Dipole studies on organometallic compounds

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DIPOLE STUDIES ON
ORGANOMETALLIC COMPOUNDS

by

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MEMORANDUM

The work described in this thesis was carried out in the Durham Colleges in the University of Durham between September 1957 and August 1960. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

The work described in this thesis has been the subject of one publication with Professor G.E. Coates and G. Calvin. (Chem. and Ind. 1959, 1628).

SUMMARY

Several new organometallic compounds of palladium(II) and gold(I) of the type $L_2PdR.X$, L_2PdR_2, and $L.AuR$, (where L is a ligand, R an organic group, and X a halogen) have been prepared and their electric polarisations, together with those of several known compounds of type L_2PdX_2 and LAuX, have been measured.

The atom polarisation of several symmetrical organometallic compounds of palladium(II) have been measured, and from these, estimates of the atom polarisations of similar compounds with permanent dipole moments have been made.

The dimethyl compounds of palladium have been studied in some detail and their configuration discussed.

From dipole moment measurements on gold(I) compounds the amount of charge transfer in the formation of the phosphorus-gold bond has been calculated.

A description of the apparatus and procedure used in making determinations of dipole moments, together with a method for estimating electron polarisations at infinite wavelength, is included in the thesis.

CONTENTS

PHYSICAL MEASUREMENTS

INTRODUCTION

The work described in this thesis is almost entirely concerned with complexes of palladium and gold(I).

(1) Palladium

Palladium chloride ($PdCl_2$) forms complexes readily with many donors and amongst the strongest of these are tertiary phosphines and arsines. The complexes are easily formed,[5] stable in air, and of the form L_2PdCl_2 where L is the ligand. Dihalobisphosphine (or arsine) palladium complexes nearly always have a trans configuration.

Calvin and Coates[22] used these complexes (and some others) to prepare normal (sigma bonded) organic derivatives of palladium by the direct action of organolithium compounds or Grignard Reagents. These compounds were of the type L_2PdRX or L_2PdR_2 where X was halogen SCN or CN and R was alkyl, aryl, or phenylethynyl. Most of them were white when pure but many decomposed when allowed to stand at room temperature, turning grey and eventually black due to the formation of elemental palladium. Triethylphosphine appeared to have the strongest stabilising effect, and a comparison of organic groups suggested that the most stable compounds were formed when R was methyl, phenylethynyl, or phenyl bearing an electron attracting group.

(2) Gold(I)

Mann, Wells and Purdie[3] prepared and investigated the monomeric halides R_3PAuX but no organic derivatives of gold(I) were reported until recently[23] when several compounds of the type R_3P-AuR' were prepared in this laboratory by the action of organolithium compounds on triethylphosphinemonochlorogold(I) and triphenylphosphinemonochlorogold(I). R' was methyl, ethyl, phenyl, or phenylethynyl.

As the compounds of palladium were expected to have square planar configuration and those of gold(I) to have colinear P-Au and Au-C bonds they were particularly suitable for dipole moment studies. Thus the purpose of the investigation was (1) the preparation of organopalladium and organogold(I) compounds suitable for dipole studies and (2) dipole moment measurements on these.

In the case of the compounds of palladium the question of cis-trans isomerism arises, and this matter can easily be resolved by dipole moment measurements. The dimethyl compounds deserve special mention in this respect as their variable configuration is of interest: they are discussed in a later section.

A source of error in accurate dipole moment measurements is the allowance made for atom polarisation. High and uncertain atom polarisations can cause substantial variations in the calculated values obtained for dipole moments if the latter are small. e.g. an error of 5 c.c. in the allowance for atom polarisation corresponds to a 10% error in the dipole moment for a compound with a moment of about 1D.

Atom polarization is due to the displacement, in an electric field, of polar groups (see p.42). These displacements may arise from the stretching of a polar bond or from a change in the angle between two polar bonds; they correspond to the displacements which occur when infra-red light is absorbed. It is, in the case of relatively simple molecules, possible to calculate atom polarizations as an additive function of the various infra-red absorptions:[24]

$$P_A = \text{const.} \sum^{j} A_j \nu_j^{-2}$$

In the above expression the atom polarization (P_A) is the sum of the terms $A_j \nu_j^{-2}$ (A_j = integrated band area - roughly the absorption intensity - of band j of frequency ν_j).

Naturally it would be feasible to compute atom polarizations in this way only when a molecule is sufficiently simple for its fundamental infra-red frequencies to be sorted out and their intensities measured.

Bearing in mind that atom polarizations are some additive function of polar bonds, the common practice of taking atom polarization as some arbitrary fraction - often five per cent - of the electron polarization at some particular wavelength - often 5893Å - seems rather irrational. That so much useful information has been obtained from dipole moment measurements derived in this manner is simply due to the fact that atom polarizations generally contribute so little to the total polarization that errors in their calculation do not matter very much.

However, quite early in the development of the application of dipole moments to chemical problems Smith and Angus[25] suggested that compounds with no permanent dipole moment, but containing large and balanced (opposed) dipoles, have abnormally large atom polarizations. Examples were beryllium acetylacetonate and basic beryllium acetate. Later, Sutton in particular[26,27] found evidence for similar effects in numerous compounds containing balanced dipoles, including benzoquinone and a variety of symmetrical acetylacetonates of metals.

That metal co-ordination complexes should have abnormally big atom polarizations would be linked to the above theory by the fact that the infra-red frequencies of the most polar bonds (metal-to-ligand) are at too low a frequency to be observed with most infra-red spectrometers, and the contribution of these deformations to the atom polarization should therefore be particularly large.

Consequently it would seem more satisfactory, in measuring the dipole moments of metal co-ordination compounds, not to compute atom polarization as 5% of R_D, but to estimate it by analogy with other co-ordination complexes of a similar constitution as possible but with balanced dipoles and therefore zero permanent dipole moment. In the latter type of compound the atom polarization is relatively easily measured as the differance between the total polarization and the electron polarization (extrapolated to infinite wavelength).

One of the simplest classes of metal co-ordination compound with balanced dipoles is the class of trans-planar complexes L_2MX_2, where L is a donor ligand such as a tertiary phosphine or arsine, M a metal such as palladium or platinum, and X a neutral ligand such as halogen or an organic group.

A certain number of data were obtained by Jensen[28] which indicate that trans complexes of palladium and platinum have fairly large atom polarizations. However, the compounds investigated by Jensen were all coloured (generally halide) complexes, and in these cases light absorption in the visible region of the spectrum can introduce error into the measurement of refractive indices.

The preparation in these laboratories of colourless organo-palladium compounds, and by Chatt at Welwyn of colourless organo-platinum compounds was considered to provide a good opportunity for the measurement of atom polarization in this class of compound, and to see whether it is possible to arrive at any general rule for the estimation of atom polarization more satisfactory than the "5% rule".

CHEMICAL PREPARATIONS

I STARTING MATERIALS, PREPARATION AND PURIFICATION

(1) Benzene

B.D.H. Analar benzene was three quarters frozen slowly with shaking every half hour. The liquid portion was rejected and the procedure repeated twice more.

The residue was refluxed with potassium for three hours under nitrogen and then distilled, the first 50 mls. or so being rejected. The benzene was stored in a flask with a drying column containing molecular sieve (Linde 4A) attached, which allowed about 400 mls of benzene to be standing in contact with the sieve before use. It was blown out of the storage vessel by dry nitrogen. The benzene had a density of 0.8736 ± 0.0002[1] gm/ml and a refractive index of 1.4979 ($\lambda = 5985$)[1] both at 25°C.

(2) Triethyl Phosphine

$$\mathrm{EtBr + Mg \longrightarrow EtMgBr}$$

$$\mathrm{PCl_3 + 3EtMgBr \longrightarrow PEt_3 + 3MgClBr}$$

Ethyl magnesium bromide (5.66 moles) was made from ethyl bromide (562 g., 5.16 moles) ethyl iodide (78 g. 0.5 moles) and Magnesium turnings (144 g., 6.0 moles) in ether (1.5 litres) in a 5 litre flask.

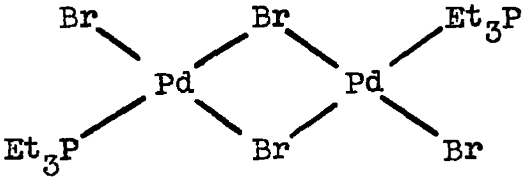
The flask was then cooled to -20°C and phosphorus trichloride (206.5 g., 1.5 moles) in ether (1.5 litres) was added dropwise over a period of 2 hours. Hissing could be heard as the phosphorus trichloride dropped into the Grignard and a yellow deposit formed on the side of the flask. The reaction mixture was stirred for a further thirty minutes and water was added followed by a solution containing ammonium chloride (11 g., 0.2 moles) in water (100 mls.) to aid in the dissolving up of magnesium salts. Ether distilled off during the addition and was collected. When hydrolysis was complete and a readily stirred mixture obtained the mixture was steam distilled until only one phase was visible in the distillate. The ether phase was fractionated under nitrogen and the fraction distilling between 123°C and 127°C collected. Yield 123 g., 68%.

Difficulty was experienced in stirring during the hydrolysis stage as the mixture tended to solidify. The solid was dispersed before the steam distillation stage by addition of a large volume of water. Frothing was encountered during the distillation and care had to be taken that the mixture did not froth over into the receiver.

(3) Bis(triethylphosphine)dibromopalladium(2)

$$Na_2PdCl_4 + 2Et_3P + 2NaBr —— (Et_3P)_2PdBr_2 + 4NaCl$$

To a solution of sodium chloropalladite $Na_2PdCl_33H_2O$ (17.5 g., 0.05 moles) and NaBr (21 g., 0.02 moles) in water, triethylphosphine (11.8 g., 0.1 moles) in ethanol (20 mls) was added from a dropping funnel with stirring. A faintly reddish precipitate was obtained which turned yellow on addition of a little more triethyl phosphine. This was due to the presence of the red bridged compound.



The yellow precipitate was filtered off, dried in an oven at 70°C, and recrystallised from acetone containing a little lithium bromide and triethylphosphine. Yield 22 g., 85%. Melting Point 134°C.

(4) Triethylphosphinemonochlorogold (I)3

$$H_2O + HAuCl_4 + 2Et_3P —— Et_3PAuCl + 3HCl + Et_3PO.$$

To a solution of brown gold chloride (Johnson and Matthey) (57.75 g., 0.15 moles) in water (150 mls) and ethanol (150 mls) cooled in an ice-salt bath under nitrogen was added triethylphosphine (43.5 mls., 0.3 moles) in ethanol (300 ml.) dropwise with stirring.

After addition of the phosphine the bath was removed and the mixture stirred for a further 30 minutes. The colour faded from bright yellow to a faint dirty brown which addition of hydrazine (1 ml. in 25 mls of water) did not dispel.

The ice bath was replaced and water (750 mls) added slowly. The solution turned pale yellow and greyish white crystals of triethylphosphine mono~~bore~~bromogold were deposited. The crystals were filtered off washed and dried. Yield 44 g. On standing for three days the solution deposited a further 9 g. of product. Total yield 53 g., 100%.

The triethylphosphinemonochlorogold was recrystallised from ethanol. Melting Point 86°C.

(5) <u>Triphenylphosphinemonochlorogold</u> (I)

$$H_2O + HAuCl_4 + 2Ph_3P \text{ —— } Ph_3PAuCl + 3HCl + Ph_3PO$$

To a solution of brown gold chloride (24 g., 0.06 moles) in water (50 mls.) was added a solution of triphenylphosphine (33 g., 0.12 moles) in ethanol (400 mls).

