}CCu(PMe_3)_3$

Phenylethynyl(trimethylphosphine)copper (2.2g., 0.0093 mole) was dissolved in benzene (25cc.) and trimethylphosphine (1.5g., 1.9cc., 0.02 mole) added to give a pale yellow solution. The benzene was removed and the solid crystallised from cyclohexane as small pale cream crystals which were collected on the sintered disc of the Schlenk tube. After pumping for a few seconds on a water pump, they were dried by blowing a stream of nitrogen through the disc. Yield (2.5g., 67.5%). (Found: C, 51.5; H, 9.4; Cu, 16.3, 16.4. $C_{17}H_{32}CuP_3$ requires C, 52.0; H, 8.2; Cu 16.2%). On pumping this solid it deepened slightly to pale yellow but only a negligible amount of volatile material was collected on a vacuum line.

<u>p-nitrophenylethynyl(bisdiethylphenylphosphine)copper</u>

$p\text{-}NO_2C_6H_4C{:}CCu(PPhEt_2)_2$.

Diethylphenylphosphine (1.9g., 1.9cc., 0.011 mole) was added to p-nitrophenylethynylcopper (2g., 0.01 mole) in benzene (20cc.) a red solution being formed immediately though part of the acetylide remained unreacted, but dissolved on addition of further phosphine (0.011 mole). After filtering off any impurity the benzene was removed until the volume was about 10cc.. Hexane (70cc.) was now added and the violet-red almost black crystals (1.5g., m.p. 75°) settled from the dark red solution, on standing for a few days. Attempts to recrystallise from acetone, methycyclohexane and various solvent combinations were unsuccessful. (Found: C, 61.6; H, 6.6; Cu, 11.7. $C_{28}H_{34}CuNO_2P_2$ requires C, 62.0; H, 6.3; Cu 11.7%).

Attempts to prepare a complex of p-nitrophenylethynylcopper with trimethylphosphine were unsuccessful. Again two equivalents of trimethylphosphine were required to dissolve one equivalent of p-nitrophenylethynylcopper forming an intense, dark-red solution. Some very dark red crystals (0.2g.) were obtained which contained: C, 49.7; H, 6.1. $C_{11}H_{13}CuNO_2P$ requires C, 46.1; H, 6.0. $C_{14}H_{22}CuNO_2P_2$ requires C, 59.55 H, 7.85%.

Mixed ethynyl complexes $RC\vdots CCu.R'C\vdots CCu.2PMe_3$

t-butylethynyl(phenylethynyl)(bistrimethylphosphine)dicopper

t-butylethynylcopper (2g., 0.0138 mole) was dissolved in benzene (30 cc.) and phenylethynylcopper (2.27g., 0.0138) added, followed by trimethylphosphine (0.0276 mole, 15cc. of a standard solution in benzene) which produced an immediate colour change from red to yellow, with solution of all the phenylethynylcopper. Thebenzene was removed, and the solid recrystallised from benzene-hexane, as small yellow crystals, 3g., m.p. 105-111°. A second recrystallisation from toluene-hexane raised the m.p. to 111-112°. (Found: C, 51.8; H, 7.0; Cu, 27.6, 27.7. $C_{20}H_{32}Cu_2P_2$ requires C, 52.05; H, 7.0; Cu 27.5%). An equimolar mixture of phenylethynyl(trimethylphosphine)copper and t-butylethynyl(trimethylphosphine)copper had m.p. 70-75 (dec.) indicating that a new compound and not the equimolar mixture had been isolated. One acetylenic stretching frequency at 2062 $cm.^{-1}$ (KBr disc) was observed in the I.R. The infra red spectra was otherwise identical with that of the equimolar mixture (ν C≡C 2058 $cm.^{-1}$) except that a weak peak at 1898 $cm.^{-1}$, a shoulder at 953 $cm.^{-1}$, and a broad absorption at 500 $cm.^{-1}$ were absent.

Reaction between methylethynylcopper, phenylethynylcopper and triethylphosphine

On addition of triethylphosphine (4.72g., 5.9cc., 0.04 mole) to propynylcopper (2.05g., 0.02 mole) and phenylethynylcopper (3.3g., 0.02 mole) suspended in benzene (30cc.), only the phenylethynylcopper dissolved, methylethynylcopper (2g.) being recovered on filtration. The benzene was removed, and the solid left, recrystallised from hexane gave yellow needles (2.6g.), presumably phenylethynyl(bistriethylphosphine)copper.

Reaction between phenylethynylcopper, isopropenylethynylcopper and trimethylphosphine

Isopropenylethynylcopper (2.5g., 0.02 mole) and phenylethynylcopper (3.3g., 0.02 mole) were suspended in benzene (30cc.), and all dissolved on addition of trimethylphosphine (0.04 mole, 26cc. of a standard solution in benzene). Removal of the benzene left an oily material, difficult to recrystallise, which gave from toluene-hexane solution, a yellow solid (2g.). (Found: Cu, 34.7; 36.4. The mixed complex requires Cu, 28.7; and the isopropenylethynyl and phenylethynyl(trimethylphosphine) complexes require Cu, 31.0, and 26.4% respectively). In view of the difficulty of isolating any pure compound, this reaction was left at this stage.

Phenylbutadiynylcomplexes with trialkylphosphines

Phenylbutadiynyl(trimethylphosphine)copper $PhC\vdots C\cdot C\vdots CCuPMe_3$

Phenylbutadiynylcopper (1.5g., 7.9 m mole) was suspended in benzene (20cc.) in which it dissolved on addition of trimethylphosphine (0.62g., 0.77cc., 8.0 m mole). After removing the benzene, and recrystallising from toluene, the complex was again recrystallised from benzene-methylcyclohexane, (m.p. decomp. > 140°). The pure complex may be recrystallised from benzene. (Found: C, 58.5; H, 5.5; Cu, 23.9, 23.6. $C_{13}H_{14}CuP$ requires C, 58.95; H, 5.3; Cu, 24.0%).

Phenylbutadiynyl(triethylphosphine)copper $PhC{\vdots}C{\cdot}C{\vdots}CCuPEt_3$

Phenylbutadiynylcopper (3g., 0.023 mole) was suspended in benzene (30cc.) and triethylphosphine (2.96g., 3.7cc., 0.025 mole) added. The benzene was pumped off and the yellow-brown residue recrystallised from hexane (4 times) affording yellow needles, m.p. 155-156 (dec.). Recrystallisation may also be carried out from propanol. (Found: C, 62.3; H, 6.7; Cu, 20.5; 20.8. $C_{16}H_{20}CuP$ requires C, 62.6; H, 6.6; Cu, 20.7%).

Bisphenylbutadiynyl(tristriethylphosphine)copper $(PhC{\vdots}C{\cdot}C{\vdots}CCu)_2(PEt_3)_3$

Addition of triethylphosphine (0.461g., 0.52cc., 3.5 m mole) to a suspension of phenylbutadiynyl(triethylphosphine)copper (1.1g., 3.5 m mole), in benzene (20cc.), which was then removed, afforded a yellow solid, soluble in warm hexane recrystallising as pale yellow transparent needles (1g., 78%, m.p. 95-96°). (Found: C, 62.4; H, 7.7; Cu, 17.4, 17.8. $C_{38}H_{55}Cu_2P_3$ requires C, 62.4; H, 7.6; Cu, 17.4%). A small amount was first isolated during a preparation of phenylbutadiynyl(tri~~m~~ethylphosphine)copper, using a slight excess of phosphine. This complex with Cu:P ratio 2:3 loses triethylphosphine on standing in air or on heating a solution in propanol, forming the monophosphine complex.

Phenylbutadiynyl(tri-n-propylphosphine)copper $PhC{\vdots}C{\cdot}CCuPPr^{n}_{3}$

Addition of tripropylphosphine (2.8g., 3.5cc., 17.5 m mole) to a suspension of phenylbutadiynylcopper (3g., 15.9 m mole) in benzene (25cc.) followed by removal of the benzene and recrystallisation of the residue from propanol gave yellow needles (3g., 54%, m.p. 87°). (Found: C, 65.2; H, 7.8; Cu, 18.3,18.3. $C_{19}H_{24}CuP$ requires C, 65.4; H, 7.5; Cu 18.2%).

Infra Red Spectra

Infra-red acetylenic stretching frequencies of the copper complexes are collected in Table 5 , page 124. They were frequently measured in solution in benzene as well as in KBr discs. Carbon tetrachloride and tetrachlorethylene are very transparent in the acetylenic region, but unfortunately they slowly react with aliphatic tertiary phosphines and their complexes Benzene absorbs quite appreciably near 2000 $cm.^{-1}$ but (with slow scanning) was found to be the most suitable solvent.

Two series of complexes were studied in more detail, $RC{:}CCu(PMe_3)_n$, (R = phenyl, isopropenyl). Solutions containing Cu:P in the ratio, 1:1, 1:2, 1:3 and 1:4 were prepared by dissolving the mono phosphine complex (10mg.) in benzene (1cc.) and adding the appropriate amount of trimethylphosphine (as a standard solution in benzene). The samples were introduced, in turn, into a 1 mm KBr cell, a blank of pure benzene in a similar cell being placed in the reference beam of the spectrometer. Table 6 , page 125 , shows the various frequencies. In the case of the isopropenyl series, addition of phosphine was accompanied by a lightening of colour of the solution, and when n = 3 and 4, the solutions were colourless. The t-butylethynyl series of complexes gave only very very weak acetylenic stretching frequencies. Extinction coefficients were calculated for the various absorptions.

SILVER ETHYNYL COMPLEXES

Phenylethynyl(trimethylphosphine)silver $PhC{:}CAgPMe_3$

Trimethylphosphine (0.035 mole, 7 ml. of a solution in hexane) was added to phenylethynylsilver (3.96g., 0.02 mole) suspended in hexane (30cc.). After shaking for 20 minutes the hexane was pumped off and the complex recrystallised from a large volume of acetone as white needles, m.p. dec 130°, (Found: C, 46.5; H, 5.3; Ag, 37.7%. $C_{11}H_{14}AgP$ requires C, 46.3; H, 4.95; Ag, 37.9%). Phenylethynyl(trimethylphosphine)silver is very light sensitive, and should be prepared in subdued light and stored in the dark. In 2.07, 2.29, 3.82 wt.% benzene (ebullioscopically) it has an association of 2.21, 1.82, 2.00.

Reaction between t-butylethynylsilver and trimethylphosphine afforded some fawn needles probably of the 1:1 complex, but no satisfactory analysis was obtained.

CHAPTER V

GOLD (I) ETHYNYL COMPLEXES

PHENYL ETHYNYL GOLD AND ITS COMPLEXES

Preparation of phenylethynylgold $(\mathrm{PhC}\vdots\mathrm{CAu})_x$

The preparation of gold acetylides must be carried out carefully to avoid formation of metallic gold. ~~Auric~~ Gold(III) bromide is reduced with sulphur dioxide to the gold(I) state in an aqueous acetone medium, avoiding the presence of excess SO_2. In aqueous ethanol solution, gold was more easily formed.

An aqueous solution of gold(III)chloride ($HAuCl_4.xH_2O$, 51% Au, 10g., 0.026g., atom gold) was filtered into a 500cc. flanged flask (of the type shown in Fig. 1, without the tap in the bottom of the flask) equipped with a 'vibromixer' stirrer and a gas lead ending just below the stirrer. A filtered aqueous sdution of potassium bromide (15g., 0.115 mole) was added and the volume made up to 200cc. with acetone, so that the acetone and water were present in roughly equal volumes. A slow stream of SO_2 was passed through with vigorous stirring, until the solution turned pale red. The SO_2 was then passed very slowly and stopped when the solution became pale yellow. Phenylacetylene (2.6g., 2.78cc., 0.0255 mole) in acetone (10cc.) was added, followed immediately by excess sodium acetate (c. 25g.

of the hydrated salt in water(100cc.). The initial pale yellow precipitate gradually thickened and after stirring for 30 minutes was filtered, washed with acetone and ether and dried at the pump. Yield of phenylethynylgold, 7g., 91%. (Found: C, 32.0; H, 1.8; Au, 65.2, 65.7. C_8H_5Au requires C, 32.2; H, 1.7%; Au, 66.1%). Phenylethynylgold on heating remains yellow to about 100°, but decomposes gradually above this temperature. It appears to possess no explosive property.