The solution slowly became colourless and white crystals of triphenylphosphinemonochlorogold (I) were deposited. These were separated, washed with ethanol and dried. Yield 30 grams 100%. Melting point 255°C (Decomposition).

(6) Bis(trimethylphosphine)dichloropalladium

To a solution of bis(dimethylsulphide)dichloropalladium (14 g., 0.02 moles) in ether (50 mls) a solution of trimethylphosphine (0.042 moles) in ether (20 mls was added dropwise under nitrogen. The light yellow bis(trimethylphosphine)dichloropalladium was thrown out of solution immediately and was collected, washed with ether and dried. Yield 13 grams (100%).

(7) Dipyridyldichloropalladium[4]

$$\underline{\text{dipy}} + (Et_2S)_2PdCl_2 \text{ —— } \text{dipy } PdCl_2 + 2Et_2S$$

To a solution of bis(diethylsulphide)dichloropalladium (14 g., 0.02 moles) in ether (50 mls) was added a solution of dipyridyl (4.0 g., 0.025 moles) in ethyl alcohol (10 mls). The orange yellow dipyridyldichloropalladium was filtered off washed with alcohol and acetone and dried. Yield 6 grams (90%), did not melt below 300°C.

(8) Bis(triethylarsine)dichloropalladium[5]

Solutions of triethylarsine (7.3 g., 0.045 moles) in ethanol (50 mls) and bis(diethylsulphide)dichloropalladium (7.1 g., 0.02 moles) in ethanol (50 mls) were run at equivalent rates into a flask with stirring. The resulting solution was reduced in volume by pumping and on cooling the remainder, orange yellow crystals separated out and were collected, washed with a little ethanol and dried. Yield 7.3 grams (73%). Melting Point 113°-116°C.

II. ORGANOMETALLIC COMPOUNDS

Most of the organometallic compounds were prepared in a similar manner and the following description is typical of the method used. Any variations are indicated in the appropriate places.

As the compounds were required for dipole moment measurements efforts were made to achieve maximum purity rather than maximum yield. Records of yields are therefore not included, as they would have little significance.

(1) Standard Reaction Procedure

Starting material (usually 0.02 moles) was placed in a 500 ml three-necked flask fitted with a glass stirrer, containing dry ether (200 mls). The flask was purged with nitrogen and a slow stream of nitrogen was maintained throughout the reaction. The mixture was stirred and the flask cooled in an acetone/carbon dioxide bath to -60°C, care being taken that the stream of nitrogen was sufficient to offset any tendency to suck back due to cooling. Grignard reagent or organo-lithium compound was added slowly from a dropping funnel. After the addition the reaction mixture was allowed to warm to 10°C then cooled to 0°C and water (100 ml.) added. The layers were separated, the organic layer pumped dry and the compound recrystallised.

Almost all compounds were recrystallised in double Schlenk tubes by cooling, as heating up in solution commonly caused decomposition.

(2) Compounds of Palladium

(1) Introduction

The starting material used was almost always bis(triethylphosphine)dibromopalladium. At first it appeared that one of the bromine atoms could be replaced if reacted with a Grignard reagent, and both with an organolithium compound i.e.

$$(Et_3P)_2PdBr_2 + RMgBr \text{ —— } (Et_3P)_2Pd(R)Br$$

$$(Et_3P)_2PdBr_2 + 2RLi \text{ —— } (Et_3P)_2PdR_2.$$

This was often found to be the case but not always as the diphenyl and diphenyl ethynyl compounds were both obtained from reaction with Grignard Reagents when attempts were being made to replace only one bromine atom.

(2) Bis(triethylphosphine)bromo(methyl)palladium[2]

$$(Et_3P)_2PdBr_2 + 2MeMgBr \text{ —— } (Et_3P)_2Pd(CH_3)Br + MgBr_2$$

The dibromide (10.0 g., 0.02 moles) was allowed to react with methyl-magnesium bromide (0.045 moles). After warming up and stirring for 30 minutes at 10°C traces of yellow starting material were still visible. The mixture was again cooled to -60°C and methylmagnesium bromide (0.005 moles) added. On allowing to warm up the coloured material reacted and a colourless solution together with a little white solid was present. After addition of water both layers were colourless and the ether layer gave a white crystalline solid. This was recrystallised from a mixture of hexane and ether. Melting point 73°C.

(3) Bis(triethylphosphine)dimethylpalladium[2]

$(Et_3P)_2PdBr_2 + 2MeLi —— (Et_3P)_2PdMe_2 + 2LiBr$

The dibromide (10.0 g., 0.02 moles) was allowed to react with methyl-lithium (0.045 moles). At 10°C there was no trace of starting material. From the ether layer a grey solid was obtained which on recrystallisation from *n*hexane gave a white solid. Melting point 47-49°C.

Evidence for the Isomerisation of bistriethylphosphine dimethyl palladium

(a) A sample of the compound was stored at room temperature under nitrogen for about six months and then recrystallised for dipole moment measurements. The melting point of the recrystallised compound was 66-67°C and its dipole moment (1.4 Debye) indicated a mixture of isomers with a preponderance of the *trans* form.

(b) A second sample of the dimethyl compound was prepared. Melting Point 47°C and a dipole moment of 4.7 Debye was recorded indicating a high proportion of the cis compound being present.

(c) A third sample of the compound with melting point 46-47°C gave a dipole moment figure of 3.6 Debye.

(d) From a solution in n-hexane which had been standing for two days a further sample with melting point 63°C was obtained. This specimen appeared to be faintly yellow. (Found: C, 45.3; H, 9.6. $C_{14}H_{36}P_2Pd$ requires C, 45.1; H, 9.7%). The dipole moment of this sample was 2.7 Debye.

Addition of a drop of triethylphosphine to a solution of the dimethyl compound caused a small steady increase in dielectric constant for a few minutes but the total increase was not sufficient for a complete change to the cis form.

Specimens with melting points as high as 77°C were isolated by sublimation.

All melting points were fairly sharp (i.e. melted over 1 or 2°) and infra-red spectra of the various specimens showed no significant differences.

(4) Bis(triethylphosphine)bromo(phenyl)palladium

$$(Et_3P)_2PdBr_2 + PhMgBr \longrightarrow (Et_3P)_2Pd(Ph)Br + MgBr_2$$

Attempts to prepare this compound under the usual conditions failed. Specimens of the diphenyl compound were obtained twice. This was considered to be due to the low solubility of the starting material in ether, and so tetrahydrofuran was tried as solvent. The solution was cooled to -20°C instead of the usual -60°C and a smaller quantity of Grignard was used.

Dibromide (10 g., 0.02 moles) was allowed to react with phenylmagnesiumbromide (0.03 moles) at -20°C.

The reaction mixture turned brown immediately (probably due to metallic palladium) and after hydrolysis and addition of ether (200 mls) the organic layer was dark brown in colour. The volume of the organic layer was reduced to about 10 ml by pumping on a water pump and the liquid decanted from the solid which had been deposited. The solid which was brown in colour was washed with 5 mls of hexane and recrystallised twice from ether. A white solid resulted. Melting Point 104°C (slight decomposition). (Found: C, 43.5; H, 7.6. $C_{18}H_{35}BrP_2Pd$ requires C, 43.2; H, 7.1%).

(5) Bis(triethylphosphine)diphenylpalladium[2]

$$(Et_3P)_2PdBr_2 + 2PhLi \text{ —— } (Et_3P)_2PdPh_2 + 2LiBr$$

The dibromide (10 g., 0.02 moles) was allowed to react with phenyl-lithium (0.045 moles). The yellow colour disappeared on allowing to warm up, and hydrolysis gave two clear layers. From the organic layer a white solid was obtained which was recrystallised from ether (twice). Melting point 94°C (very sharp with immediate decomposition).

(6) Bis(triethylphosphine)di(phenylethynyl)palladium[2]

$$(Et_3P)_2PdBr_2 + 2Ph\text{-}C{\equiv}C\text{-}MgBr \text{ —— } (Et_3P)_2Pd(Ph\text{-}C{\equiv}C)_2 + 2LiBr$$

The dibromide (10 g., 0.02 moles) was allowed to react with phenylethynyl-lithium (0.045 moles). After hydrolysis a faintly brown solid was filtered off which on recrystallisation from hot ethanol (twice) gave a white solid. Melting Point 164°C (decomposition).

(7) Bis(triethylphosphine)bromo(p-chlorophenyl)palladium

$$(Et_3P)_2PdBr_2 + p\text{-}ClPhMgBr \text{ —— } (Et_3P)_2PdBr(pClPh) + MgBr_2$$

The dibromide (5 g., 0.01 moles) was allowed to react with p-chlorophenylmagnesiumbromide (0.015 moles) in tetrahydrofuran the reaction being carried out at $-20^\circ C$. The reaction mixture turned brown on hydrolysis. Ether (100 mls) was added to aid in separation and from the organic layer a brown solid was obtained. Recrystallisation from a mixture of hexane (70%) and ether (30%) gave a white solid. Melting Point $118^\circ C$. (Found: C, 40.7; H, 6.7. $C_{18}H_{34}BrClP_2Pd$ requires C, 40.6; H, 6.4%).

(8) <u>Bis(triethylphosphine)bromo(p-bromophenyl)palladium</u>

$$(Et_3P)_2PdBr_2 + p\text{-}BrPhMgBr \text{ —— } (Et_3P)_2PdBr(pBrPh) + MgBr_2$$

The <u>dibromide</u> (7.5 g., 0.015 moles) was allowed to react with p-bromophenylmagnesiumbromide (0.025 moles) with tetrahydrofuran as solvent, the reaction mixture being cooled to $-20^\circ C$. The yellow colour of the solution faded but did not disappear even after stirring at room temperature for 30 minutes. A positive colour test for the Grignard Reagent was obtained however and so the mixture was cooled and hydrolysed. Ether (100 mls) was added and a grey solid which was present was filtered off.

From the organic layer a grey solid was obtained which on recrystallisation (twice) from a mixture of hexane (80%) and ether (20%) gave a white solid. Melting Point, $144^\circ C$ (no decomposition). (Found: C, 37.5; H, 5.9.

$C_{18}H_{34}Br_2P_2Pd$ requires C, 37.3; H, 5.9%). The grey solid which was filtered off after hydrolysis was tested for palladium with negative result.

p-Bromophenylmagnesium bromide and p-chlorophenylmagnesiumbromide were prepared by mixing solutions of anhydrous magnesium bromide in ether with equivalent solutions of p-bromophenyl-lithium and p-chlorophenyllithium respectively as the direct formation of the Grignards from magnesium and the aryl dihalides is an unsatisfactory method.

(9) Bis(triethylphosphine)di(p-bromophenyl)palladium

$$(Et_3P)_2PdBr_2 + 2\ p\text{-}BrPhLi \longrightarrow (Et_3P)_2Pd(pBrPh)_2 + 2LiBr.$$

The dibromide (5 g., 0.01 moles) was allowed to react with p-bromophenyl-lithium (0.05 moles). The solution turned milky white and on hydrolysis a white solid was thrown out of solution. This was filtered off and washed with water, acetone and ether. The compound did not melt below 240°C but began to darken at 130°C. (Found: C, 44.1; H, 6.1. $C_{24}H_{38}Br_2P_2Pd$ requires C, 44.2; H, 5.9%).

(10) Bis(triethylphosphine)di(p-chlorophenyl)palladium

$$Et_3P)_2PdBr_2 + 2p\text{-}ClPhLi \longrightarrow (Et_3P)_2Pd(pClPh)_2 + 2LiBr$$

The dibromide (7.5 g., 0.15 moles) was allowed to react with p-chlorophenyl-lithium (0.035 moles). A white insoluble product was obtained on hydrolysis (as above) and this after washing with water acetone and ether gave a white solid. Melting point 164°C (decomposition). (Found: C, 50.7; H, 6.9. $C_{24}H_{38}Cl_2P_2Pd$ requires C, 51.2; H, 6.8%).

(11) Bis(triethylphosphine)cyano(methyl)palladium[2]

Bis(triethylphosphine)bromo(methyl)palladium (2 g., 0.0045 moles) in methanol (20 mls) was added to a saturated solution of potassium cyanide (1.3 g., .02 moles) in methanol in a beaker. A strong odour of triethylphosphine was noticeable almost immediately. The mixture was allowed to stand for two hours and then cold water (200 mls) was added. An oily white precipitate was thrown out of solution and the beaker was allowed to stand for three hours in an ice salt bath. After scratching white crystals were obtained. These were recrystallised from hexane. Melting Point 78°C (softens 73°C). M, cryoscopically in 1.69% benzene solution 397.5; in 3.75% solution 397.5. $C_{14}H_{33}N.P_2Pd$ requires M, 384.

(12) Bis(trimethylphosphine)dimethylpalladium

$$(Me_3P)_2PdCl_2 + 2MeLi \longrightarrow (Me_3P)_2PdMe_2 + 2LiCl$$

Bis(trimethylphosphine)dichloropalladium (6.6 g., 0.02 moles) was allowed to react with methyl-lithium (0.045 moles). Slight decomposition took place and the organic layer yielded a brown solid which on recrystallisation from ether (three times) gave a white solid. Melting point 84-90°C. Despite two further recrystallisations no sharper melting point could be obtained and it appears probable that on heating isomerisation takes place giving a mixture of the cis and trans forms. (Found: C, 33.7; H, 8.7. $C_8H_{24}P_2Pd$ requires C, 33.3; H, 8.4%).

(13) Reaction between Bis(trimethylphosphine)dichloropalladium and phenyl-lithium

The dichloride (6.6 g., 0.02 moles) was allowed to react with phenyl-lithium (0.045 moles). The mixture turned faintly green and darkened as it warmed up until it was quite black. After hydrolysis quantities of diphenyl and metallic palladium were isolated but no organopalladium compound was obtained.

(14) Bis(triethylarsine)dimethylpalladium

$$(Et_3As)_2PdCl_2 + 2MeLi \longrightarrow (Et_3As)_2PdMe_2 + 2LiCl$$

Bis(triethylarsine)dichloropalladium (8.3 g., 0.02 moles) was allowed to react with methyl-lithium (0.06 moles). Blackening was observed and the organic layer after separation was faintly green in colour. The organic layer was dried with magnesium sulphate and pumped dry during which operation it turned black and the residue was a black mass. The black mass was extracted with acetone and the extract cooled in a double Schlenk tube. A cream coloured solid which quickly showed signs of decomposition was obtained. The solid was recrystallised twice from n-hexane containing a trace of triethylarsine and filtrations were done with the aid of a vacuum pump instead of a water pump to exclude all water vapour. A cream coloured solid was obtained. Melting Point: 49°C (decomposition). (Found: C, 36.4; H, 8.1. $C_{14}H_{36}As_2Pd$ requires C, 36.4; H, 7.8%).

(15) Dipyridyldimethylpalladium[2]

$$\text{dipy PdCl}_2 + 2\text{MeLi} \longrightarrow \text{dipy PdMe}_2 + 2\text{LiCl}$$

Several attempts were made to prepare this compound and obtain a correct analysis and it was found that, if the starting materials were prepared under anhydrous conditions, and the compound was recrystallised and analysed quickly, then this could be achieved.

The dichloride (6.6 g., 0.02 moles) was allowed to react with methyl lithium (0.06 moles). A little blackening took place and after hydrolysis the insoluble dimethyl compound which was orange in colour was filtered off, recrystallised from acetone and dried on the vacuum pump. Melting Point 155°C (decomposition). (Found: C, 48.8; H, 5.1. $C_{12}H_{14}N_2Pd$ requires C, 49.2; H, 4.8%).

Initially a specimen of the compound which showed no visible sign of change after keeping for a few days was recrystallised and analysed. The figure for carbon analysis was found to be about five per cent low and the melting point which had previously been observed as 153°C was not apparant. The compound began to decompose at 130°C and became progressively more black.

(16) Reaction between mesityl-lithium and dipyridyl-dichloropalladium

The dichloride (6.6 g., 0.02 moles) was allowed to react with mesityl-lithium (0.045 moles). The reaction mixture turned black after addition of a few drops of mesityl-lithium and on adding water a brown ethereal layer and a black sludge were obtained. Metallic palladium and dipyridyl were isolated but no organopalladium compound was obtained.

(17) Reaction between p-tolylmagnesiumbromide and bis-(triethylphosphinedibromopalladium)

The dibromide (10 g., 0.02 moles) in tetrahydrofuran (150 mls) was allowed to react with p-tolylmagnesium-bromide (0.025 moles) at -20°C. The yellow colour of the reaction mixture faded as it warmed up then began to turn brown and on hydrolysis turned black. From the organic layer a black solid was obtained which on extraction with, and recrystallisation (three times) from an ether hexane mixture gave a grey-white crystalline solid. Melting Point 127-128°C.

The analysis figures were incompatible with either a mono p-tolyl compound or a di p-tolyl compound however.

(18) Mixed Organopalladium Compounds

Two attempts to prepare mixed organopalladium compounds, (i.e. compounds with two different organic groups attached to the palladium atom) met with no success.

Bis(triethylphosphinebromo(methyl)palladium was allowed to react with phenyl-lithium and with phenylethynyl-magnesium bromide i.e. $(Et_3P)_2Pd(Me)Br + PhLi$ ——

$(Et_3P)_2Pd(Me)Br + PhC{\equiv}CMgBr$ ——

In both cases blackening took place and no organo palladium compound was obtained.

Calvin and Coates[2] however have prepared bis(triethylphosphine)phenyl(p-trifluoromethyl)palladium.

$(Et_3P)_2Pd(p\text{-}CF_3C_6H_4)Ph.$

(19) Bis (tri-n-propylphosphine)dimethylpalladium

$$(nPr_3P)_2PdCl_2 + 2MeLi \text{ —— } (nPr_3P)_2PdMe_2 + 2\ LiCl$$

Bis(tri-n-propylphosphine)dichloropalladium (10 g., 0.02 moles) was allowed to react with methyl-lithium (0.045 moles). The colour of the solution faded slowly until the mixture was colourless and on hydrolysis two clear layers were obtained. The organic layer gave an oil which was dissolved in n-hexane and cooled overnight. A small amount of a colourless crystalline solid was obtained. Melting point 60°C. (Found: C, 52.9; H, 10.8; $C_{20}H_{48}P_2Pd$ requires C, 52.5; H, 10.6%).

III. COMPOUNDS OF GOLD

(1) Introduction

Organometallic compounds of gold were prepared by reaction of triethylphosphinemonochlorogold (I) with the requisite organolithium compound.

i.e. $Et_3PAuCl + RLi \longrightarrow Et_3PAuR + LiCl$

The desired product was usually found in the organic layer after hydrolysis and the aqueous layer after varying periods of time almost invariably deposited metallic gold which probably came from unstable soluble gold compounds of the form $(R_2AuEt_3P)^-Li^+$. Addition of large excesses of organolithium compound led to small yields.

(2) Triethylphosphinemonomethylgold (I)[2]

$$Et_3PAuCl + MeLi \longrightarrow Et_3PAuMe + LiCl$$

Monochloride (7 g., 0.02 moles) was allowed to react with methyl-lithium (0.025 moles). A faint pink colour was observed during the addition of methyl-lithium (probably due to colloidal gold) and this darkened to purple as the mixture warmed up.

A white solid was obtained from the organic layer. Melting Point 62°C. (Recrystallised from ether).

The aqueous layer began to show signs of metallic gold after about thirty minutes.

(3) Triethylphosphinemonophenylgold (I)[2]

$Et_3PAuCl + PhLi \longrightarrow Et_3PAuPh + LiCl$

Monochloride (7 g., 0.022 moles) was allowed to react with phenyl-lithium (0.025 moles). The pink organic layer gave a faintly pink solid which on recrystallisation from ether gave a white solid. Melting Point 68°C. The aqueous layer turned purple in a few minutes after separation. (M in 1.26% nitrobenzene solution 394.6; in 2.93% solution 404.1; in 4.75% solution 401.7: $C_{12}H_{20}AuP$ requires M, 392.4.)

(4) Triethylphosphinemonophenylethynylgold

$Et_3PAuCl + PhC{\equiv}CLi \longrightarrow Et_3PAuC{\equiv}CPh + LiCl$

The monochloride (7 g., 0.02 moles) was allowed to react with phenylethynyl lithium (0.025 moles). The reaction mixture turned to a green-yellow colour as the organolithium compound was added and remained this colour. After hydrolysis an insoluble green-yellow solid was filtered off. This proved to be the gold compound which on recrystallisation from acetone gave a yellow solid. Melting Point 84-87°C. Two further recrystallisations from methanol gave a yellow solid. Melting Point 83-85°C. On cooling the solid became a much deeper green yellow but reverted to its original colour on warming up again. (Found: C, 40.3; H, 4.8. M cryoscopically in 2.82% benzene solution 592.8; in 4.61% solution 542.5; in 5.91% solution 551.6. M cryoscopically in 1.08% nitrobenzene solution 486.1; in 2.42% solution 495.5; in 5.26% solution 483.7. $C_{14}H_{20}AuP$ requires C, 40.1; H, 4.8%; M, 416.5).

On allowimg to stand for a few days the compound reverted to a greyish white form with the same melting point (83-85°C) as the coloured compound. The grey compound did not change colour on cooling.

(5) Triethylphosphinemonoethylgold

$$Et_3PAuCl + EtLi \;\text{———}\; Et_3PAuEt + LiCl$$

The monochloride (7 g., 0.02 moles) was allowed to react with ethyl-lithium (0.21 moles). After hydrolysis and separation the organic layer began to darken. It was pumped dry and the dark solid obtained recrystallised from ether and then n-hexane (three times). A grey/white solid was obtained. Melting Point 51°C. (slight decomposition).

The solid was very soluble in ether and effervesced steadily with ethyl alcohol and vigorously with alcoholic

HCl. (Found: C, 28.0; H, 6.1; $C_8H_{20}AuP$ requires C, 27.9; H, 5.9%).

(6) Triethylphosphinemonoiodogold (I)[6]

$$Et_3PAuCl + NaI \longrightarrow Et_3PAuI + NaCl$$

The monochloride (3.5 g., 0.01 moles) was dissolved in acetone and added to a saturated solution of sodium iodide in acetone (100 mls).

The precipitated sodium chloride was filtered off and a little more solution of sodium iodide was added to complete the conversion. The acetone solution was then added to a large volume of water and the triethylphosphinemonoiodogold filtered off and recrystallised from an acetone water mixture. White solid Melting Point 68°C. (Found: C, 16.3; H, 3.5. $C_6H_{15}AuP$ requires C, 16.3; H, 3.4%).