Complexes of phenylethynylgold

The complexes were generally prepared by suspending phenylethynylgold in benzene and adding a slight excess of the donor, followed by removal of the benzene and recrystallisation of the solid from the solvent stated. In most cases warming encouraged decomposition of the complex, with the formation of gold; they were, therefore, generally recrystallised by cooling a solution of the complex at room temperature, to -20° in a "deep-freeze" or to lower temperatures over an acetone/CO_2 bath. Reagents were added under nitrogen, but once the compound had been formed it was handled and recrystallised in air. The complexes must be stored in the cold, and more essentially in the dark. When pure, they are all colourless, and they were obtained in quantitative yields.

Phenylethynyl(ammine)gold $PhC{\vdots}CAuNH_3$

In the presence of ammonia, phenylethynylgold turns to a colourless complex, insoluble in all common solvents. It is best prepared by adding an ammoniacal acetone solution to phenylethynyl(n-octylamine)gold, when it is precipitated as colourless crystals, dec. > 120°. (Found: C, 32.3; H, 2.8, Au, 62.5, 62.3. C_8H_8AuN requires C, 30.5; H, 2.6; Au, 62.5%).

Phenylethynyl(isopropylamine)gold $PhC⋮CAuNH_2Pr^i$

Excess isopropylamine was added to a benzene (10cc.) suspension of phenylethynylgold (1.1g.). The benzene and excess amine were removed and the complex crystallised from acetone as fine colourless needles (1g.). (Found: C, 36.7; H, 4.1; Au, 54.8, 55.1. $C_{11}H_{14}AuN$ requires C, 37.0; H, 3.95; Au, 55.2%). The complex darkens rapidly above 115°, is soluble in hot acetone and benzene, and insoluble in carbon tetrachloride, chloroform, ether and methylcyclohexane.

Phenylethynyl(n-pentylamine)gold $PhC⋮CAuNH_2C_5H_{11}{}^n$

Similarly prepared to the above complex, this was crystallised as white feathery needles by cooling to -20° its solution in 1,2-dimethoxyethane. (Found: C, 40.9; H, 4.8; Au, 51.1, 51.0. $C_{12}H_{16}AuN$ 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 warm acetone, chloroform, and carbon tetrachloride, but insoluble in ether and in hexane.

Phenylethynyl(n-octylamine)gold $PhC⋮CAuNH_2C_8H_{17}{}^n$

Similarly prepared, but more soluble in similar solvents, this complex was crystallised as colourless needles from 1,2-dimethoxymethane, m.p. dec. above 120°. (Found: C, 45.0; H, 5.6; Au, 45.7, 45.8. $C_{16}H_{24}AuN$ 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, 4.42, 5.73 wt. % benzene).

Phenylethynyl(n-nonylamine)gold $PhC{\vdots}CAuNH_2C_9H_{19}{}^n$

This complex crystallised as colourless needles from 1,2-dimethoxyethane, m.p. 117-118° (decomp., and darkening above 105°). (Found: C, 46.6; H, 5.9; Au, 44.6, 44.4. $C_{17}H_{26}AuN$ 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). Both this and the octylamine complex are not sufficiently soluble in nitrobenzene at its freezing point to carry out molecular weight measurements.

Phenylethynyl(di-n-butylamine)gold $PhC{\vdots}CAuNH(C_4H_9{}^n)_2$

Crystallised from acetone as colourless needles m.p. 91-92° (decomp.), a solution of this complex in benzene darkens rapidly and is unsuitable for dipole moment or molecular weight measurements. (Found: C, 45.5; H, 5.7; Au, 46.2, 46.3. $C_{16}H_{24}AuN$ requires C, 40.7; H, 4.2; Au, 51.4%).

Phenylethynyl(pyridine)gold

Excess pyridine was added to phenylethynylgold suspended in 1,2-dimethoxyethane. On cooling to -20°, fawn needles separated, decomp. above 80°. (Found: C, 42.0, 40.1; H, 3.0, 2.6; Au, 52.1, 52.3. $C_{13}H_{10}AuN$ requires C, 41.4; H, 2.7; Au, 52.25%). The pure complex lost pyridine when suspended in benzene and phenylethynylgold (identified by I.R. spectra and gold analysis) was recovered. Phenylethynyl(pyridine)gold is insoluble in most solvents, dissolving on addition of excess pyridine. Pyridine did not replace octylamine from a benzene solution of its phenylethynylgold complex.

Phenylethynylgold and some tertiary amines

Phenylethynylgold dissolved in a benzene solution containing an excess of triethylamine or tributylamine. The solutions darkened rapidly on standing and after 1½ hours a black sludge separated. Phenylethynylgold does not react with bipyridyl.

Phenylethynyl(trimethylphosphine)gold $PhC\vdots CAuPMe_3$

This complex was crystallised as colourless very fine powder from a toluene-hexane mixture, m.p. 190-191° (decomp.). (Found: C, 33.9, H, 3.9. $C_{11}H_{14}AuP$ requires C, 35.3; H, 3.8%). It is insoluble in benzene and difficult to obtain in well defined crystals.

Phenylethynyl(triphenylphosphine)gold $PhC\vdots CAuPPh_3$

This complex was crystallised as very pale cream plates from a benzene-methylcyclohexane mixture, m.p. 163-164° (decomp.) (Found: C, 56.1; H, 3.8; Au, 35.1; M, cryoscopically in benzene

533, 482, 482. $C_{26}H_{20}AuP$ requires C, 55.7; H, 3.6; Au, 35.2%, M, 561. It is soluble in acetone, benzene, chloroform, carbon tetrachloride, slightly soluble in ether, and insoluble in hexane.

Bisphenylethynyl(1,2-diphenylphosphino-ethane)digold

$(PhC{\vdots}CAu)_2Ph_2PCH_2CH_2PPh_2$.

1,2-diphenylphosphino-ethane (0.8g., 2 m mole) was added to phenylethynyl(n-octylamine)gold (1.7g., 4 m mole) in chloroform (20cc.). The solution was filtered to remove any impurity and ethanol added until a precipitate just began to form. On standing, fine white needles (decomp. above 200°) separated and were filtered off. (Found: C, 49.9; H, 3.7; Au, 39.7. $C_{42}H_{34}Au_2P_2$ requires C, 50.6; H, 3.4; Au, 39.6%). It is insoluble in cold benzene, in contrast to the other phosphine and similar complexes.

Phenylethynyl(triphenylphosphite)gold $PhC{\vdots}CAuP(OPh)_3$

This complex was obtained as colourless feathery needles from ethanol, m.p. 113-114°. (Found: C, 50.8; H, 3.2; Au 32.3, 32.0; M, cryoscopically in benzene 548, 596, 578, 596. $C_{26}H_{20}AuO_3P$ requires C, 51.3; H, 3.3; Au, 32.4%; M, 609).

Phenylethynylgold and trialkylphosphites

Phenylethynylgold readily dissolves in benzene solutions of trimethyl or triethylphosphite, but the exceedingly soluble complexes were obtained as oils and attempts to purify them were unsuccessful.

Phenylethynyl(triethylarsine)gold $PhC\vdots CAuAsEt_3$

This complex was isolated both as pale yellow needles and as fine grey needles, in each case crystallising from ether cooled to -25°, m.p. 67-68°. (Found: C, 35.9; H, 4.7; Au, 42.7; M, cryoscopically in 0.46, 0.66, 1.01 wt. % benzene, 474, 484, 460. $C_{14}H_{20}AsAu$ requires C, 36.5; H, 4.6; Au, 42.8%; M, 460).

Phenylethynyl(triethylstibine)gold $PhC\vdots CAuSbEt_3$

On addition of triethylstibine (1 mol.) to phenylethynylgold (3g.) a pale yellow solution was formed. Removal of the benzene left an oily material, difficult to recrystallise, only a small amount of fairly pure material being obtained from propanol. (0.2g., m.p. 96-97°. Found: C, 32.7; H, 3.2. C $C_{14}H_{20}AuSb$ requires C, 33.1; H, 4.0%). A product with identical infra red spectrum was also obtained by displacement of n-octylamine, from its phenylethynylgold complex, by triethylstibine. It was recrystallised from methanol as pale off-white needles, m.p. 60-70°. (Found: C, 31.5; H, 4.5%). Phenyl(triethylstibine)gold is difficult to purify and is not very stable darkening rapidly in air though more slowly under nitrogen. It was handled under nitrogen in a Sohlenck tube.

Phenylethynyl(n-butylisocyanide)gold $PhC\vdots CAuCNBu^n$.

was crystallised from ether as colourless feathery needles, m.p. 40.5-41.5°. (Found: C, 41.0; H, 3.8; Au, 51.5, 51.5; M, cryoscopically in 1.00, 1.50, 1.79, 1.99 wt. % benzene, 386, 409, 417, 412. $C_{13}H_{14}AuN$ requires C, 40.9; H, 3.7; Au, 51.7%; M, 382). It is soluble in chloroform, acetone, benzene and ethanol, and insoluble in hexane.

Phenylethynyl(p-tolylisocyanide)gold $PhC{:}CAuCN\ C_6H_4\underline{p}\text{-}CH_3$ was isolated as 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. $C_{16}H_{12}AuN$ requires C, 46.3; H, 2.9; Au 47.5%).

Phenylethynyl(o-ethylphenylisocyanide)gold $PhC{:}CAuCNC_6H_4\underline{o}C_2H_5$ was crystallised as colourless needles from 1,2-dimethoxyethane, m.p. 107-108°. (Found: C, 47.5; H, 3.4; Au, 45.7; 45.7; M, cryoscopically in 0.95, 1.43, 1.72, 1.91 wt. % benzene, 439, 400, 446, 427. $C_{17}H_{14}AuN$ requires C, 47.55; H, 3.3; Au, 45.9%; M, 429).

With the exception of the amine complexes and that formed by 1,2-diphenylphosphino-ethane, most complexes were freely soluble in organic solvents except saturated hydrocarbons.

Dipole Moment Data

Atom Polarisations are assumed to be 10cc. for each gold atom in the molecule.

$\mathrm{PhC\!:\!CAuPPh_3}$

wt. fraction 10^6 w	Δc(cm)	Specific Volume V	$10^7\Delta$ n
3882	0.561	1.1433	4529
6028	0.759	1.1410	7066
7642	1.032	1.1411	7790
10487	1.512	1.1386	11957
18784		1.1350	21200

$$\alpha = \frac{d\Delta c}{dw} \times 0.06227 \qquad \beta = \frac{dV}{dw} = -0.5507 \qquad \gamma = \frac{dn}{dw} = 0.1132$$

$$= 8.9631$$

Total Polarisation = 1044 cc.

Electron Polarisation = 133.1 cc. $\mu = 6.7$ D.

$\mathrm{PhC\!:\!CAuP(OPh)_3}$

10^6 w	Δ c	V	$10^7\Delta$ n
4402	0.270	1.1422	4167
6803	0.319	1.1411	6522
8609	0.563	1.1402	7790
15440	0.936	1.1364	14312

$$\alpha = 3.7854 \qquad \beta = -0.5305 \qquad \gamma = 0.09529$$

Total Polarisation = 544.6 cc.

Electron Polarisation = 140.9 cc. $\mu = 4.4$ D.

$PhC\vdots CAuAsEt_3$

$10^6 w$	Δc	V	$10^7 \Delta n$
4647	0.708	1.14343	4076
7220	1.087	1.14013	5616
10109	1.493	1.13857	7066
13334	2.069	1.13618	9421
19472		1.13212	13689

$\alpha = 9.4339$ $\beta = -\ 0.6450$ $\gamma = 0.07025$

Total Polarisation = 885.2 cc.