(7) Triethylphosphinemonobromogold (I)[7]

$$H_2O + HAuCl_4 + 2Et_3P + KBr \longrightarrow Et_3PAuBr + 3HCl + Et_3P + KCl$$

To a solution of brown gold chloride (8 g., 0.02 moles) in water (20 mls) and ethanol (20 mls) was added a solution of potassium bromide (15 g., 0.12 moles) in water (20 mls). The mixture was cooled in an ice bath and ethanol (50 mls) was added. A solution of triethylphosphine (6 mls 0.04 moles) in ethanol (20 mls) was added dropwise with stirring under nitrogen. After the addition of the triethyl phosphine the solution went red and then orange, Addition of triethylphosphine (2 mls) caused the mixture to turn faintly pink. Water (100 mls) was added and the grey white solid obtained recrystallised from alcohol. Melting Point 88-90°C.

(8) Reaction between n-propyl-lithium and triethylphosphinemonochlorogold (I)

The monochloride (7 g., 0.02 moles) was allowed to react with n-propyl-lithium (0.021 moles). A brown oil was obtained from the organic layer from which no crystals could be obtained. The oil decomposed slowly over several days yielding metallic gold.

(9) Reaction between mesityl-lithium and triethylphosphinemonochlorogold (I)

Mesityl-lithium was prepared in 92% yield in tetrahydrofuran at -40°C from mesitylbromide and lithium shot.

Monochloride (7 g., 0.02 moles) in tetrahydrofuran (150 mls) was allowed to react with mesityl-lithium (0.021 moles). Ether (100 mls) was added to aid in separation after hydrolysis, and from the organic layer a brown oil was obtained which would not deposit crystals and appeared to be quite stable.

(10) Reaction between n-butyl lithium and triethylphosphinemonochlorogold (I)

The monochloride (7 g., 0.02 moles) was allowed to react with n-butyl-lithium (0.021 moles). A brown oil was obtained from the organic layer. On cooling this gave faintly brown crystals which reverted to the oil on warming up. The oil appeared to be quite stable.

(11) Reaction between p-tolyl-lithium and triethylphosphinemonochlorogold (I)

A white stable oil was obtained after cooling a hexane solution of the brown oil from the organic layer.

(12) Reaction between p-chlorophenyl-lithium and triethylphosphinemonochlorogold (I)

Again a brown oil was isolated from which no crystals could be obtained.

(13) Reaction between potassiumdiphenylphosphide and triethylphosphinemonochlorogold (I)

Potassiumdiphenylphosphide was prepared from diphenylphosphine (9.3 g., .05 moles) in tetrahydrofuran (150 mls) and potassium wire (5 g., 0.12 moles). The solution turned bright red and then on standing dark brown. It was decanted from the potassium wire and titration of a sample indicated that the total alkali (0.086 moles) was almost twice the expected amount.

The solution of potassiumdiphenylphosphide (75 mls) was added dropwise to the monochloride (7 g., 0.02 moles) in tetrahydrofuran (150 mls) cooled to -40°C. After hydrolysis a yellow oil settled out which on scratching gave a sticky yellow solid. The solid was washed with acetone several times and dried. It proved to be almost completely insoluble in all solvents and was probably a polymer. Attempts to break down the polymer chain by heating with triethylphosphine in xylol failed. As the compound could not be recrystallised no analysis was carried out.

(14) Reaction between potassiumdiphenylarsine and triethylphosphinemonochlorogold (I)

Potassiumdiphenylarsine was prepared in a similar manner to potassiumdiphenylphosphine from diphenylarsine (0.05 moles) and potassium wire (0.12 moles). Again the alkali titration was almost twice the expected figure.

The solution of potassium diphenylarsine (75 mls) was added dropwise to the monochloride (7 g., 0.02 moles) in tetrahydrofuran (150 mls) at -40°C.

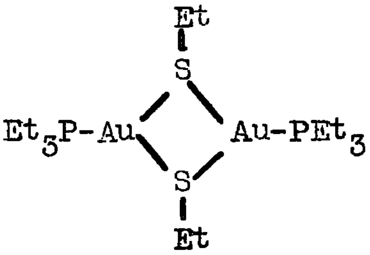
After hydrolysis a yellow oil was obtained which solidified after cooling and scratching. The solid proved to be almost insoluble in any solvent but with triethylphosphine in benzene it went into solution finally yielding an oil. With phenyl dimethylphosphine in benzene an oil was obtained also.

(15) Reaction between sodiumphenylsulphide and triethylphosphinemonochlorogold (I)

Sodiumphenylsulphide (.05 moles) was prepared by adding diphenylsulphide (.05 moles) to a solution of sodium ethoxide (0.05 moles) in ethanol.

The monochloride (7 g., 0.02 moles) in tetrahydrofuran (150 mls) was allowed to react with sodiumphenylsulphide (0.02 moles) at -40°C. After hydrolysis a white oil was obtained which on cooling gave a white mass. This was recrystallised from acetone (twice) and gave a white crystalline solid. Melting point 94-95°C. (Found: C, 34.4; H, 4.9; M cryoscopically in 1.82% benzene solution. 471.1; in 3.96% solution 522.0; in 5.27% solution 560.2. M cryoscopically in 1.06% nitrobenzene solution 434.8; in 2.39% solution 451.3; in 3.56% solution 474.9. $C_{12}H_{20}AuSP$ requires C, 34.0; H, 4.7%; M. 424.4).

As the compound showed some association in benzene solution it was hoped that by using a slightly stronger donor i.e. diethylsulphide, a dimer of the form



might be obtained.

(16) Reaction between Sodiumethylsulphide and Triethylphosphinemonochlorogold (I)

From the reaction of sodiumethylsulphide (0.02 moles) with the monochloride (0.02 moles) a thick colourless evil smelling oil was obtained which decomposed on attempts to purify it by vacuum distillation, giving metallic gold and triethylphosphine as easily recognisable products.

(17) Triphenylphosphinemonomethylgold (I)

$$Ph_3PAuCl + MeLi \text{ ——— } Ph_3PAuMe + LiCl$$

The monochloride (10 g., 0.02 moles) was allowed to react with methyl-lithium (0.025 moles). A white solid was obtained from the reaction mixture after hydrolysis. This was filtered off, washed and recrystallised from hot acetone. Melting Point 175°C (Decomposition). (Found: C, 48.0; H, 3.7; Au, 41.95. $C_{19}H_{18}AuP$ requires C, 48.1; H, 3.8; Au 41.5%). Decomposition occurred almost instantaneously in the aqueous layer.

(18) Triphenylphosphinemonophenylgold (I)

$$Ph_3PAuCl + PhLi \text{ ——— } Ph_3PAuPh + LiCl$$

The monochloride (10 g., 0.02 moles) was allowed to react with phenyl-lithium (0.025 moles). A brown solid was filtered off after hydrolysis (the brown colour was probably due to the phenyl-lithium). It was recrystallised three times from hot ether and then from ether together with a little charcoal. A white solid was obtained. Melting Point 164°C. (began to decompose at 130°C). (Found: C, 52.8; H, 3.9; Au, 37.2. $C_{24}H_{20}AuP$, requires C, 53.8; H, 3.7; Au, 36.8%).

(19) <u>Triphenylphosphinemonoethylgold (I)</u>

$$Ph_3PAuCl + EtLi \longrightarrow Ph_3PAuEt + LiCl$$

The monochloride (10 g., 0.02 moles) was allowed to react with ethyl-lithium (0.921 moles). The reaction mixture turned greenish yellow and then turned to pink as the mixture warmed up.

From the organic layer a faintly pink solid was obtained (the pink colour being due to metallic gold). On recrystallisation from ether (twice) a white solid was obtained. The compound decomposes and melts about 130°C if heated up quickly but the melting point was not very certain. (Found: C, 49.5; H, 4.4. $C_{20}H_{20}AuP$ requires C, 49.2; H, 4.1%).

(20) <u>Triphenylphosphinemonomesitylgold (I)</u>

$$Ph_3PAuCl + Mesityl\text{-}Li \longrightarrow Ph_3PAuMesityl + LiCl$$

The monochloride (10 g., 0.02 moles) was allowed to react with mesityl-lithium (0.021 moles). A light brown oil was obtained from the organic layer which on prolonged pumping (eight hours) gave a light brown solid. This solid was recrystallised from ether giving a white solid which did not melt but began to decompose at 100°C. (Found: C, 55.7; H, 4.7. $C_{27}H_{26}AuP$ requires C, 56.0; H, 4.5%).

IV. COMPOUNDS OF PLATINUM

(1) Preparation of trans-Bis(~~m~~triethylphosphine)diphenylplatinum[8]

Phenylmagnesiumbromide was prepared from magnesium (1.3 g.) bromobenzene (8.4 g.) and ether (40 mls). Benzene (150 mls) was added and most of the ether removed by distillation.

The flask was allowed to cool, trans-bis(~~m~~triethylphosphine)-dichloroplatinum (3.5 g.) was added and the mixture refluxed for 1 hour, then cooled. After hydrolysis with dilute hydrochloric acid the crude product was isolated and chromatographed on an alumina column. Elution with petroleum ether (b.p. 60-80°C) gave trans-bis(~~m~~triethylphosphine)-diphenylplatinum (2.3 g.). Melting Point 177-180°C.

PHYSICAL MEASUREMENTS

I. GENERAL THEORY OF DIPOLE MOMENT MEASUREMENTS

It was pointed out by Faraday[9] that the molecules of a dielectric when placed in an electric field become 'polarised' i.e. a separation of charge takes place. One end of the molecule acquires a small positive charge, the other a negative charge of the same magnitude.

Clausius[10] and Mosotti[11] treated this idea mathematically and derived the relation known as the Clausius and Mosotti law.

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{1}{d} = p \qquad (1)$$

Where p is the specific polarisation d is the density and ε the dielectric constant of the substance.

For a number of materials of low dielectric constant p remains constant despite changes in temperature and pressure, and is almost the same for the liquid or solid states.

It was shown by Maxwell[12] that for such materials the dielectric constant is related to the refractive index n for the same frequency of radiation by

$$n^2 = \varepsilon \varphi \qquad (2)$$

where φ is the magnetic permeability of the material.

As φ is almost equal to unity for all except ferromagnetic substances then if the values of the refractive index obtained in the visible region of the spectrum are extrapolated to the wavelength at which the dielectric constant is measured (virtually infinite wavelength) then

$$\varepsilon = n_\infty^2 \qquad (3)$$

For substances of high dielectric constant ε is almost invariably greater than n_∞^2 .

It was shown by Lorenz[13] and Lorentz[14] that $\frac{n^2-1}{n^2+2}\,\frac{1}{d} = r$ where r is a constant, independent of temperature, known as the specific refraction. The product of the specific refraction and the molecular weight M is known as the molecular refraction R .

$$\text{Thus} \qquad R = \frac{n^2-1}{n^2+2}\,\frac{M}{d} \qquad (4)$$

Molecular refractions are within certain limits additive and by allocation of certain values to certain atoms and bonds molecular refractions may be compiled. In view of this it would be expected that the molecular polarisation P obtained by multiplying the specific polarisation by the molecular weight would also be additive. It is found however that P is only additive for compounds of low dielectric constant where $\varepsilon = n_\infty^2$.

Debye[15,16] indicated that this behaviour could be explained by assuming that although a molecule as a whole is neutral the centres of positive and negative charge do not usually coincide and the molecule has a permanent doublet or dipole which tends to orientate itself in an electric field of relatively low frequency. (i.e. radio frequency). Thus the molecule shows polarisation by orientation besides charge displacement.

Indeed it would be fortuitous if any molecule other than a symmetrical one did not have some net permanent dipole due to the variation in electronegativity of the atoms of which the molecule is composed.

The magnitude of the electronic charge is 4.8×10^{-10} e.s.u. and distances between small atoms 1 to 2×10^{-8} cms. It is found that dipole moments of most molecules lie between 0 and 9×10^{-18} e.s.u. or 0-9 Debye. (1 Debye = 1×10^{-18} e.s.u.). A further contribution to the total polarisation of a molecule is that due to the relative displacement of the atoms of the molecule in an electric field.

If a molecule contains polar bonds so that the atoms carry different effective charges then the nuclei are displaced with respect to one another and this produces an induced dipole the effect of which is superimposed on the permanent dipole if present and the dipole due to the displacement of the electrons with respect to the nucleus.

This type of polarisation is known as atom polarisation and together with orientation polarisation (due to orienting of permanent dipoles) and electron polarisation (that due to displacement of electrons) goes to make up the total polarisation.

Thus Total polarisation = Atom Polarisation +
Orientation Polarisation +
electron polarisation

$$\text{or} \quad TP = {}_{A}P + {}_{O}P + {}_{E}P \qquad (5)$$

For molecules with no permanent dipole and no atom polarisation the total polarisation is the same as the electron polarisation or $TP = {}_{E}P$, and is identical with R if the value of n is obtained by extrapolation to infinite wavelength. As the values of R obtained for infinite wavelength usually only differ by 1 or 2 c.c. from those obtained at visible frequencies, often no correction for the difference is made in dipole moment calculations.

The Clausius and Mossotti theory considers each molecule as a sphere of dielectric and assumes that for small displacements of electrons with respect to the nucleus the induced moment m is proportional to the field F.

$$\text{i.e.} \quad m = \gamma F \qquad (6)$$

γ is called the polarisability of the molecule and is equal to the moment induced by a field of unit strength.

The treatment gives an equation for the Molecular polarisation known as distortion polarisation,

$P = \frac{4}{3}\pi N \gamma$ where N is Avagado's number.

The Debye treatment which is concerned with a molecule with a permanent dipole μ inclined at an angle to an electric field F gives an expression for the molecular orientation polarisation

$${}_{O}P = \frac{4}{3}\pi \frac{N\mu^2}{3kT} \qquad (7)$$

where k is Boltzmann's constant and T is the absolute temperature.

Thus the total polarisation is given by

$${}_{T}P = \frac{4}{3}\pi N \left(\gamma + \frac{\mu^2}{3kT}\right) \qquad (8)$$

$\frac{4}{3}\pi N \gamma$ represents the polarisation a molecule would have in the absence of a permanent dipole and this may be divided up into atom polarisation and electron polarisation. From equation I(7):

$$\mu = \sqrt{\frac{9k}{4\pi N} \quad {}_{o}PT}$$

$$= 0.012812 \sqrt{{}_{o}PT}.$$

As all the dipole moment measurements with which this work is concerned were carried out at 25°C then this can be further reduced to

$$\mu = 0.2212 \sqrt{{}_{o}P} \qquad (9)$$

II. EVALUATION OF RESULTS

The expression for the polarisation of a solution, due to Debye[15,16] is:-

$$P = P_1 f_1 + P_2 f_2 = \frac{\varepsilon - 1}{\varepsilon + 2} \; \frac{M_1 f_1 + M_2 f_2}{d} \qquad (1)$$

where P_1 P_2 f_1 and f_2 are the total polarisations and mole fractions of solvent and solute respectively. Halverstadt and Kumler[17] 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. $\varepsilon = a + \alpha w_2$ and $v = b + \beta w_2$ where a and b are the dielectric constant and specific volume of the solvent, w_2 is the weight fraction of the solute), they derived an expression for the specific total polarisation at infinite dilution of the solute p_2 .

$$p_2 = \frac{3 \alpha V_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} (v_1 + \beta) \qquad (2)$$

By plotting ε against w_2 and v against w_2, α and β may be evaluated.

In a similar manner the electron polarisation Ep_2 can be expressed as

$$Ep_2 = \frac{6\gamma n_1 v_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n^2 + 2}(v_1 + \beta) \qquad (3)$$

where the assumption is made that $n = n_1 + \gamma w_2$ where n_1 is the refractive index of the solvent.

To obtain dipole moments by measurements on solutions the dielectric constant refractive index and density of a number of solutions must be determined. By plotting ε, v, and n against w_2, obtaining α, β, and γ from the graphs, and fitting them in the equations then the total polarisation and electron polarisation of the compound being studied may be obtained.

At low concentrations ($w_2 \leqslant 0.02$) the plots are usually very close to straight lines[17] and linear plots of n against w_2 may be obtained at still higher concentrations.

III. PHYSICAL MEASUREMENTS

(1) Dielectric Constant Measurements

Benzene was used as the solvent in all cases and the dielectric constants of air (ε_1), and benzene (ε_2) were assumed to be known. The principle used was the measurement of the change in capacitance which occurred when the dielectric of a condenser was charged.

The condenser was the cell (see Figure 1) the dielectric of which could be changed easily by blowing out with nitrogen and replacing with the required liquid. If ε_3 is the dielectric constant of the solution and C_1, C_2 and C_3 the capacitances of the cell filled with air, benzene and solution respectively, then provided the lead capacitances remain constant

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

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

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

A heterodyne beat capacitance meter similar to the one designed by Hill and Sutton[18] was used to measure the capacitance change in the cell. This consisted of two units. The lower one was principally a beat frequency generator made up of two similar radio frequency oscillators one of fixed frequency f_0 (approximately 10^5 c.p.s.) and one of variable frequency f_1 incorporating the measuring system. Also in the lower unit were the requisite circuits for mixing, demodulating, and beat frequency amplification. The two oscillators were made as nearly identical as possible so that any disturbances, e.g. fluctuations in temperature or supply voltage, affected both equally.

The upper unit contained a power pack, an audio frequency oscillator, and a cathode ray tube. The audio oscillator with frequency f_2 of about 1000 c.p.s. could be varied by a coarse and a fine control to allow accurate adjustment. The X plates of the cathode ray tube carried the output from the beat frequency generator and the Y plates that of the audio frequency oscillator. Some difficulty was encountered in making the apparatus sufficiently stable.

When first constructed the system, particularly with the cell in circuit, was very unstable. An appreciable drift occurred between switching the cell out and in again and a steady zero reading for the cell filled with benzene could not be obtained.

Improvements were brought about by replacing the silver-mica condensers in the frequency determing stages of the oscillators by rigid, air spaced, metal plate condensers and by making all leads as rigid as possible.

A further increase in stability was obtained by substituting a thick copper lead taken through a one inch earthed copper tube filled with polythene for the external coaxial cable lead from the main unit to the cell.

Finally the low tension supply to the valve heaters (which was not stabilised) was replaced in the case of the valves in the frequency determining stages of the oscillators, by lead acid accumulators.

The apparatus was then sufficiently stable to measure to 0.004 pf.

A transistor stabilised low tension supply was substituted for the lead acid accumulators several months later, and has since proved most satisfactory.

The measuring system was as shown in Figure II, C was the cell, D an air spaced, uncalibrated, variable condenser, as was F, and M was a calibrated concentric cylinder variable condenser with a micrometer screw having a capacitance change of 3.68 pfs per cm. (cms.

in length not in capacitance). S was a switch by which the cell could be replaced by F, and M in the circuit of the variable radio frequency oscillator.

The cell was a modified form of the Sayce Briscoe[19] type with plates of platinum burnt onto the glass instead of deposited silver. This made the cell much more robust and allowed washing out with strong acid if necessary. The capacitance was about 50 pfs. The 25°C thermostat in which the cell was immersed was filled with transformer oil to reduce stray capacitances.

Procedure

The cathode ray tube was used to obtain the necessary relationship between the output frequency of the beat frequency generator and that of the audio frequency oscillator. As it was possible to obtain two identical beat frequencies, one with $f_o > f_1$ and one with $f_1 < f_o$ care was taken to always work with $f_o > f_1$. By varying F the output from the beat frequency generator was tu~~r~~ned to give a figure of eight on the cathode ray tube corresponding to $f_o - f_1 = 2f_2$ this ratio prevented any likelihood of the oscillators pulling and was used as balance point in all measurements.

The cell was washed out twice and then filled with dry benzene the benzene used in washing out being expelled by a stream of nitrogen from a cylinder. The cell and contents were allowed to come to thermal equilibrium (10 minutes was found to be a sufficient time) and F was adjusted until the figure of eight was obtained on the cathode ray tube. D and M were then switched in and by adjustment the figure of eight was again obtained. The cell was switched back in and the figure of eight again obtained and then D and M switched in again and adjusted. As changes in capacitance in the circuit containing F and the cell appeared to cause slight changes in the frequency of the circuit containing F, D, and M and vice-versa it was always necessary to adjust each circuit twice at least. When a steady figure of eight was obtained on both sides of the switch indicating that the capacitances on both sides of the switch ~~indicating that the capacitances on both sides~~ had the same value then the reading on M was noted. As M was calibrated in centimeters in length (0 to 2.5) and as the capacitance of M increased as the reading in centimeters decreased it was always arranged that when a balance was obtained with benzene in the cell, M should read approximately 2.4 centimeters.

The benzene was then blown out with dry nitrogen and the cell washed out and filled with the solution under test. The process of adjustment was repeated but this time only F and M were adjusted so that the change in capacitance could be read off on M.

The zero reading (i.e. the reading with the cell filled with benzene) was checked after each solution, as it occasionally showed a tendency to drift during a set of measurements.

(2) Specific Volume Measurements

A Sprengel type pyknometer of about 4 mls capacity fitted with ground glass caps to prevent evaporation was used. It was calibrated by filling with distilled water and weighing and checked by making density determinations on benzene, both operations being carried out at 25°C. The density of benzene at 25°C is about 0.8736 g/ml[1] and the results obtained had a maximum deviation of ± 0.0002 g/ml from this figure.

Procedure

The dry pyknometer was filled and placed in a 25°C thermostat for 15 minutes. The meniscus of the liquid was adjusted to the graduation mark by applying a piece of filter paper to the tip of the opposite limb and the pyknometer was removed from the thermostat, dried with tissue paper and the caps put in place. It was hung on the balance for twenty minutes to allow to come to hygrometric equilibrium with the atmosphere and then weighed.

(3) Refractive Index Measurements

A Pulfrich refractometer with a divided cell was used. Silicone rubber proved to be a satisfactory cement, the main difficulty being removal of the cell from the prism when a leak occurred. The cell could be washed out with aqua regia without causing apparant harm to the cementing.

The refractometer was enclosed in a 25°C air thermostat. The thermostat consisted of a large box (approximately 2 ft x 2 ft x 2 ft) fitted with a glove and a terylene window through which one could take readings and see to make adjustments without opening the box.

The box was heated by an electrical sheet heater placed directly in front of a fan. The temperature was controlled by an a/c bridge thermoregulator with a platinum resistance thermometer as the arm of the bridge inside the box. A quick response to temperature fluctuations was obtained with this system. A temperature difference of 0.2°C was observed between various parts of the box but temperatures in particular places did not vary by more than 0.1°C.

Temperature control by water circulation proved unsatisfactory probably due to inefficiency of the circulating pump and the low thermal conductivity of the prism glass.

Initially a sodium lamp was used as a light source and later for refractivities at various wavelengths mercury, cadmium and hydrogen lamps. As filters were necessary and as the intensities of some of the lines (particularly those of the hydrogen lamp) were not very high this proved to be an unsatisfactory method.