Electron Polarisation = 85.9 cc. $\underline{\mu = 6.2\ D}$

$PhC\vdots CAuCNBn^n$

$10^6 w$	Δc	V	$10^7 \Delta n$
3739	0.965		
4690	1.060	1.14176	
6417	1.422	1.14026	5797
8954	1.985		7247
10367		1.13853	
13324		1.13681	11051
19136			15940

$\alpha = 13.917$ $\beta = -\ 0.5880$ $\gamma = 0.08300$

Total Polarisation = 1062 cc.

Electron Polarisation = 81.2 cc. $\underline{\mu = 6.9\ D}$

$PhC\vdots CAuCNC_6H_4\ o\text{-}C_2H_5$ - See page 57

$PhC\vdots CAuNH_2C_5H_{11}{}^{n}$

10^6 w	Δc	V	$10^7\Delta$n
4354	0.058	1.14217	2174
7390	0.103	1.14010	4348
12850	0.161	1.13593	7609
17104	0.216	1.13391	10690

$\alpha = 0.7784$ $\beta = 0.6290$ $\gamma = 0.05925$

$PhC\vdots CAuNH_2C_8H_{17}{}^{n}$

10^6 w	Δc	V	$10^7\Delta$n
4468		1.14280	
8499		1.14039	4892
12796		1.13916	17971
16703		1.13604	10327
18281			11232
6719	0.109		
9168	0.130		
11595	0.205		

$\alpha = 0.7939$ $\beta = -0.5175$ $\gamma = 0.06200$

$PhC{:}CAuNH_2C_9H_{19}{}^n$

10^6 w	Δc	V	$10^7\Delta n$
5381	0.046		
7365	0.099		
7457		1.14085	4167
10679		1.13910	5797
12978	0.164		
14594		1.13717	7066

$\alpha = 0.7845$ $\beta = -0.5050$ $\gamma = 0.0545$

From m.w. measurements in benzene the degree of association of the amine complexes at an average concentration at which the dielectric constant measurements were made is approximately 2.8. Comparison of the values of α for the amine complexes with those for other complexes shows that the solutions contain much less polar species.

Reactions carried out to investigate the relative donor strengths of various ligands to phenylethynylgold

About 0.5g. complex was dissolved in benzene or 1,2-dimethoxyethane and a slight excess over one equivalent of the appropriate ligand was added. After removal of volatile material (in vacuo), the complex remaining was recrystallised and identified by its melting point and infra-red spectra.

The following reactions were thus demonstrated:

(1) $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ + $\mathrm{PEt_3} \longrightarrow \mathrm{RPEt_3}^{*}$ + octyl$^{\mathrm{n}}$ $\mathrm{NH_2}$

(2) $\mathrm{RAsEt_3} + \mathrm{PEt_3} \longrightarrow \mathrm{RPEt_3}^{*} + \mathrm{AsEt_3}$

(3) RCN$\underline{\mathrm{p}}$-tolyl + $\mathrm{PEt_3} \longrightarrow \mathrm{RPEt_3}^{*}$ + $\underline{\mathrm{p}}$-tolyl NC†

(4) $\mathrm{RP(OPh)_3} + \mathrm{PEt_3} \longrightarrow \mathrm{RPEt_3}^{*} + \mathrm{P(OPh)_3}$

(5) $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ + $\mathrm{AsEt_3} \longrightarrow \mathrm{RAsEt_3}^{*}$ + octyl$^{\mathrm{n}}$ $\mathrm{NH_2}$

(6) $\mathrm{RNH_2}$ pentyl$^{\mathrm{n}}$ + $\underline{\mathrm{p}}$-tolyl NC $\longrightarrow$ RCN$\underline{\mathrm{p}}$-tolyl* + pentyl$^{\mathrm{n}}\mathrm{NH_2}$

(7) $\mathrm{RAsEt_3}$ + $\underline{\mathrm{p}}$-tolyl NC $\longrightarrow$ RCN$\underline{\mathrm{p}}$-tolyl* + $\mathrm{AsEt_3}^{\dagger}$

(8) $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ + $\mathrm{SbEt_3} \longrightarrow \mathrm{RSbEt_3}^{\ddagger}$ + octyl$^{\mathrm{n}}\mathrm{NH_2}$

(9) $\mathrm{RAsEt_3} + \mathrm{SbEt_3} \longrightarrow \mathrm{RAsEt_3}$ unchanged

(10) RCN$\underline{\mathrm{p}}$-tolyl + $\mathrm{P(OPh)_3} \longrightarrow \mathrm{RP(OPh)_3}^{*}$ + $\underline{\mathrm{p}}$-tolylNC†

(11) $\mathrm{RPEt_3} + \mathrm{PPh_3} \longrightarrow \mathrm{RPPh_3}^{\ddagger} + \mathrm{PEt_3}^{\dagger}$

(12) $\mathrm{RPEt_3} + \mathrm{P(OPh)_3} \longrightarrow \mathrm{RPEt_3}$ unchanged

(13) $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ + $\mathrm{Pr^iNH_2} \longrightarrow \mathrm{RNH_2Pr^{i}}^{*}\downarrow$ + octyl$^{\mathrm{n}}$ $\mathrm{NH_2}$

(14) $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ + $\mathrm{NH_3} \longrightarrow \mathrm{RNH_3}^{\ddagger}\downarrow$ + octyl$^{\mathrm{n}}$ $\mathrm{NH_2}$

(15) $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ + pyridine $\longrightarrow$ $\mathrm{RNH_2}$ octyl$^{\mathrm{n}}$ unchanged

R = phenylethynylgold, PhC:CAu

* identified by m.p. and I.R. spectrum

‡ identified by I.R. spectrum

† identified by smell

TERTIARYBUTYLETHYNYLGOLD AND SOME DERIVATIVES

Preparation of t-butylethynylgold $Bu^tC:CAu$

This was prepared by the method used for phenylethynylgold. t-Butylacetylene (2.06g., 2.7cc., 0.0258 mole) was added to the solution after the reduction of gold(III) chloride (10g. hydrate), followed by sodium acetate (25g.) in water (100cc.). A pale yellow precipitate formed and gradually thickened. Water was then added until the flask was almost full, and after stirring for 30 minutes the solid was filtered off, washed with water and dried in vacuo. Yield: 6g., 77%). t-Butylethynylgold can be crystallised from propanol as small fine crystals, decomp. above 150°, or from hexane (by cooling a solution over acetone/CO_2). (Found: C, 26.2; H, 3.3; Au, 70.6, 70.5; M, ebullioscopically in 1.48, 2.46, 2.93, 3.47, 4.47 wt. % benzene, 1166, 1192, 1154, 1118, 1112. $(C_6H_9Au)_4$ requires C, 25.9; H, 3.3; Au, 70.9%, M, 1113). It is soluble in benzene, chloroform and hexane, slightly soluble in acetone and insoluble in methanol.

Frequently on recrystallising the crude material, some remained insoluble in the boiling solvent and was recovered as a purplish-white powder, insoluble in most organic solvents. It appears to be a more polymeric form of t-butylethynylgold, and on addition of trimethylphosphine to an ether suspension it afforded a complex identical (mixed m.p. and infra-red spectrum) with that from the tetramer.

t-Butylethynyl(ammine)gold $\mathrm{Bu^tC\vdots CAuNH_3}$

Addition of excess ammonia to $\mathrm{(Bu^tC\vdots CAu)_4}$ (2g.) suspended in acetone (20cc.) gave a white precipitate which dissolved on warming. The hot filtered solution deposited colourless feathery needles (1.0g.), and a further 0.5g. were recovered after concentration of the mother liquor, decomp. above 155°. (Found: C, 25.4; H, 4.2; Au, 66.5, 66.6; N, 4.66. $\mathrm{C_6H_{12}AuN}$ requires C, 24.4; H, 4.1; Au, 66.8; N, 4.74%). A solution in boiling benzene loses ammonia to give t-butylethynylgold.

t-Butylethynyl(trimethylphosphine)gold $\mathrm{Bu^tC\vdots CAuPMe_3}$

Addition of trimethylphosphine (3.65 m mole in ether 5cc.) to a solution $\mathrm{(Bu^tC\vdots CAu)_4}$ (1g., 0.9 m mole) in benzene (10cc.) discharged the yellow colour immediately. Removal of benzene and recrystallisation from a 1,2-dimethoxyethanehexane mixture afforded colourless plates, 1g., m.p. 194-196° (decomp). (Found: C, 30.4; H, 5.1; Au, 55.7; 55.8. $\mathrm{C_9H_{18}AuP}$ requires C, 30.5; H, 5.1; Au, 55.6%).

t-Butylethynyl(triphenylphosphine)gold $\mathrm{Bu^tC\vdots CAuPPh_3}$

Addition of triphenylphosphine in benzene to a benzene solution of t-butylethynyl(ammine)gold, followed by removal of benzene, and crystallisation of the solid remaining from a 1,2-dimethoxyethane-hexane mixture afforded $\mathrm{Bu^tC\vdots CAuPPh_3}$ as colourless crystals, m.p. 192-195° (decomp.). (Found: C, 52.3; H, 4.4. $\mathrm{C_{24}H_{24}AuP}$ requires C, 51.4; H, 4.3%).

Other reactions of phenylethynylgold

The reaction between phenylethynylgold and phosphine

Phenylethynylgold (2.166g.) was suspended in benzene (25cc.) and phosphine (from Zn_3P_2 and dil. H_2SO_4) bubbled through the stirred suspension, which turned orange, though no colour was imparted to the benzene. The suspension was filtered (N_2 atmosphere) and the solid washed with benzene, and analysed: C, 2.9; H, 2.1; Au, 84.8, 85.4%. H_2AuP requires C, 0.0; H, 0.88%; Au, 85.7%. Yield: 1.59g., 95.2%. It was insoluble in all common solvents and was fairly air-stable. All the absorption frequencies in the infra-red spectrum could be attributed to phosphorus-hydrogen linkages.

The filtrate from the reaction was distilled until half the benzene and any free phosphine had been removed. It was then added to ammoniacal copper(I) chloride solution giving phenylethynylcopper (1.09g.), corresponding to 95% of the phenylethynyl group present in the starting material. The benzene layer, now free from phenylacetylene was reduced to dryness, there being no residue. This experiment is consistent with the reaction

$$PhC{\vdots}CAu + PH_3 \longrightarrow PhC{\vdots}CH + (AuPH_2)_x$$

t-Butylethynylgold and phosphine react similarly.

The reaction between quaternary ammonium or phosphonium iodides and PhC⋮CAu

Phenylethynylgold and tetraethylammonium iodide

Phenylethynylgold (4g., 13.4 m mole) was suspended in ethanol (10cc.). On addition of tetraethylammonium iodide (3.5g., 13.6 m mole) the suspension was replaced by a mixture of a grey crystalline precipitate and gold powder, which was then filtered off and extracted with hot acetone, gold (1.3g., 50%), and colourless needles (1.8g.) which crystallised from the acetone on cooling, being recovered. The colourless needles contained: C, 58.9; H, 5.64; Au, 32.7, 32.9%, but no iodine, and had m.p. 198-200° (decomp.). The ethanolic filtrate from the reaction afforded unreacted tetraethylammonium iodide (1.3g., m.p. 312°).

A similar reaction gave fine colourless crystals (m.p. 174-176° (decomp.) from acetone) containing, on analysis, Au, 26.1, 26.8%. The compound from the two first had absorption due to acetylenic stretching, at approx. 2141 and 2096 cm.$^{-1}$. The second compound had one only, at 2146 cm.$^{-1}$.

The compound $(PhC{\vdots}C)_2AuNEt_4$, if formed would require C, 54.4; H, 5.7; Au, 37.2%.

Phenylethynylgold and trimethylphenylphosphonium iodide

On addition of trimethylphenylphosphonium iodide (2.8g., 10 m mole) in methanol (20cc.) to a suspension of phenylethynylgold

(3g., 10m mole) in methanol (10cc.), the phenylethynylgold dissolved and gold (1g.) was precipitated and filtered off. Removal of the methanol from the filtrate, and recrystallisation of the solid thus obtained from an acetone-ethanol mixture afforded small white needles, 1g., m.p. 149-150°. (Found: C, 59.7; H, 4.4; Au, 25.5. $(\mathrm{PhC{:}C})_2\mathrm{AuPMe}_3\mathrm{Ph}$, if formed, requires, C, 54.3 H, 4.2; Au, 35.8%.). This solid had one acetylenic frequency at 2144 cm.$^{-1}$.

DISCUSSION

CHAPTER VI

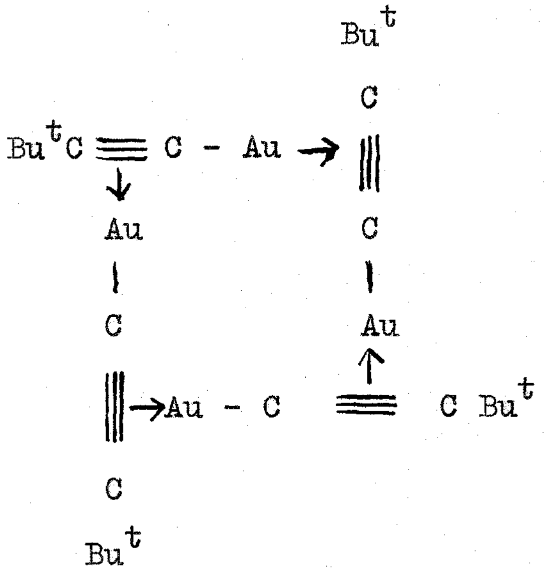
DISCUSSION

Copper(I), Silver(I) and Gold(I) derivatives of monoacetylenes $\mathrm{RC{\vdots}CM}$.

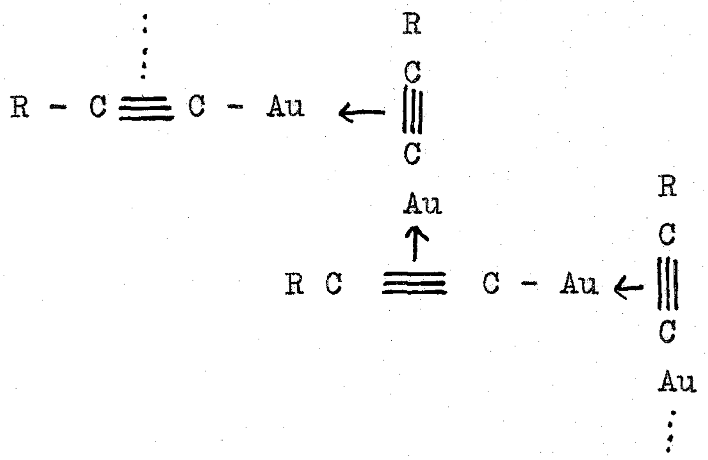
The structure of the polymeric copper and silver ethynyls $\mathrm{RC{\vdots}CCu(Ag)}$ is still unknown. With the exception of t-butylethynylcopper which is octameric ebullioscopically in benzene, this figure agreeing with the cryoscopic values obtained by other workers,[92,141] all the copper acetylides are insoluble in all common organic solvents other than those with which they react (e.g. some amines). A possible structure has been suggested,[1] as described earlier, but any experimental evidence may not be forthcoming for some time since it is exceedingly difficult to obtain sufficiently well-defined crystals suitable for X-ray crystal structure determinations. The copper and silver ethynyls were prepared by the well-established methods, as powders which required prolonged pumping, in vacuo, to dry them. The arylethynylcopper compounds were in general slightly soluble in isopropylamine and diethylamine; the complexes formed are only weak and extraction of phenylethynyl- and mesitylethynyl copper by these amines in a Soxhlet apparatus in a nitrogen atmosphere, afforded micro-crystalline material, extraction being slower with the secondary amine. Further extractions with isopropylamine by Mr. P. W. R. Corfield[142] of this department afforded similar crystals which unfortunately were "twinned" and, thus, unsuitable for detailed X-ray study. Repetition of the work of F. Straus who obtained[133] phenylethynylcopper as "a fine mass of yellow crystalline needles" from copper(II) phenylpropiolate in the presence of various amines only provided powdery solids.

Some of the alkylethynylsilvers are moderately soluble in certain organic solvents, in particular in chloroform, carbon tetrachloride and acetone. t-Butylethynylsilver, the most soluble silver ethynyl, was extracted with benzene, cyclohexane, isopropylamine and diethylamine, some decomposition resulting in the higher boiling solvents, but in all cases feathery needles were obtained.

The only goldethynyl hitherto described is the unstable acetylide Au_2C_2. A general method developed to prepare goldethynyls $(R\cdot C\vdots CAu)_x$ consists of adding the acetylene and sodium acetate solution, to a freshly reduced solution of gold(III) chloride containing sodium bromide, and has been used to prepare the new compounds, phenylethynylgold(I) and t-butylethynylgold(I). Phenylethynylgold, a yellow powder, resembles its copper analogue in appearance and is presumably a similar co-ordination polymer. It is insoluble in common organic solvents, but differs in being soluble in and forming isolatable complexes with a considerably greater variety of donor solvents, and is no doubt a typical gold(I)ethynyl. t-Butylethynylgold is also similar to its copper analogue in that it is soluble in many organic solvents, but whereas t-butylethynylcopper is octameric ebullioscopically in benzene the pale-yellow gold compound is tetrameric. If the co-ordination number of the gold is two, as is most common for gold(I), the compound is likely to have the square structure



An insoluble form of t-butylethynylgold was also obtained as a pale purplish-white powder (the colour almost certainly being due to a trace of metallic gold) which is probably a polymer of similar structure to that of phenylethynylgold:



The infra-red spectra of the two forms were almost identical, with slight difference in the acetylenic stretching region (Table 8, page 128).

These organic group IB ethynyls could not be made to explode, including the pale yellow paranitrophenylethynylsilver which is reported[134] to explode on heating. It appears that only the acetylides, M_2C_2, (M = Cu, Ag, Au) and the derivatives of monohaloacetylenes XC⋮CM (X = halogen, M = Cu, Ag, no gold compounds are yet described) possess this property.

Co-ordination complexes of copper(I), silver(I) and gold(I) ethynyls

Ethynylcopper(I) complexes with tertiary phosphines

Difficulties due to the inconveniently high solubilities of the triethylphosphine complexes reported previously[92] were largely overcome by the use of trimethylphosphine, the more symmetrical molecule usually resulting in higher melting points and lower solubilities.

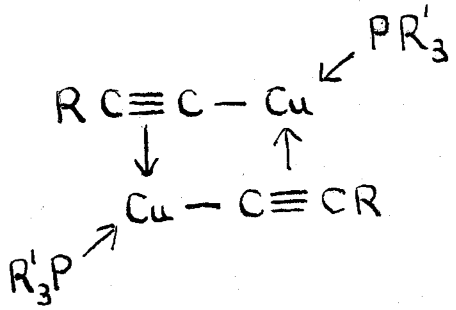
The yellow monophosphine complexes (Table 2a) prepared by addition of the required amount of the tertiary phosphine to a suspension of the insoluble copper ethynyl in an organic solvent,

TABLE 2a

Degree of association of mono-phosphine complexes

	cryoscopically				ebullioscopically	
	in benzene		in nitrobenzene			
	wt.%	n	wt.%	n	wt.%	n
$CH_2:CMeC\vdots CCuPMe_3$	1.77	3.34	1.23	2.12		
	2.18	3.28	1.90	2.31		
	2.49	3.37	2.34	2.24		
	2.66	3.39	2.64	2.16		
			2.85	2.04		
					in acetone	
$Bu^tC\vdots CCuPMe_3$	2.78	2.67	1.65	2.01	0.50	2.4
	3.35	2.79	1.94	2.04	1.00	2.6
	3.84	2.73	2.29	1.99		
	4.20	2.74	2.49	2.05		
					in benzene	
$PhC\vdots CCuPMe_3$	0.91	2.60	0.39	1.94	1.59	3.18
	1.81	2.75	0.41	1.99	1.80	2.62
	2.41	2.80	0.53	2.04	3.01	2.67
	2.91	2.79	0.61	2.06	3.80	2.62
	3.07	2.70	0.73	1.88		
	6.36	2.70	0.99	2.05		
$PhC\vdots CCuPEt_3$	0.68	2.93	0.44	2.00		
	1.16	2.70	0.97	2.02		
	1.27	2.54	1.50	1.89		
	2.00	2.64	2.05	2.03		
	2.63	2.70				
$PhC\vdots CCuPPh_3$	too sparingly soluble					
$\underline{p}NO_2C_6H_4C\vdots CCuPPh_3$	1.14	2.10	0.39	1.12		
	1.77	2.07	0.49	0.94		
	2.18	2.02	0.64	0.92		
	2.44	1.96	0.76	1.14		

followed by filtration and crystallisation, are usually dimeric in nitrobenzene and slightly associated in benzene (between 2.6 and 3.3). The nitrobenzene solutions may well contain dimer molecules of structure



in which case the copper atoms have the co-ordination number three. It could also be possible that the solvent acts as a donor as well as ethynyl groups thus allowing the more usual four-co-ordination. *para*Nitrophenylethynyl(triphenylphosphine)copper is exceptional in being monomeric in nitrobenzene and dimeric in benzene. It is unlikely that nitrobenzene could behave as a donor of sufficient strength to break the dimer. This complex was obtained in two modifications. In non-polar solvents it formed orange solutions, from which orange crystals were recovered; on allowing these crystals to stand in contact with ethanol in which they are insoluble, they gave a powdery red material. Unfortunately yellow-green phenylethynyl(triphenylphosphine)copper is too sparingly soluble for molecular weight