Instead, six interference filters (Jenaer Glasswork Schott and Gen.) were used together with a microscope lamp as light source. These were checked by determining refractivities of benzene with the red and blue lines of the hydrogen lamp and with the sodium D lines. Refractivities determined by using the filters were in agreement, and so the lamps were discarded in favour of the filters. The intensity of light transmitted by the red filter (λ max* = 7090Å) was very low and to increase this a projection lantern was substituted for the microscope lamp.

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* (The interference filters transmitted appreciable intensity of light over a narrow wavelength range. λ max was the wavelength at which the filter had its highest degree of transmission.)

This arrangement proved to be very satisfactory and easy to use.

The sodium D line was used in all the earlier measurements, and later the red interference filter with $\lambda_{max} = 6620$Å. For the symmetrical compounds, refractive indices at several wavelengths were measured to allow an estimation of the electron polarisation at infinite wavelength to be made.

Procedure

A solution was placed in one side of the divided cell and a sample of pure dry benzene in the other. A polythene cap was placed over the top of the cell to prevent evaporation and the liquids allowed to come to thermal equilibrium (usually taking about 20 minutes). The extinction angles were read off from the refractometer and the difference obtained by subtraction. As differences rather than absolute refractivities were of primary importance, this technique minimised any errors which might be caused by temperature fluctuations.

CALCULATION OF RESULTS

(1) Dielectric Constants

The change in capacitance in the cell was measured on the calibrated condenser M. The dielectric constant of benzene was taken as 2.2727 and that of air as 1.0006.

The change in capacitance of the cell when filled with air and then with benzene was 69.05 pfs, and was measured by connecting an N.P.L. calibrated condenser in parallel with the cell and finding the necessary change in capacitance to restore the balance when the dielectric was changed from air to benzene.

From equation III(I).

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

$\varepsilon_1 = 1.0006$ $\varepsilon_2 = 2.2727$ $C_2-C_1 = 69.05\text{pfs}$

C_3-C_2 was the change in capacitance measured on M.

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

If l is the reading on the condenser in cms. As the capacitance change per cm was 3.68 pfs, then

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

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

$$\frac{d\varepsilon}{dw} = \frac{1.2721 \times 3.38}{69.05} \quad \frac{dl}{dw}$$

$$= 0.06227 \quad \frac{dl}{dw} \qquad (1)$$

$\frac{dl}{dw}$ is the slope of the graph obtained by plotting the reading on the calibrated condenser against weight fraction. $\frac{d\varepsilon}{dw}$ corresponds to α in equation II(2).

(2) Specific Volumes

Volume of pyknometer was 4.1458 mls.

$$\text{Specific volume} = \frac{4.1458}{Wg.}$$

Where Wg is the weight of solution in the pyknometer.

$$v = b + \beta w_2 = \frac{4.1458}{Wg.}$$

$$\beta = \frac{d\left(\frac{4.1458}{Wg.}\right)}{dw_2} \qquad (2)$$

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

(3) Refractive Indices

The relationship between the extinction angle and the refractive index of the solution was given by

$$n = /\text{Sin } A \sqrt{N^2 - \text{Sin}^2 B} + \text{Cos } A \text{ Sin } B.$$

Where A was the refractive angle of the prism

B the angle of emergence, and

N the refractive index of the prism.

However on plotting a graph of extinction angle against refractive index a linear relationship was observed and thus the computation of Δn values was comparatively simple. The difference in the extinction angle of the solvent and solution was read off directly from the refractometer, and the relationship between extinction angle and refractive index was found to be:-

$$1 \text{ min of arc} = 1082 \times 10^{-7}$$

A plot of Δn against w gave $\frac{dn}{dw}$ which corresponds to γ in equation II(3).

(4) Total Polarisation

From equation II(2) i.e. $p_{2\infty} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + \frac{\epsilon_1 - 1}{\epsilon_1 + 2}(v_1 + B)$

$v_1 = 1.1447$ $\epsilon_1 = 2.2727$

Then $p_2 = 0.1881\alpha + 0.2979\,(1.1447 + \beta)$ (3)

(5) Electron Polarisation

From equation II(3) i.e. $Ep_2 = \frac{6n_1\gamma v_1}{(n_1^2+2)^2} + \frac{n_1^2 - 1}{(n_1^2+2)}(v_1 + B)$

$v_1 = 1.1447$ $n_1 = 1.4979$ (for Sodium D line)

Then:

$Ep_2 = 0.5712\gamma + 0{,}2932\,(1.1447 + \beta)$ for

$\lambda = 5985\text{Å}$ (4)

For $\lambda = 7090$ $E.p._2 = 0.5715 + 0.2927\,(1.1447 + \beta)$

$\lambda = 6620$ $E.p._2 = 0.5714 + 0.2929\,(1.1447 + \beta)$

$\lambda = 5910$ $E.p._2 = 0.5712 + 0.2931\,(1.1447 + \beta)$

$\lambda = 5440$ $E.p._2 = 0.5711 + 0.2933\,(1.1447 + \beta)$

$\lambda = 4780$ $E.p._2 = 0.5706 + 0.2938\,(1.1447 + \beta)$

$\lambda = 4340$ $E.p._2 = 0.5702 + 0.2944\,(1.1447 + \beta)$

Values of $E.p._2$ at infinite wavelength were obtained by assuming that the values obtained for various values of λ fitted a simple equation of the form

$$Ep_2 = A + \frac{B}{\lambda^2}$$

The $E.p._2$ values were plotted against $\frac{1}{\lambda^2}$ and the curve obtained was extrapolated to $\frac{1}{\lambda^2} = 0$. This gave a value for A which was taken as $E.p._2$ at infinite wavelength.

V. ERRORS IN MEASUREMENT

(1) Errors in ε_1, n_1 and v_1

Everard, Hill and Sutton[21] showed that small errors in those quantities were of negligible importance in dipole moment measurements. As no large variations were observed when plotting graphs of ε , n and v against w, values of $\varepsilon_1 = 2.2727$, $n_1 = 1.4949$ ($\lambda = 5895$) and $v_1 = 1.1447$ were used in all calculations (benzene being used as solvent in all cases).

(2) Errors in α, β and γ

These were considered to be not larger than 2% as any big errors were shown by deviations from linearity in the corresponding plots.

Errors of 2% in β have negligible effect upon μ . For a compound of molecular weight 500 an error of 2% in α causes an error of 0.02 D in a moment of about 1D, whilst an error of 2% in γ causes an error of 0.012 D. Thus the total error in a moment of 1D is 0.032 D or 3.2%.

In moments of about 3.5 D the error is 0.052 D or 1.5% and for larger moments the percentage error decreases.

(3) Errors in Electron Polarisation

In almost all electron polarisation determinations the Sodium D line was used.

Differences between electron polarisation values determined for the Sodium D line and for infinite wavelength, on several compounds in the latter stages of the work were not greater than 1 c.c. This constitutes a possible error of 0.02 D in a moment of 1 D (i.e. 2%) whilst for a moment of 3.5 D the error is 0,01 D (i.e. 0.3%).

(4) Errors due to Atom Polarisation

Measurements on symmetrical palladium compounds of the type L_2PdR_2 where R was Ph, p.ClPh, p.BrPh gave values of atom polarisation of between 14 c.c. and 21 c.c. When R was C ≡ CPh the value was very high (28.9 c.c.) whilst when R was Cl, Br or I the value was about 26.5 c.c. (Chatt and Shaw[20] obtained high values for the atom polarisations of their acetylenic derivatives of platinum.)

In view of these figures it is possible that errors due to uncertain atom polarisation values are as high as 4 c.c. corresponding to an error of 0.1 D (i.e. 10%) in moments of 1 D and an error of 0.04 D (i.e. 1.1%) in moments of 3.5 D.

(5) Total error

Moments of about 1 D are very uncertain as the possible total error is about 17%. For moments of 3.5 D the error is unlikely to be greater than 0.1 D (i.e. 3%).

VI. RESULTS OF DIPOLE MOMENT MEASUREMENTS

(1) Compounds of Palladium with Permanent Dipole Moments

Bis(triethylphosphine)bromo(methyl)palladium

$10^6 w$	v	$10^6 \Delta n$
4981	1.1428	334
9846	1.1406	647
13392	1.1392	808
16378	1.1376	1047

$\frac{d\varepsilon}{dw} = 4.4210$ $\frac{dv}{dw} = -0.4474$ $\frac{dn}{dw} = 0.06375$

$TP_2 = 455.2$ c.c. $EP_2 = 105.5$ c.c. $AP_2 = 19$ c.c. $\mu = 4.02$ D

Bis(triethylphosphine)bromo(phenyl)palladium

10^6	v	$10^6 \Delta n$
6002	1.1421	379
8326	1.1416	561
14007	1.1392	975
20357	1.1365	1442
24487	1.13	1729

$\frac{d\varepsilon}{dw} = 3.1596$ $\frac{dv}{dw} = -0.4049$ $\frac{dn}{dw} = 0.073$

$TP_2 = 407.4$ c.c. $EP_2 = 129.3$ c.c. $AP_2 = 20$ c.c. $\mu = 3.55$ D

Bis(triethylphosphine)bromo(p-bromophenyl)palladium

10^6w	v	$10^6\Delta n$
4994	1.1430	2181
10378	1.1397	5965
13472	1.1388	8569
20187	1.1355	14072

$\frac{d\varepsilon}{dw} = 0.9341$ $\frac{dv}{dw} = -0.490$ $\frac{dn}{dw} = 0.0675$

$TP_2 = 214.6$ c.c. $EP_2 = 133.5$ c.c. $AP_2 = 23.5$ c.c. $\mu = 1.66$ D

Bis(triethylphosphine)bromo(p-chlorophenyl)palladium

10^6w	v	$10^6\Delta n$
3784	1.1438	108
9651	1.1412	615
16164	1.1381	1073
20031	1.1363	1405

$\frac{d\varepsilon}{dw} = 1.0025$ $\frac{dv}{dw} = -0.460$ $\frac{dn}{dw} = 0.0669$

$TP_2 = 209.8$ c.c. $EP_2 = 127.7$ c.c. $AP_2 = 22.9$ c.c. $\mu = 1.70$ D

Bis(triethylphosphine)bromo(mesityl)palladium

$10^6 w$	v
4782	1.1429
8674	1.1416
11341	1.1406
12186	1.1403

$\frac{d\varepsilon}{dw} = 2.8490$ $\frac{dv}{dw} = -0.3500$

$TP_2 = 414.0$ c.c. EP_2(calculated) $= 143.3$ c.c. $\mu = 3.5$ D

Bis(triethylphosphine)cyanomethylpalladium

$10^6 w$	v	$10^6 \Delta n$
5656	1.1431	273
11547	1.1410	597
17190	1.1391	919
22184	1.1374	1157

$\frac{d\varepsilon}{dw} = 6.8428$ $\frac{dv}{dw} = -0.3376$ $\frac{dn}{dw} = 0.0546$

$TP_2 = 586.6$ c.c. $EP_2 = 102.8$ c.c. $AP_2 = 23$ c.c. $\mu = 4.74$ D

Bis(triethylphosphine)dimethylpalladium

$10^6 w$	v	$10^6 \Delta n$
3094	1.1439	122
6037	1.1429	291
8306	1.1421	453
9818	1.1418	506

$\frac{dv}{dw} = -0.3070$ $\frac{dn}{dw} = 0.0503$ $EP_2 = 103.3$ c.c.