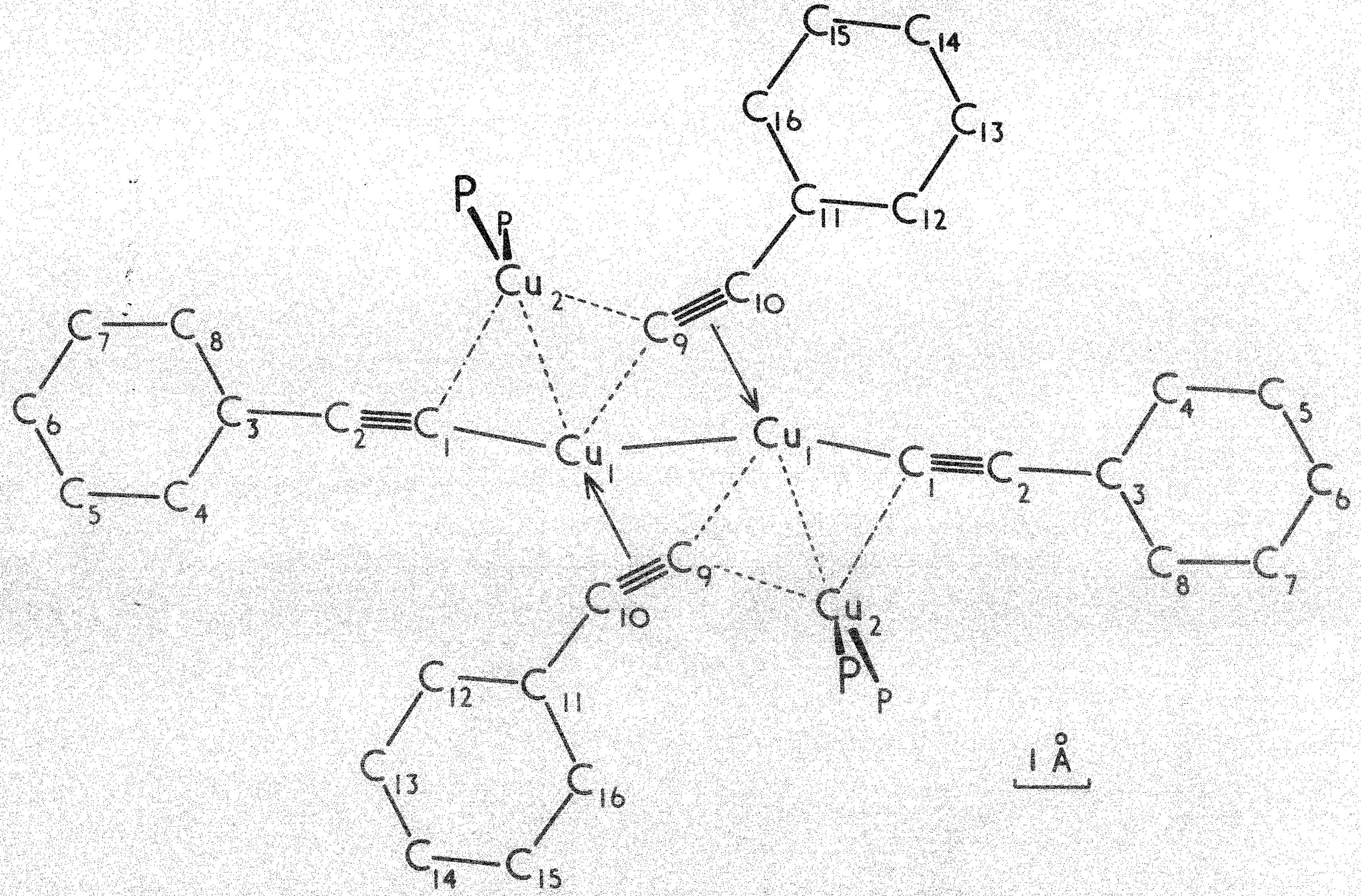


Fig. 5. – The phenylethynyl(trimethylphosphine) copper (I) tetramer
(after CORFIELD and SHEARER)

determinations. These triphenylphosphine complexes are air-stable unlike the trialkylphosphine complexes. Propynylcopper did not form a triphenylphosphine complex and did not readily yield isolable phosphine complexes. The complexes isolated were very air sensitive and exceedingly soluble in hexane, but they dissociate in the absence of an excess of the phosphine. The stability of the trimethylphosphine complexes ($Me_3PCuC{\vdots}CR$, R = Me, Bu^t, Ph, isopropenyl) isolated increases in the order Me $\ll$ isopropenyl $<$ Bu^t $<$ Ph.

The structure (Figure 5 opposite) of the complex $PhC{\vdots}CCuPMe_3$ has been examined crystallographically by Dr. H.M.M. Shearer and Mr. P.W.R. Corfield of this department. It contains tetrameric units $(PhC{\vdots}CCuPMe_3)_4$ each with a zig-zag chain of four copper atoms; two phosphine molecules are bound to each of the terminal copper atoms, the central two atoms being not co-ordinated to phosphorus. Two of the four acetylene groups have a different environment from the other two. Apart from the phosphine groups (the methyls not being shown in the figure) which lie above and below the plane of the paper the structure is nearly flat. The acetylene groups are bent, particularly those (C_9 and C_{10}) which form "broadside-on" π bonds to copper. The other kind are clearly σ-bonded to the copper together with some "end-on" π bonding. The environment of Cu_2 is roughly trigonal (with respect to the phosphines and Cu_1 and tetrahedral) with respect to the phosphines and carbon atoms C_1 and C_9. The copper atoms Cu_1 appear to have five ligands in a plane but if the possibility of Cu-Cu bonding is ignored although the Cu-Cu distances are close to those in metallic copper, then Cu_1 can be regarded as trigonally co-ordinated and Cu_2 as tetrahedrally co-ordinated.

Several bisphosphine complexes were isolated though they were more difficult to purify. They support further the view that ethynylcopper(I) complexes are co-ordination polymers in which polymerisation is reduced by tertiary phosphines successfully competing with ethynyl groups as ligands. When two phosphine groups are co-ordinated to each copper atom the complexes are monomeric and 3 covalent. (Table 2b).

TABLE 2b

Degree of association cryoscopically, bisphosphine Complexes

	in benzene		in nitrobenzene	
	wt.%	n	wt.%	n
$Bu^tC{\equiv}CCu(PMe_3)_2$	0.31	1.00	0.18	0.43
	0.71	0.98	0.62	0.75
	1.41	0.98	1.13	0.88
	1.85	0.98	1.47	0.84
$PhC{\equiv}CCu(PMe_3)_2$	0.63	0.98	0.53	0.93
	0.86	1.12	0.78	1.00
	1.17	1.35	1.09	0.95
	1.71	1.37	1.34	0.98
$\underline{p}\text{-}NO_2C_6H_4C{\equiv}CCu(PPhEt_2)_2$	0.61	0.57	0.32	0.38
	0.94	0.63	0.50	0.26
	1.28	0.69		

The t-butylethynyl complex dissociates in nitrobenzene solution, though if nitrobenzene was acting as a donor and partially replacing the phosphine, the same cryoscopic result would be obtained. However the paranitrophenylethynyl complex is dissociated in both benzene and nitrobenzene. Dissociation could also be responsible for the t-butyl and phenyl complexes melting over a range of several degrees.

Progressive addition of tertiary phosphine causes a marked lightening of colour. For example, t-butylethynylcopper which is orange-red yields a yellow-green mono(trimethylphosphine) complex and a colourless bisphosphine complex.

In the case of the aliphatic ethynylcoppers and of phenylethynylcopper, to dissolve a certain amount of the ethynyl in benzene, one equivalent of an aliphatic phosphine is required. paraNitrophenylethynylcopper appears to be exceptional and two equivalents of the phosphine are required - apparently the bisphosphine complex is more stable than the monophosphine complex (which was never isolated) and is formed in preference. paraBromophenylethynylcopper, although not studied in detail, behaves similarly, two equivalents of triethylphosphine being required to dissolve a given amount of the ethynyl. It seems that the electrophilic nature of the nitro and bromo groups draws electrons from the copper atom which can then more readily accept two phosphine molecules. If this is a likely explanation then mesitylethynylcopper might be expected to form a 1:1 complex as phenylethynylcopper does, and in fact a known weight of mesitylethynylcopper dissolved readily in benzene on addition of one equivalent of trimethylphosphine.

One trisphosphine complex $PhC{:}CCu(PMe_3)_3$ was isolated, but it dissociated in solution and had a strong smell of trimethylphosphine. It is presumably monomeric and analagous to the previously reported[34] isocyanide complex $PhC{\vdots}CCu(CN\underline{p}\text{-}tolyl)_3$.

The presence of ethynyl groups in two different environments in the complex $(PhC{:}CCuPMe_3)_4$ suggests that it should be possible to prepare a complex of the type $[R\ C\ CCu,\ R'C{:}CCu(PMe_3)_2]_2$ in which two ethynyl radicals are incorporated into the molecule. This was achieved in one case where R = Ph, $R' = Bu^t$, and the complex had a sharp melting point between those of the two complexes $PhC{\vdots}CCuPMe_3$ and $Bu^tC{\vdots}CCuPMe_3$. An equimolar mixture of these two complexes melted thirty degrees lower with decomposition and so confirmed that a new compound and not the equimolar mixture had been prepared.

TABLE 2c

Association, cryoscopically, of $PhC{\vdots}CCu\ Bu^tC{\vdots}CCu\ 2PMe_3$

in benzene		in nitrobenzene	
wt.%	n	wt.%	n
1.69	1.44	1.14	0.96
2.54	1.44	1.71	1.00
3.05	1.42	2.05	1.02
3.39	1.38	3.28	0.96

Molecular weight measurements (Table 2c) correspond to those found for $[PhC{\vdots}CCuPMe_3]_4$ and presumably the complex has a similar structure to the tetramer in which two of the phenyls are replaced by t-butyl groups.

It is interesting to note that when 2 mols. of triethylphosphine are added to an equimolar suspension of propynylcopper and phenylethynylcopper in benzene, the propynylcopper remained unchanged, phenylethynylbistriethylphosphinecopper being formed. To prepare a mixed complex of the above type it therefore seems necessary that there must be a minimum difference between the stabilities of the related constituent complexes.

The diacetylene complexes $PhC\vdots C\cdot C\vdots CCuPR_3$ (R = Me, Et, Pr^n) prepared were unexpectedly found to be less air-sensitive than the monoacetylene compounds. In contrast the diacetylenes (e.g. $PhC\vdots C\cdot C\vdots CH$ which decomposes above 0°C) are much less stable than the monoacetylenes. Whereas $PhC\vdots C\cdot$[illegible]$CuPEt_3$ reverted to yellow amorphous $PhC\vdots CCu$ after exposure to air for a few days the corresponding butadiynyl complex decomposed slowly over several months and the trimethylphosphine complex appeared unchanged after a year. Molecular weight measurements (Table 2d) indicate that they are associated similarly to the monophosphine complexes.

An interesting complex with a Cu:P ratio 2:3 was characterised. It was isolated in an unsuccessfull attempt to prepare a bisphosphine complex over which it would therefore seem to possess extra stability. It loses triethylphosphine

TABLE 2d

Association, cryoscopically, of phenylbutadiynyl complexes $\mathrm{PhC{\vdots}C{\cdot}C{\vdots}CCuL}$

L	benzene		nitrobenzene	
	wt. %	n	wt.%	n
PMe_3	too sparingly soluble			
PEt_3	1.10	3.27	1.13	1.97
	1.40	3.29	1.75	2.04
	1.71	3.05	2.15	2.11
	1.77	3.23	2.43	2.13
PPr_3^n	2.52	3.36	1.05	2.00
	3.78	3.19	1.40	2.00
	4.54	3.11	1.68	2.04
	5.09	3.01	2.11	1.95
$(PEt_3)_{\frac{3}{2}}$	0.91	0.71	0.57	0.91
	1.31	0.51	0.99	1.03
	1.64	0.63	1.49	0.95
	1.82	0.69	1.87	0.96

on standing in air or on heating a solution in propanol, giving the monophosphine complex and from an x-ray study Dr. Shearer and Mr. Corfield confirm this Cu:P ratio. They report that the space group is similar to that of $\mathrm{(PhC{\vdots}CCuPMe_3)_4}$ and the data are consistent with a structure different from that of $\mathrm{PhC{\vdots}C{\cdot}CuPMe_3}$ only in that three instead of two phosphine groups are bound to the terminal copper atoms (Cu_2 in figure 5) of the Cu_4 chain. In nitrobenzene this complex dissociates as a dimer [i.e. $\mathrm{(PhC{\vdots}C{\cdot}C{\vdots}CCu)_2(PEt_3)_3}$, with two copper atoms per molecule] and it is more extensively dissociated in benzene. (Table 3d).

Silverethynyl complexes

Little work was carried out on silver complexes as previous preliminary investigations[1] showed them to be similar to their analagous copper complexes. They also seem to be less easy to purify than the copper compounds which is probably chiefly due to the fact that they are quite sensitive to light. Phenylethynyl(trimethylphosphine)silver $PhC{:}CAgPMe_3$ which is less soluble than its copper analogue, is dimeric ebullioscopically in benzene.

Co-ordination compounds of gold(I) ethynyls

The first gold(I)ethynyl complex, the phosphine complex $PhC{:}CAuPEt_3$, was prepared[146] from bromo(triethylphosphine)-gold(I) and phenylethynyllithium. The reaction between phenylethynylgold and triethylphosphine gave an identical complex confirming the isolation of phenylethynylgold. By similar direct reactions between phenylethynylgold and donor molecules it has been possible to prepare a range of complexes many of which could not have been obtained by the reaction of an organolithium reagent on a gold(I) halide. In this way complexes of phenylethynylgold with ammonia, primary and secondary amines, tertiary phosphines arsines and stibines, phosphites and *iso*cyanides were prepared.

The complexes with triphenylphosphine, triphenylphosphite, triethylarsine, n-butylisocyanide and *o*-ethylphenylisocyanide, are monomeric in benzene as would be expected for gold(I) compounds. The complex with triethylstibine was air-sensitive and unstable, and no molecular weight measurements were carried out, but it would be surprising if it were not monomeric too. Phenylethynyl(triethylphosphine)gold has been previously reported to have an association of 1:1 to 1.2 in nitrobenzene and about 1.3 in benzene.[122] A diphosphine complex was also obtained, in which 2 molecules of phenylethynylgold give $PhC{:}CAu \longleftarrow PPh_2CH_2CH_2Ph_2P \longrightarrow AuC{:}CPh$ This complex was less soluble than the other phosphine complexes, being insoluble in cold benzene.

These monomeric complexes, in which the Au-C and P-Au bonds are co-linear, are particularly suited to dipole moment measurements. The dipole moments (Table 3) are with the exception of the triphenylphosphite complex, in the range 6.2 - 7.1 D.

TABLE 3

Dipole moments of some phenylethynylgold(I) complexes

$Ph_3PAuC\vdots CPh$	6.7
$(PhO)_3PAuC\vdots CPh$	4.4
$Et_3AsAuC\vdots CPh$	6.2
$Bu^nNCAuC\vdots CPh$	6.9
o-$C_2H_5C_6H_4NCAuC\vdots CPh$	7.05
* $Et_3PAuC\vdots CPh$	6.55

included for comparison

* Et_3PAuMe	5.5
* Ph_3PAuMe	5.6
* Et_3PAuEt	5.5

* measured by Dr. P. Dixon

The triphenylphosphite complex is peculiar, particularly if the moment of triphenylphosphite itself is in the same direction as triphenylphosphine, i.e. $\overset{-}{P} - \overset{+}{C}$ which is likely. The effect of changing Et_3P by Ph_3P causes an increase in moment of 0.15D which is similar to the increase on going from Et_3PAuMe to Ph_3PAuMe, but which is not in the expected sense, as triphenylphosphine is known to be a better electron-acceptor than triethylphosphine and this would tend to decrease the dipole. The _o_-ethylphenylisocyanide complex might also be expected to have a lower moment than n-butylisocyanide complex instead of the observed increase of 0.15D. In this region of 7D the observed moments are particularly accurate, having an error not greater than 0.02D.

Phenylethynylgold forms a stable colourless ammine $(PhC\equiv CAuNH_3)_x$ in the presence of ammonia analagous to the less stable phenylethynyl(ammine)copper. It is insoluble in all common organic solvents. Crystalline complexes with four primary aliphatic amines were isolated. The isopropyl and n-pentylamine complexes were too sparingly soluble for molecular weight determinations suggesting they may be associated in some way and the n-octyl- and n-nonylamine complexes had apparant degrees of association, which increased with concentration, in the range 2.6 - 4.1. Ebullioscopic methods are impracticable since the amine complexes, the least thermally stable of the phenylethynylgold complexes isolated, decompose fairly quickly in solution on warming and the solutions darken slowly at room temperature. Since benzene solutions of these complexes evidently contain two or more molecular species it is not possible to calculate dipole moments, however dielectric measurements of their benzene solutions indicate the presence of species which are much less polar than the other complexes studied. The acetylenic stretching frequencies (see page 117) in these complexes are similar to those found in the monomeric complexes, and suggest that the acetylenic group is not involved to any appreciable extent in co-ordination to gold to make up a polymeric structure. The co-ordination number of the gold is evidently greater than two.

Complexes with the secondary amines, di-n-butylamine and piperidine were characterized. The piperidine complex was soluble in benzene, and solutions of the di-n-butylamine complex turned red very readily, depositing a black sludge and rendering them useless for molecular weight or dipole moment determinations. The only tertiary amine to yield an isolatable complex was pyridine, and the complex reverted to phenylethynylgold when placed in organic solvents containing no excess pyridine. Aliphatic tertiary amines dissolve benzene suspensions of phenylethynylgold giving solutions which darken readily and deposit gold.

The relative donor strength of the various ligands, mentioned so far, towards phenylethynylgold was established by a series of displacement reactions given in detail on page 96 .The resulting order was found to be

PPh_3 > PEt_3 > $P(OPh)_3$ > *p*tolylNC > $AsEt_3$ > $SbEt_3$

> ammonia, primary and secondary amines > tertiary amines

It is also almost certain that $NH_3 > RNH_2 > R_2NH$, the secondary amine complexes showing a markedly lower stability than primary amine complexes. It is interesting that triphenylphosphine will replace triethylphosphine from its complex, triphenylphosphine being a stronger π acceptor; the series in fact appears to be largely determined by the extent to which the ligand is able to accept electrons from the gold *d* orbitals. In this respect, it is interesting to note the position of the isocyanide ligand and that triethylstibine will replace amines.

Several other ligands were tried as donors to phenylethynylgold. Trimethylphosphite and triethylphosphite gave complexes which were oils at room temperature. Diethylsulphide, diphenylacetylene methyl and phenylcyanide and carbon monoxide at atmospheric pressure did not yield complexes. Phenylethynylgold was extracted slowly by dimethylsulphide (using a Soxhlet apparatus) but the resulting solution continually deposited gold. Phosphorus(III) chloride, which has been seen to be a better co-ordinating ligand than the alkylphosphines to some metals in low valency states[143] due to its greater acceptor properties, did not appear to form a complex with phenylethynylgold.

Since fairly weak donors such as triethylstibine form complexes with phenylethynylgold, it might be expected that, quaternary ammonium and phosphonium iodides would give salts of the type $[Et_4N]^+ [PhC{:}CAuI]^-$ in which the iodine acts as a donor. Phenylethynylgold does in fact dissolve in cold alcoholic solutions of these iodides, but the white crystalline solids obtained from these solutions (together with some gold metal) did not contain iodine. Analytical data did not agree with another possible compound $[R_4N(P)]^+ [(PhC{:}C)_2Au]^-$ and more than one product may result from this reaction.

Phosphine, itself, did not give a complex of phenylethynylgold but acted as an acid to give polymeric $(AuPH_2)_x$ which is insoluble in all common inert solvents, and darkens on keeping. In view of this and of recent work[144] on the reaction of palladium complexes with secondary phosphines, it would be interesting to look at the reaction of phenylethynylgold with primary and secondary phosphines.

A few complexes of the other gold ethynyl prepared, t-butylethynylgold, were isolated. Similar complexes to those of phenylethynylgold were obtained with ammonia, trimethyl- and triphenyl- phosphines. The ammine, $Bu^tC{\vdots}CAuNH_3$ is moderately soluble in various organic solvents, in contrast to the phenyl analogue, but unfortunately a solution in benzene loses ammonia on boiling, and its degree of association could not be determined.

CHAPTER VII

INTERPRETATION AND DISCUSSION OF INFRA-RED SPECTRA

The acetylenic stretching frequencies

Disubstituted acetylenes absorb light in the range[145] 2190 - 2260 cm.$^{-1}$. Co-ordination between acetylenic groups and the metal atomsshould result in a reduction of the stretching frequency because of electron flow from the occupied πu bonding orbitals of the acetylene to the metal and because of electron flow from occupied metal d orbitals to unoccupied πg acetylene antibonding orbitals. Both these effects should reduce the acetylenic bond order, and hence the stretching frequency. Effects of this type have been described previously; for example, the acetylenic stretching frequency of ditertiarybutylacetylene is reduced by about 200 cm.$^{-1}$ when it is π-bonded to platinum,[146] and similar effects have been found in heavy metal complexes of olefins.[147]

In agreement with the view[1] that the alkyl and arylethynyl-copper(I) compounds, $(RC{\vdots}CCu)_x$ are co-ordination polymers in which there is substantial back co-ordination from filled copper 3d orbitals to the acetylenic antibonding orbitals, these compounds have been found to absorb in the region 1920-1960 cm.$^{-1}$ which is 270 - 300 cm.$^{-1}$ lower than the range characteristic of disubstituted acetylenes. (Table 4).

TABLE 4

Stretching frequencies of the acetylenic group in RC⋮CM

R·	M = $\frac{1}{2}$ Hg	Cu	Ag
Me·	2156	1955	2061
Et·	2165	1952	ca. 2040[a,c]
Pr^n·	2164[a] 2175[b]	1942	2045
Bu^t·	2180 2146 2188 2154	absent	2055
Ph·	2149	1933	2055
$\underline{p}NO_2C_6H_4$·	absent[a,c]	1929	2042
mesityl-	2142	1933[c] (v.w.)	2026
$\underline{p}BrC_6H_4$·	2160	1942	2048
PhC⋮C·	2204 2098	2180[a,c]	2190

measured in [a] KBr disc, [b] benzene solution, [c] Nujol mull

It can be seen that this effect is less marked in the corresponding silver compounds whose acetylenic frequencies are in the range 2020-2060 $cm.^{-1}$, a reduction of only 150-200$cm.^{-1}$. The acetylenic frequencies of the corresponding ethynylmercury(II) compounds are included in Table 4 for comparison as examples of disubstituted acetylenes containing 'normal' ethynyl-metal bonds. On substituting copper and silver for mercury the decrease in ν(C⋮C) is about 200 and 100 $cm.^{-1}$ respectively. In the case of t-butylethynylcopper(I) no absorption that could be due to an acetylenic vibration could be detected either in a potassium bromide disc or in solution in tetrachlorethylene. This could be connected with the mass of a copper atom being fairly near that of the butyl group. However, no similar frequency could be detected in the case of bis*p*-nitrophenylethynylmercury and in the case of phenylbutadiynyl-copper and -silver the frequencies observed are obviously due to one of the two acetylene groups which is apparantly not involved in the structure of the co-ordination polymer.

Phenylethynylgold absorbs very weakly at 1973 cm.$^{-1}$ which is about 175 cm.$^{-1}$ lower than the absorption in the mercury compound and near that in phenylethynylcopper. t-Butylethynylgold has three weak absorptions between 2030 and 1950 cm^{-1} (see Table 8, page 118) which are similarly lower. Co-ordination between the metal and the acetylene decreases in the sense Cu > Au > Ag in these uncomplexed ethynyls, $(RC\vdots CM)_x$.

In the case of the ethynylcopper(I) compounds complex formation with a tertiary phosphine raises $\nu(C\vdots C)$ by nearly 100 cm.$^{-1}$ from that observed in $(RC\vdots CCu)_x$, and it is peculiar that the frequency of the acetylenic absorptions is much the same whether the complex contains one, two or more molecules of phosphine. Table 5 lists the acetylenic frequencies of the copperethynyl complexes for which two or more $\nu(C\vdots C)$ bands were observed in the spectra of the solid complexes pressed in a potassium bromide disc.