(a) $\frac{d\varepsilon}{dw} = 0.9583$ $TP_2 = 160.3$ c.c. $\mu = 1.4$ D

(b) $\frac{d\varepsilon}{dw} = 6.7874$ $TP_2 = 569.3$ $\mu = 4.7$ D

(c) $\frac{d\varepsilon}{dw} = 4.1410$ $TP_2 = 395.6$ c.c. $\mu = 3.6$ D

(d) $\frac{d\varepsilon}{dw} = 2.2880$ $TP_2 = 253.6$ c.c. $\mu = 2.7$ D

Bis(trimethylphosphine)dimethylpalladium

10^6 w	v	$10^6 \Delta n$
5333	1.1418	433
8560	1.1405	578
10568	1.1398	704
11593	1.1393	812

$\frac{d\varepsilon}{dw} = 11.495$ $\frac{dv}{dw} = -0.395$ $\frac{dn}{dw} = 0.06805$

$TP_2 = 978.4$ c.c. $EP_2 = 74.8$ c.c. $\mu = 6.6$ D

Bis(triethylarsine)dimethylpalladium

10^6 w	v	$10^6 \Delta n$
5339	1.1414	289
7041	1.1408	325
10492	1.1393	560
13848	1.1378	777

$\frac{d\varepsilon}{dw} = 7.2233$ $\frac{dv}{dw} = -0.5442$ $\frac{dn}{dw} = 0.0533$

$TP_2 = 708.7$ c.c. $EP_2 = 95.2$ c.c. $\mu = 5.4$ D

(2) Compounds of Gold with Permanent Dipole Moments

(10 c.c. has been allowed for atom polarisation in each case).

Triethylphosphinemonochlorogold (I)

$10^6 w$	v	$10^6 \Delta n$
11283	1.1374	398
21138	1.1303	868
32709	1.1221	1371
43276	1.1149	1910

$\frac{d\varepsilon}{dw}^{*} = 22.17$ $\quad \frac{dv}{dw} = -0.700$ $\quad \frac{dn}{dw} = 0.04767$

$TP_2 = 1509$ c.c. $\quad EP_2 = 54.5$ c.c. $\quad \mu = 8.4$ D

$\frac{d\varepsilon}{dw}$ was derived from other solutions of lower concentration.

Triethylphosphinemonomethylgold (I)

$10^6 w$	v	$10^6 w$	$10^6 \Delta n$
3437	1.1426	27676	704
6151	1.1411	42786	1307
8772	1.1393	57135	1972
10275	1.1383	63172	2142

$\frac{d\varepsilon}{dw} = 10.36$ $\quad \frac{dv}{dw} = -0.62$ $\quad \frac{dn}{dw} = 0.041$

$TP_2 = 695$ c.c. $\quad EP_2 = 58.3$ c.c. $\quad \mu = 5.5$ D

$\frac{dn}{dw}$ was derived from another set of solutions.

Triethylphosphinemonophenylgold(I)

$10^6 w$	v	$10^6 \Delta n$
4118	1.1432	103
5078	1.1424	235
7576	1.1417	398
9580	1.1396	540
10758	1.1391	578

$\frac{d\varepsilon}{dw} = 10.96$ $\frac{dv}{dw} = -0.5779$ $\frac{dn}{dw} = 0.06187$

$TP_2 = 875.6$ c.c. $EP_2 = 79.1$ c.c. $\mu = 6.2$ D

Triethylphosphinemonophenylethynylgold(I)

$10^6 w$	v	$10^6 \Delta n$
5280	1.1425	451
7449	1.1414	613
11124	1.1390	959
14575	1.1370	1244

$\frac{d\varepsilon}{dw} = 11.58$ $\frac{dv}{dw} = -0.5901$ $\frac{dn}{dw} = 0.08533$

$TP_2 = 976$ c.c. $EP_2 = 8.8$ c.c. $\mu = 6.55$ D

Triethylphosphinemonoethylgold(I)

$10^6 w$	v	$10^6 \Delta n$
5818	1.1396	217
10437	1.1369	343
10487	1.1371	343
12195	1.1358	415

$\frac{d\varepsilon}{dw} = 9.5273$ $\frac{dv}{dw} = -0.5978$ $\frac{dn}{dw} = 0.03471$

TP_2 = 673.3 c.c. EP_2 = 62.1 c.c. μ = 5.4 D

Triethylphosphinemonoiodogold(I)

$10^6 w$	v	$10^6 w$	$10^6 \Delta n$
2290	1.1425	18510	1173
4998	1.1404	25300	1625
5442	1.1394	40613	2418
6962	1.1387		

$\frac{d\varepsilon}{dw} = 17.4356$ $\frac{dv}{dw} = -0.8280$ $\frac{dn}{dw} = 0.06237$

TP_2 = 1492.6 c.c. EP_2 = 56.8 c.c. μ = 8.36 D

Triethylphosphinemonobromogold

$10^6 w$	v	$10^6 \Delta n$
2763	1.1420	1624
5866	1.1398	3248
7222	1.1388	4150

$\frac{d\varepsilon}{dw} = 19.3037$ $\frac{dv}{dw} = -0.7229$ $\frac{dn}{dw} = 0.0572$

$TP_2 = 1485$ c.c. $EP_2 = 61.8$ c.c. $\mu = 8.32$ D

Triphenylphosphinemonochlorogold(I)

$10^6 w$	V	$10^6 \Delta n$
2147	1.1429	325
5520	1.1411	667
6382	1.1405	775
8300	1.1394	1029

$\frac{d\varepsilon}{dw} = 16.4704$ $\frac{dv}{dw} = 0.6236$ $\frac{dn}{dw} = 0.1305$

$TP_2 = 1610.4$ c.c. $EP_2 = 112.5$ c.c. $\mu = 8.5$ D

Triphenylphosphinemonomethylgold(I)

$10^6 w$	v	$10^6 \Delta n$
2505	1.1437	
5164	1.1415	595
5713	1.1418	650
10761	1.1386	1225

$\frac{d\varepsilon}{dw} = 7.6343$ $\frac{dv}{dw} = -0.6186$ $\frac{dn}{dw} = 0.1138$

$TP_2 = 753$ c.c. $EP_2 = 101.8$ c.c. $\mu = 5.6$ D

Triphenylphosphinemonophenylgold(I)

$10^6 w$	v	$10^6 \Delta n$
2321	1.1431	307
5401	1.1410	704
6439	1.1415	848
9552	1.1396	1118

$\frac{d\varepsilon}{dw} = 8.2944$ $\frac{dv}{dw} = -0.5648$ $\frac{dn}{dw} = 0.1310$

$TP_2 = 930$ c.c. $EP_2 = 131.3$ c.c. $\mu = 6.2$ D

(3) Symmetrical Compounds of Palladium

Bis(triethylphosphine)diphenylpalladium

$10^6 w$	v	$10^6 \Delta n$
11181	1.1403	902
12317	1.1398	10104
16891	1.1385	1300
21095	1.1372	1715

$\frac{d\varepsilon}{dw} = 0.3705$ $\frac{dv}{dw} = -0.3100$ $\frac{dn}{dw} = 0.0816$

$TP_2 = 158.2$ c.c. $EP_2 = 144.5$ c.c. $(\lambda = \infty)$ $AP_2 = 13.7$ c.c.

Bis(triethylphosphine)di(phenylethynyl)palladium

$10^6 w$	v	$10^6 \Delta n$
6035	1.1420	650
10000	1.1408	1083
13820	1.1395	1570
21380	1.1372	2346

$\frac{d\varepsilon}{dw} = 0.5884$ $\frac{dv}{dw} = -0.3175$ $\frac{dn}{dw} = 0.1086$

$TP_2 = 194.7$ c.c. $EP_2 = 165.8$ c.c. $(\lambda = \infty)$ $AP_2 = 28.9$ c.c.

Bis(triethylphosphine)di(p-bromophenyl)palladium

10^6w	v	$10^6\Delta n$
4412	1.1419	325
10115	1.1392	794
14511	1.1373	1191
20578	1.1346	1734

$\frac{d\varepsilon}{dw} = 0.4234$ $\frac{dv}{dw} = -0.4400$ $\frac{dn}{dw} = 0.0893$

TP_2 = 189.7 c.c. EP_2 = 168.5 c.c. ($\lambda = \infty$) AP_2 = 21.2 cc.

Bis(triethylphosphine)di(p-chlorophenyl)palladium

10^6w	v	$10^6\Delta n$
4832	1.1429	342
9975	1.1405	794
15063	1.1380	1191

$\frac{d\varepsilon}{dw} = 0.4670$ $\frac{dv}{dw} = -0.4800$ $\frac{dn}{dw} = 0.0974$

TP_2 = 161.8 c.c. EP_2 = 141.6 c.c. ($\lambda = \infty$) AP_2 = 20.2 c.c.

Bis(triethylphosphine)dibromopalladium

$10^6 w$	v	$10^6 \Delta n$
6386	1.1404	343
9346	1.1386	560
13780	1.1360	866
20267	1.1328	1282

$\frac{d\epsilon}{dw} = 0.4670$ $\frac{dv}{dw} = -0.5917$ $\frac{dn}{dw} = 0.06606$

$TP_2 = 127.0$ c.c. $EP_2 = 100.4$ c.c. $AP_2 = 26.6$ c.c.

Bis(triethylphosphine)dichloropalladium

$10^6 w$	v	$10^6 \Delta n$
6410	1.1407	353
11411	1.1387	689
15183	1.1372	873
22829	1.1339	1327

$\frac{d\epsilon}{dw} = 0.4982$ $\frac{dv}{dw} = -0.3953$ $\frac{dn}{dw} = 0.0577$

$TP_2 = 131.2$ c.c. $EP_2 = 104.6$ c.c. $AP_2 = 26.6$ c.c.

Bis(triethylphosphine)diiodopalladium

$10^6 w$	v	$10^6 \Delta n$
5338	1.1402	361
12145	1.1361	956
14958	1.1345	1173
20144	1.1315	1679

$\frac{d\varepsilon}{dw} = 0.4892$ $\frac{dv}{dw} = -0.5980$ $\frac{dn}{dw} = 0.0885$

$TP_2 = 152.1$ c.c. $EP_2 = 125.8$ c.c. $AP_2 = 26.3$ c.c.

(4) Symmetrical Compounds of Platinum

transBis(triethylphosphine)dichloroplatinum

$10^6 w$	v	$10^6 \Delta n$
5361	1.1405	2166
9889	1.1383	4148
14173	1.1356	5772
19414	1.1330	8123

$\frac{d\varepsilon}{dw} = 0.4219$ $\frac{dv}{dw} = -0.5600$ $\frac{dn}{dw} = 0.04275$

$TP_2 = 127.4$ c.c. $EP_2 = 98.4$ c.c. $AP_2 = 29$ c.c.

transBis(triethylphosphine)diphenylplatinum

$10^6 w$	v	$10^6 \Delta n$
4282	1.1412	271
9586	1.1399	614
14919	1.1376	975
19197	1.1354	1300

$\frac{d\varepsilon}{dw} = 0.3130$ $\frac{dv}{dw} = -0.4240$ $\frac{dn}{dw} = 0.0670$

$TP_2 = 160.2$ $EP_2 = 146.2$ c.c. ($\lambda = \infty$) $AP_2 = 14.0$ c.c.

Diphenylbutadiyne

$10^6 w$	v
5935	1.1417
10101	1.1409
15905	1.1398
19970	1.1394

$\frac{d\varepsilon}{dw} = 0.6787$ $\frac{dv}{dw} = -0.1888$

$TP_2 = 82.4$ c.c. $EP_2 = 78.7$ c.c. ($\lambda = \infty$) $AP_2 = 3.7$ c.c.