TABLE 5

Acetylenic stretching frequencies of ethynylcopper(I) complexes[x]

$\mathrm{Bu^tC⁝CCuPMe_3}$		2050 $\mathrm{cm^{-1}}$	(vw)
$\mathrm{PhC⁝CCuPMe_3}$		2019 (w),	2045 (m)
$\mathrm{PhC⁝CCu(PMe_3)_2}$		2035 (m),	2048 (m)
$\mathrm{PhC⁝CCu(PMe_3)_3}$		2034 (s),	2051 (vw)
$\mathrm{PhC⁝CCuPEt_3}$	a	2018 (s) 2020 (s),	 2048 (m)
$\mathrm{PhC⁝CCuPPh_3}$		2043 (m)	
$\mathrm{p\text{-}NO_2C_6H_4C⁝CCuPPh_3}$		2015 (s)	
$\mathrm{p\text{-}NO_2C_6H_4C⁝CCu(PPhEt_2)_2}$		2025 (s)	
$\mathrm{PhC⁝C\cdot C⁝CCuPMe_3}$		2161 (s),	1981 (m)
$\mathrm{PhC⁝C\cdot C⁝CCuPEt_3}$	b	2159 (s), 2167 (s),	1988 (m) 1988 (m)
$\mathrm{(PhC⁝C\cdot C⁝CCu)_2(PEt_3)_3}$	a	2165 (s), 2171 (s),	2008 (m) 2009 (m)
$\mathrm{PhC⁝C\cdot C⁝CCuPPr^n_3}$	b	2164 (s), 2166 (s),	1984 (m) 1986 (m)
$\mathrm{Bu^tC⁝CCu(PhC⁝CCu)(PMe_3)_2}$		2062 (m)	

[x] Spectra measured in KBr discs except: [a] in benzene, [b] in tetrachlorethylene.

cf.	$\mathrm{PhC⁝CAgPMe_3}$	2075 (w)
	$\mathrm{PhC⁝CAuPMe_3}$	2095 (m)

vw very weak, w, weak, m, medium, s, strong absorption

The silver and gold complexes $\mathrm{PhC⁝CAg(Au)PMe_3}$ are added since they show that ν(C:C) increases in the series $\mathrm{PhC⁝CMPR_3}$ in the sense M = Cu < Ag < Au and that the change from $\mathrm{(RC⁝CCu)_x}$ to

$RC\vdots CCuPR_3$ (about 100 cm.$^{-1}$) is much greater than that from $(RC\vdots CAg)_x$ to $R\,C\vdots CAgPR_3$ (about 20 cm.$^{-1}$) but not as great as that from $(RC\vdots CAu)_x$ to monomeric $RC\vdots CAuPR_3$ (about 130 cm.$^{-1}$).

In the butadiynyl complexes it can be seen that one of the two acetylene groups is not involved in co-ordination, and the other is involved slightly more than the acetylenic group in the mono-ethynyl complexes.

Two series of copper complexes $RC\vdots CCu(PMe_3)_n$ (R = Ph· and CH_2:CMe·) were studied in some detail. Trimethylphosphine was added to the 1:1 complex dissolved in benzene, so that the ratio of phosphine to $RC\vdots CCu$ was increased to 2:1, 3:1 and 4:1 (i.e. n = 2,3 and 4). The acetylenic absorptions observed for these different solutions containing increasing P:Cu ratios are shown in Table 6. Extinction coefficients are included in parenthesis.

TABLE 6

Effect of P:Cu ratio on $\nu(C\vdots C)$ in benzene solution of $RC\vdots CCu(PMe_3)_n$

R·	n = 1	n = 2	n = 3	n = 4
Ph·	2025 (40)			
		2038 (101)	2041 (101)	2035 (82)
	2053 (40)	2061 (66)	2061 (168)	2061 (224)
	2086 (5)	2087 (17)	2087 (10)	2086 (5)
CH_2:C Me·	*2013 (36)	2021 (53)	2017 (49)	2017 (25)
	2035 (37)		2039 (58)	2039 (113)
	2063 (15)	2064 (33)	2062 (51)	2062 (80)
	2089 (2.5)	2089 (7.5)	2089 (5)	

Colour of solution * yellow, pale yellow, colourless

They are useful as a measure of the relative strengths of the various absorptions, but since the solutions contain mixtures of more than one complex no particular significance can be attached to them.

It is significant that in the isopropenyl series solutions for which the P:Cu ratios were three and four were quite colourless, and therefore could not contain appreciable amounts of the bright yellow 1:1 complex.

The acetylenic frequencies in the complexes of phenylethynylgold are collected in Table 7. There is no apparent relation between the frequency and the nature of the ligand and it is remarkable that the frequencies fall within such a narrow range 2107 - 2134 $cm.^{-1}$, (with the exception of that of $PhC{:}CAuPMe_3$ at 2095 $cm.^{-1}$), close to those of phenylethynyl-nickel[75b], -palladium[75c] and -platinum(II)[75a] complexes with triethylphosphine (2100 - 2108 $cm.^{-1}$).

These frequencies are displaced very little from that of bisphenylethynylmercury(II) (2149 $cm.^{-1}$) and π bonding between the metal and the acetylene is therefore not significantly larger.

The acetylene frequencies in the t-butylethynylgold complexes prepared are peculiar since three (and in one case four) weak bands are formed.

TABLE 7

Acetylenic stretching frequencies in complexes PhC:CAuL

L	$\nu(C{\vdots}C)$ cm^{-1}	L	$\nu(C{\vdots}C)$ cm^{-1}
NH_3	2120^{a} 2121^{e}	PMe_3	2095^{a}
$Pr^{i}NH_2$	2122^{a}	PEt_3	2109^{a}
n-$C_5H_{11}NH_2$	2126^{a} 2127^{b}	PPh_3	2123^{a} *vw* 2129^{b} *vw*
n-$C_8H_{17}NH_2$	2122^{a}	$\frac{1}{2}(Ph_2PCH_2)_2$	2125^{d}
n-$C_9H_{19}NH_2$	2125^{a}	$AsEt_3$	2113^{a} 2128^{b}
$Bu_2^{n}NH$	2131^{a}	$SbEt_3$	2107^{a}
piperidine	2130^{a}	$P(OPh)_3$	absent
pyridine	2134^{a}		

	$\nu(C{\vdots}C)$cm.$^{-1}$	$\nu(C{\vdots}N)$cm.$^{-1}$
$Bu^{n}NC$	2130^{a} 2134^{c}	2249^{a} 2253^{c}
p-tolylNC	absent^{a}	2232^{a}
o-$C_2H_5C_6H_4NC$	absent^{a,b}	2218^{a} 2211^{b}

[a] KBr disc, [b] benzene, [c] carbon tetrachloride, [d] Nujol mull,

[e] hexachlorobutadiene.

TABLE 8

Acetylenic stretching frequencies in $Bu^tC⁝CAu$ and its complexes

	ν(C⁝C) cm.$^{-1}$		(KBr)	
$(Bu^tC⁝CAu)_4$	2027 (w)		2002 (w)	1982 (w)
$(Bu^tC⁝CAu)_x$	2000 (sh)		1972 (sh)	1956 (w)
$Bu^tC⁝CAuNH_3$	2110 (w)		2004 (w)	1968 (vw)
$Bu^tC⁝CAuPMe_3$	2150 (vw)	2122 (m)	2041 (vw)	1980 (vw)

The frequencies at 2110 and 2122 are similar to those in the corresponding phenylethynylgold complexes and it is strange that the other frequencies are similar to those in the uncomplexed t-butylethynylgold.

Isocyanide frequencies in the gold complexes

The stretching frequency of the isocyanide groups (Table 7) bonded to phenylethynylgold are about 100 cm.$^{-1}$ greater than those of the free isocyanides, the differences (bonded) - (free) being 10, 98 and 81 cm.$^{-1}$ for the n-butyl-, p-tolyl-, and o-ethylphenyl- isocyanides respectively. Recently Cotton and Zingales[148] have reported increases of (40-70 cm.$^{-1}$ in some isocyanide complexes of) silver(I) and manganese(II). They find that this effect increases with increase in positive charge on the metal to which the isocyanide is co-ordinated, that is to say an increase as back co-ordination from the metal decreases. In the gold, complexes the increase in the frequencies are much larger than those described by Cotton and Zingales and the gold atom carries a fractional negative charge. It seems likely, therefore, the increase in $\nu(\mathrm{N{\equiv}C})$ on co-ordination is due to a rise in the bond order of the isocyanide from less than three in the free isocyanide to three in the co-ordinated isocyanide. Thefrequencies of normal cyanide groups (2220 - 2260 $\mathrm{cm.}^{-1}$) are in fact similar to those observed for the isocyanides co-ordinated to the gold atom.

N - H frequencies in the gold-amine complexes

The N - H frequencies (Table 9) observed in the phenylethynylgoldamine complexes were lower than those found in the free amines, by some 100 $\mathrm{cm.}^{-1}$.

TABLE 9

N - H Stretching frequencies in the complexes $\mathrm{PhC{\equiv}CAu}$ amine

amine	N - H * in complex		N - H ** in free amine	
NH_3	3328	3247 cm^{-1}		
$n\text{-}C_5H_{11}NH_2$	[a] 3287	3232	3380	3301
$n\text{-}C_8H_{17}NH_2$	3283	3226	3385	3306
$n\text{-}C_9H_{19}NH_2$	3264	3224	3377	3306
$n\text{-}(C_4H_9)_2NH$	3167		3298	
piperidine	3179		3278	

* All KBr discs, except [a] in hexachlorobutadiene

** Taken as liquid films.

This decrease on co-ordination is similar to that of

100-150 cm.$^{-1}$ found in some platinum complexes[149] and some complexes of other metals.[150] The interpretation of the spectra of amine complexes is frequently complicated by hydrogen bonding (for example, the spectrum of $PPr^{n}_{3}\cdot NH_3\cdot PtCl_2$ has six N -H stretching bands even in carbon tetrachloride[149]), however, the spectra of the gold-amine complexes are much simpler and little hydrogen bonding seems to occur even in the solid. The bands in the primary and secondary amine complexes are relatively sharp, as sharp as those due to C -H vibrations, and even in the ammonia complexes in which hydrogen bonding effects would be greatest the bands were only slightly broader than the C - H stretching frequencies.

Both the ammonia complexes studied had bands at 1241 cm.$^{-1}$ (m) in $PhC{\vdots}CAuNH_3$ and at 1253 cm.$^{-1}$ (s) in $Bu^{t}C{\vdots}CAuNH_3$ which were absent in the uncomplexed ethynyl and which can be assigned to a rocking mode. The t-butyl complex showed N - H deformation frequencies at 1623 and 1613 cm.$^{-1}$ which were obscured in the phenyl complex by bands due to the presence of the phenyl group.

Metal-carbon frequencies

Absorptions, which were generally weak, occurred in the copper and silver ethynyls $RC{\vdots}CCu(Ag)$ in the regions 514-520 and 510-530 cm.$^{-1}$ respectively, and in the gold ethynyls $(PhC{\vdots}CAu)_x$ and $(Bu^{t}C{\vdots}CAu)_x$ at 526 and 524 cm.$^{-1}$ respectively. In the t-butyl series $(Bu^{t}C{\vdots}CCu)_8$, $(Bu^{t}C{\vdots}CAg)_x$ and $(Bu^{t}C{\vdots}CAu)_4$ similar absorptions were at a slightly higher frequency than in and at 539, 526, and 560 cm.$^{-1}$, respectively, in comparison with the other ethynyls. These frequencies are attributed to a metal-ethynyl stretching vibration since they are found in the different ethynyls, and by comparison with some previously reported Pt-C[151] and Hg-C[152] stretching frequencies and with that of Au-Me stretching at 532 cm.$^{-1}$ in Et_3PAuMe[57]. On a mass effect along one would expect the frequencies to differ in the sense Cu > Ag > Au, but the observed order, and that of the t-butyl series in particular, suggests that the gold-carbon bonds are stronger than the copper-carbon and silver-carbon bonds.

The ethynyl metal(I) complexes absorb within the narrow range 520-530 cm.$^{-1}$ in nearly all cases, and these absorptions, also attributed to metal-ethynyl stretching, are weak particularly in the gold complexes. Table 10, collects some of these frequencies which were well-defined, omitting in particular complexes with triphenylphosphite and triphenylphosphine in which the required absorptions are obscured by ligand bands.

TABLE 10

(a) Metal-ethynyl stretching frequencies in $RC\equiv C-M$

	M →	Cu	Ag	Hg
R	Me	absent	absent	absent
↓	Et	510 vw	512 w	531 m
	Pr	514 w	510 w	544 m
	Bu^t	539 m	526 m	542 m, 464 w
	Ph	521 ms 512 ms	530 m 510 w	528 m

Table 10 continued

$\mathrm{BrC_6H_4}$	-	518 <u>m</u>	519 <u>m</u>
$\mathrm{NO_2C_6H_4}$	509 <u>w</u>	516 <u>w</u>	515 <u>w</u>
mesityl	absent	absent	absent

(b) <u>Metal-ethynyl stretching frequencies in $\mathrm{RC{\vdots}C\text{-}M\text{-}L}$</u>

$\nu(\mathrm{C - Cu})$

$\mathrm{PhC{\vdots}CCuPMe_3}$	524
$\mathrm{PhC{\vdots}CCuPEt_3}$	522 <u>w</u>
$\mathrm{Bu^tC{\vdots}CCuPMe_3}$	529 <u>w</u>
$\mathrm{CH_2{:}CMeC{\vdots}CCuPMe_3}$	541 <u>m</u>, 519 <u>w</u>
$\mathrm{PhC{\vdots}C{\cdot}C{\vdots}CCuPR'_3}$	512 - 515 <u>w</u> (R' = Me, Et, $\mathrm{Pr^n}$)
$\mathrm{(PhC{\vdots}C{\cdot}C{\vdots}CCu)_2(PEt_3)_3}$	513 <u>w</u>

$\nu(\mathrm{C - Ag})$

$\mathrm{PhC{\vdots}CAgPMe_3}$	521 <u>w</u>

$\nu(\mathrm{C - Au})$

$\mathrm{Bu^tC{\vdots}CAuNH_3}$	533 <u>mw</u>
$\mathrm{Bu^tC{\vdots}CAuPMe_3}$	538 <u>mw</u>

<u>$\mathrm{PhC{\vdots}CAu - L}$</u>

L	$\nu(\mathrm{C - Au})$	L	$\nu(\mathrm{C - Au})$
		pyridine	526
$\mathrm{n\text{-}C_5H_{11}NH_2}$	526	$\mathrm{PEt_3}$	526
$\mathrm{n\text{-}C_8H_{17}NH_2}$	524	$\mathrm{AsEt_3}$	520
$\mathrm{n\text{-}C_9H_{19}NH_2}$	526		

Table 10 continued

$(n-C_4H_9)_2NH$	529	Bu^nNC	526
piperidine	524	*p*-tolylNC	526

APPENDIX I

STABLE TERTIARY PHOSPHINE COMPLEXES OF TRIMETHYLGOLD

The only co-ordination stabilized derivatives of trimethylgold, which itself decomposes above -40°, previously described are various amine complexes,[153] and a thiol complex Me_2AuSPh, which is probably dimeric. The preparation of one of the most stable of these bistrimethyl(1:2 diaminoethane)gold, $Me_3AuNH_2CH_2CH_2H_2NAuMe_3$ was repeated to ensure that the technique of preparing trimethylgold (from methyl-lithium and gold bromide at -65°) had been acquired, and it has been found to be a suitable starting material for preparing complexes with stronger donors. Solutions in ether, of this complex, rapidly turn blue at room temperature.

Addition of triphenylphosphine to trimethylgold at -65° afforded the colourless crystalline stable complex, Me_3AuPPh_3, which is the first organo-gold(III) phosphine complex to be described. It melts at 120° with evolution of ethane. Further decomposition studies have shown that on heating:

$$Me_3AuPPh_3 \longrightarrow C_2H_6 + MeAuPPh_3 \longrightarrow \tfrac{1}{2}C_2H_6 + Au + PPh_3$$

This mode of decomposition takes place in solution and it is remarkable that no gases other than ethane are formed. In this respect it resembles the decomposition of methylsilver to ethane and silver as the only products, even when the decomposition is carried out in alcohol.[52] The yields of ethane were:

solid Me_3AuPPh_3 $\xrightarrow{120^\circ}$ 87.2% C_2H_6
Me_3AuPPh_3 in xylene $\xrightarrow{120^\circ}$ 56.8% C_2H_6
solid $MeAuPPh_3$ $\xrightarrow{175^\circ}$ 95% C_2H_6
$MeAuPPh_3$ in diphenyl $\xrightarrow{175^\circ}$ 48% C_2H_6

The complex trimethyl(trimethylphosphine)gold, m.p. 23°, is formed when trimethylphosphine is added to the ethylenediamine complex in ether, at -20°. It can be purified by sublimation at room temperature (0.004 mm pressure) on to a cold finger at -78°.

It now seems likely that other complexes (e.g. with isocyanides and possibly arsines), of trimethylgold may be prepared.

Infra-red spectra of these gold(III) complexes show two absorptions which are assigned to C-Au asymmetrical and symmetrical stretching at 504 and 477 in the ethylenediamine complex, and at 541 and 498 $cm.^{-1}$ in the trimethylphosphine complex. This region is more complicated in the triphenylphosphine complex due to ligand bands, but similar assignments are made to the absorptions at 530 and 512 $cm.^{-1}$. It is apparent that C-Au bonding is stronger in the phosphine complexes than in the ethylenediamine complex.

Experimental

Anhydrous gold(III)bromide

Prepared by adding excess bromine to dry gold powder as described by Gibson and Colles[154], but omitting the glass beads. After removal of excess bromine, the crystalline product is stored over caustic soda, and handled under nitrogen. It is only very slightly soluble in ether.

Trimethyl(1:2 diaminoethane)gold[153] $Me_3AuNH_2CH_2CH_2H_2NAuMe_3$

Trimethylgold was prepared from gold bromide (11.5g., 0.026 mole) and methyl-lithium at -65°. Ethylenediamine (1 cc., excess) was added and after stirring for one hour, the solution was allowed to warm up. Addition of water (50cc.) followed by removal of the ether from the organic layer gave a white solid which was recrystallised from ether-petroleum (40-60°) mixture. Yield 4.1g., 57%, m.p. 94° (explodes).

Trimethyl(trimethylphosphine)gold Me_3PAuMe_3

Trimethylphosphine (Excess of a standard solution in ether) was added to the ethylenediamine complex (0.5g.) in ether (10cc.) at -20°. After adding water (10cc.) the ether layer was separated and the ether removed to give oily droplets which solidified on cooling below 0°. Sublimation of this oil at 0.004 mm/23° on to a cold finger at -78° afforded colourless Me_3AuPMe_3, m.p. 23°. (Found: C, ; H, Au, 61.6. $C_6H_{18}AuP$ requires C, ; H, Au, 61.9%).

Trimethyl(triphenylphosphine)gold Me_3AuPPh_3

Triphenylphosphine (6.8g., 0.026 mole) in ether (20cc.) was added to trimethylgold (from gold bromide 11.3g., 0.26 mole) in ether (150 cc.) at -65°. After stirring for 45 minutes the solution was allowed to warm up and water (50cc.) added. Gold (2.4g.) was filtered off and the ether layer, which contained triphenylphosphine and the required complex, separated. This mixture was separated by elution through an alumina column, the triphenylphosphine remaining on the column. The solid from the ether eluent was crystallised from hexane affording Me_3AuPPh_3, 5.3g., 41% m.p. 120° (decomp). (Found:
and 50·2 5·0
C, 51.1; H, 4.7; Au, 39.5. $C_{21}H_{24}AuP$ requires C, 50.0; H, 4.8; Au 39.1%).

Thermal Decomposition of Me_3AuPPh_3

On heating trimethyl(triphenylphosphine)gold (0.3516g.) in vacuo, at 120° for half an hour ethane (20.64 N cc., corresponding to 87% of the total available'methyl groups', identified by I. R. spectra), gold, and triphenylphosphine (m.p. 79°) were obtained.

Decomposition of a further 0.1646g., in xylene for half an hour at 120° afforded 4.15 N cc. ethane corresponding to 56.8% available methyl groups. A qualitative decomposition in xylene at 120°, gave methyl(triphenylphosphine)gold after removal of the xylene, identified by m.p. 175° (decomp.) and I.R. spectra.

Thermal decomposition of $MeAuPPh_3$

Decomposition of methyl(triphenylphosphine)gold (0.2700g.) at 175° for half an hour gave ethane (5.79 N cc. corresponding to 94.8% available methyl groups), gold and triphenylphosphine (m.p. 79°). Decomposition of a further 0.4568g., in diphenyl, at 175° for half an hour gave 5.49 N cc. ethane, corresponding to 48.3% available methyl groups.

APPENDIX II

THE FAR INFRA-RED SPECTRA OF SOME GOLD COMPOUNDS

It is only recently that spectrometers have become available for investigation of the infra-red region between 20 and 50μ. One such instrument, a Grubb Parsons double beam grating spectrometer has been installed in this department, and assignments have been made to absorption bands present in the spectra of some gold compounds.

The spectra of the compounds listed in Table 11 (page 141) are fairly simple in the region 22-50μ, there being generally no more than two or three bands.

Gold-phosphorus stretching frequencies

Comparison of the spectra of some gold-phosphine complexes with each other, and with some other tertiary phosphine complexes has shown that bands which are attributed to νAu-P occur in the range 347 - 391 $cm.^{-1}$ In the complexes, $(Me_3P)_2NiCl_2$, $(Me_3P)_2NiBr_2$ and $(Me_3P)_2NiI_2$, frequencies attributed to νNi-P occur at 361 w, 360w, and 366s respectively.

In the series Me_3PAuX (X = Cl, Br, I) (Table 11), there is a steady decrease in ν Au-P as the atomic weight of the halogen increases, that is to say as the double bond character of Au-X increases there is a corresponding decrease in the gold-phosphorus bond order. In comparison with these frequencies, that at 357 m in Me_3PAuMe is at a much lower wave number than would be expected.

Gold-halogen frequencies

Some transition metal- chlorine stretching frequencies have already been reported[155] for the complex halides of rhenium, palladium, osmium iridium and platinum to be in the range 313-358 cm.$^{-1}$, and in some of these complexes isotopic splitting of the metal-chlorine bands are observed. The monochlorogold compounds in the table show this isotopic splitting particularly well, and two frequencies due to νAu-^{35}Cl and νAu-^{37}Cl are present in these complexes. The νAu-^{35}Cl frequencies are generally in the range 311-329 cm^{-1}. In the complexes Me_2SAuCl, $Me_3AsAuCl$, Me_3PAuCl, the νAu-Cl frequency decreases as the π-bonding strength of the donor atom ($P > As > S$) increases, but there is no similar regular change in the analagous bromo- series.

Gold- bromine stretching frequencies occur in the region 210-233 cm.$^{-1}$; gold-iodine frequencies lie outside the range of the spectrometer.

Other assignments in the 22-50μ region

In the trimethylphosphine complexes, in the table, the only other band besides the metal- ligand and metal-halogen absorptions, is one occurring in the region 270-300 cm.$^{-1}$ and which, by analogy with a similar band in Me_3PO[156] at 256 cm.$^{-1}$ and in Me_3PCl_2[157] at 302 cm.$^{-1}$, is attributed to a

PC_3 bending vibration.

In the triphenylphosphine complexes a weak absorption at 444 in Ph_3PAuCl and 441 $cm.^{-1}$ in Ph_3PAuBr must be due to a vibration of the triphenylphosphine group.

TABLE 11

INFRA-RED Au - P, Au - Cl and Au - Br STRETCHING FREQUENCIES

Compound	Au-P	Au-Cl	Au-Br
Me_3PAuCl	381 m	311s, 303sh	
Me_3PAuBr	378 s		224 s
Me_3PAuI	371 s		
Et_3PAuCl		312s, 305sh	
Et_3PAuBr			210 s
Ph_3PAuCl		329s, 323ms	
Ph_3PAuBr			233s, 229sh
$Me_3PAuC{\equiv}CPh$	347 s		
$Me_3PAuC{\equiv}CBu^t$	368 m		
Me_3PAuMe_3	391 w		
Me_3PAuMe	357 m		
Et_3PAuMe	388 vw		
	νAu-S		
Me_2SAuCl	344 m	324.5s 319.5sh	
Me_2SAuBr			228 m

Table 11 continued

	ν Au-As			
$Me_3AsAuCl$	265 s	317s	312s	
$Me_3AsAuBr$	absent			210 s
Me_3AsAuI	268 s			

Experimental

Samples of the compounds were ground in nujol and the mulls mounted between cesium iodide discs. In the case of halides other than iodides, halogen exchange with the cesium iodide was overcome by using thin polythene sheets between the mulls and the discs.

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