(5) Specimen of Results and Calculation for Bis(triethylphosphine)diphenylpalladium

Making up of Solutions

Wt. of flask	44.2696	30.8522	34.0326	38.6519
Wt. of flask & compound	44.4693	31.1386	34.3900	39.0650
Wt. of flask & compound & benzene	62.1308	54.1047	55.1921	58.2450
Wt. of compound	0.1997	0.2864	0.3574	0.4131
Wt. of compound & benzene	17.8612	23.2525	21.1595	19.5831
Weight fraction	0.011181	0.012317	0.016891	0.021095

Density Measurements

Wt. of pyknometer & solution	23.3061	23.3083	23.3119	23.3160
Wt. of pyknometer	19.6648	19.6648	19.6648	19.6648
Wt. of solution	3.6413	3.6435	3.6471	3.6512
Specific volume	1.1403	1.1398	1.1385	1.1372

Dielectric Constant Measurements

Zero reading (cms)	2.386	2.403	2.408	2.412
solution reading (cms)	2.320	2.330	2.307	2.281
Δc (cms)	0.066	0.073	0.101	0.130

Refractivity Measurements

All readings are in minutes and seconds of arc measured on the Pulfrich Refractometer.

	Zero Reading				
$\lambda = 6620$	8-30	16-50	17-50	20-30	24-30
$\lambda = 5910$	12-00	20-20	21-20	24-10	28-10
$\lambda = 5440$	16-10	24-30	25-30	28-10	32-00
$\lambda = 4780$	25-30	33-40	35-10	37-20	41-30
$\lambda = 4340$	35-30	44-00	45-00	47-30	51-20
change in angle		8-20	9-20	12-00	15-50
$10^6 \Delta n$		9021.	1010	1300	1715

From the graphs:

The slope of the Δc against w graph was 5.95

$$\frac{d\varepsilon}{dw} = 0.06227 \times \text{slope} = 0.3705$$

$$\frac{dv}{dw} = -0.3100$$

As the Δn values for each solution were the same for all values of λ then the slope of the Δn against w graph was the same for all the values of λ.

Thus:

$$\frac{dn}{dw} = 0.0816$$

Total Polarisation

$TP_2 = M(0.1881\alpha + 0.2979(v_1 + \beta))$ $M = 497$ $v_1 = 1.1447$

$TP_2 = 497(0.1881 \times 0.3705 + 0.2979(1.1447-0.3100))$

$= \underline{158.22 \text{ c.c.}}$

Electron Polarisation

$EP_2\ (\lambda = 6620\text{Å}) = M(0.5714\gamma + 0.2929(v_1 + \beta))$

$= 497(0.5714 \times 0.0816 + 0.2929(1.1447-0.3100)$

$= \underline{144.68 \text{ c.c.}}$

Similarly for $\lambda = 5910$ $EP_2 = 144.75$

$\lambda = 5440$ $EP_2 = 144.83$

$\lambda = 4780$ $EP_2 = 145.02$

$\lambda = 4340$ $EP_2 = 145.25$

From the graph of EP_2 against $\frac{1}{\lambda}2$ EP_2 at $\frac{1}{\lambda}2 = 0 = 144.5$ c.c.

$AP_2 = TP_2 - EP_2 = 158.2 - 144.5$

$= \underline{13.7 \text{ c.c.}}$

VII. DISCUSSION

The Dimethyl Compounds of Palladium

With the exception of the dimethyl compounds all the known coordination compounds of palladium (II) have trans configuration in non-chelate complexes.

Bis(trimethylphosphine)dimethylpalladium clearly has a cis configuration (μ = 6.6 D) and the variable moments of bis(triethylphosphine)dimethylpalladium have been discussed in an earlier part of this thesis. The possibility of a trend toward trans configuration with increase of the chain length in a trialkylphosphine was considered. However, a sample of bis (tri-n-propyl phosphine)dimethylpalladium which was prepared had a moment of 5.4 D, indicating that if the sample was a mixture it contained chiefly the cis isomer. The bistriethylphosphine complex, which was the first to be investigated, thus seems to be anomalous.

Bis(triphenylphosphine)dimethylpalladium (μ = 4.6 D[22]) and bis(triethylarsine)dimethylpalladium (μ = 5.4 D) both appear to consist principally of the cis isomer.

Bipyridyldimethylpalladium which is fairly stable at room temperature was too insoluble to carry out dipole moment measurements but it must surely have a cis configuration, yet all attempts to prepare chelating cis diaryls[22] have met with failure.

Palladium (II) halides, whether co-ordinated to phosphines, arsines, sulphides or any non-chelating donor molecules, are so labile that in no case have cis and trans isomers of the same compound been isolated. The same appears to be true of the palladium alkyls and aryls. Whereas cis-palladium dihalides have been isolated only when the metal is co-ordinated to tertiary stibines (or to chelating donor molecules), it appears that the cis forms of dimethyl derivatives of palladium are stable relative to the trans when the metal is co-ordinated to tertiary phosphines or, in the one instance examined, to a tertiary arsine. All the other organo-palladium compounds prepared had a trans structure; these include both the diaryls, di(phenylethynyls) and the halo-alkyls and -aryls.

Complexes of platinum (II) are much less labile than those of palladium (II) and both cis and trans isomers of many complexes have been prepared. Chatt and Shaw[29] similarly were able to obtain both cis and trans diaryls of platinum (II); though they managed to prepare both cis and trans bis(triethylphosphine)dimethylplatinum (II) the trans isomer was prepared only with considerable difficulty.

Atom Polarisation in Palladium Compounds

From measurements on the symmetrical palladium compounds the following data were obtained:

	EP_2	AP_2	% of EP_2	5% EP_2	15% EP_2	AP_2 - 5% EP_2
$(Et_3P)_2PdPh_2$	144.5	13.7	9.5	7.2	21.6	6.5
$(Et_3P)_2Pd(C{\equiv}CPh)_2$	165.8	28.9	17.4	8.3	24.9	20.6
$(Et_3P)_2Pd(p\text{-}BrC_6H_4)_2$	168.5	21.2	12.6	8.2	24.6	13.0
$(Et_3P)_2Pd(p\text{-}ClC_6H_4)_2$	141.6	20.2	15	7.1	21.3	13.1
$(Et_3P)_2PdCl_2$	104.6	26.6	25.4	5.2	15.6	21.4
$(Et_3P)_2PdBr_2$	100.4	26.6	26.4	5	15	21.6
$(Et_3P)_2PdI_2$	125.8	26.3	20.9	6	18	20.3

The EP_2 values of the organopalladium compounds are those determined by extrapolation to infinite wavelength. Those for the dihalides are for wavelength λ = 6620Å.

Even allowing for considerable errors in EP_2 values it can clearly be seen from the table that AP_2 does not approximate to a fixed percentage of EP_2.

The 5% rule is obviously inapplicable as shown in the final column of the table. The smallest departure in AP_2 from 5% of EP_2 is observed in the diphenyl compound. The difference (6.5 c.c. higher than 5% EP_2) would change the calculated dipole moment by 0.13 D or 13% if the moment were 1D, by by 0.066 D or 3.3% if it were 2 D, and by 0.03 D or 1% if it were 3D.

The corresponding figures where the deviation from the 5% rule is large, as in the diphenylethynyl compound, would be 0.4 D 40%, 0.23 D 11½%, and 0.16 D 5⅓%.

Chatt and Shaw[20,29] allow 15% of EP_2 for the contribution of AP_2 in their compounds of platinum and this would appear to be a better approximation than the 5% rule for palladium, although it would be high for the diphenyl compound and low for the dihalides.

A major contribution to the atom polarisation of the compounds will be due to the bending of the phosphine metal bond. If 6 c.c. is allowed as the contribution of each of these bonds then this leaves approximately 1 c.c. as the contribution of each of the phenyl groups in the diphenyl compound. The atom polarisation of benzene itself is 1.1 c.c.[30] The atom polarisation of the corresponding platinum compound $(Et_3P)_2PtPh_2$ was determined also and this proved to be 14 c.c., very close to that of the palladium compound. Consequently it seems likely that the atom polarisation attributable to the phosphine-platinum group has a value of 6 c.c. too.

The atom polarisation of chlorobenzene is 3.9 c.c.,[30] and the total atom polarisation for two phosphine palladium bonds plus twice the value for chlorobenzene, (19.8 c.c.)

is very close to the value for $(Et_3P)_2Pd$ ($\underline{p}$-$ClC_6H_4)_2$ (20.2 c.c.). The atom polarisation of bromobenzene would be expected to be a little higher due to the larger bromine atom, and the observed atom polarisation of $(Et_3P)_2Pd$ ($\underline{p}$-$BrC_6H_4)_2$ is 21.2 c.c.

The high atom polarisation of the diphenylethynyl compound is at the moment inexplicable. The atom polarisation of diphenylbutadiyne is about 3.7 c.c. (slightly less than that expected from twice the sum of benzene and acetylene) and this together with the 12 c.c. for the phosphine metal bonds constitutes only 16 c.c., leaving a further 13 c.c. to be explained. The metal carbon bond will be polar though it is unlikely to be highly polar, but the phenylethynyl group is quite long and consequently will bend relatively slowly, i.e. it is quite likely that it will have a small force constant and therefore a high atom polarisation. (Chatt and Shaw[20] obtained a high atom polarisation also for the corresponding platinum compound).

The dihalides too have high atom polarisations and these must be in part due to the polar metal to halogen bonds. Such a high value (26.6 c.c.) for the dichloro compound is rather surprising in view of the comparative lightness of the chlorine atom although the metal chlorine bond is likely to be more polar than Pd-Br or Pd-I.

The Unsymmetrical Compounds of Palladium

The moments of the unsymmetrical compounds are as follows:

	(D)
$(Et_3P)_2PdMeBr$	4.02
$(Et_3P)_2PdMeCN$	4.79
$(Et_3P)_2Pd(\underline{p}\text{-}BrC_6H_4)Br$	1.66
$(Et_3P)_2Pd(\underline{p}\text{-}ClC_6H_4)Br$	1.70
$(Et_3P)_2PdPhBr$	3.55

The moment of $(Et_3P)_2PdMeBr$ is 4.02 and that of $(Et_3P)_2PdMeCN$ 4.74 D. The difference is surprisingly small when the moment of cyanogen bromide (2.9 D) is considered. There appears to be no apparent reason for this as the compound is monomeric cryoscopically in benzene, although the melting point is not very sharp (softening took place over about 5°C before it melted) and the compound constantly had the odour of triethylphosphine.

The moments of $(Et_3P)_2Pd$ $(\underline{p}\text{-}BrC_6H_4)Br$ and $(Et_3P)_2Pd(\underline{p}ClC_6H_4)Br$ are both about 1.7 D and that of $(Et_3P)_2PdPhBr$ 3.6 D. If the difference is attributed to the phenyl-halogen bond moment which will be in opposition to the overall moment then this moment is larger than in chlorobenzene (about 1.6 D) and bromobenzene (about 1.5 D).

In bromobenzene and chlorobenzene there is a mesomeric effect i.e. a small drift of negative charge back into the ring thus opposing the overall moment which has the halogen atom at its negative end. The negative charge on the metal atom (arising from co-ordination to two phosphorus atoms) will tend to prevent this happening, and thus the difference in the moment of say $(Et_3P)_2PdPhBr$ and $(Et_3P)_2Pd(\underline{p}\text{-}BrC_6H_4)Br$ should be comparable with the moment of a typical alkyl bromide, normally about 1.8-1.9 D.

Allowance for Atom Polarisation in Unsymmetrical Compounds

By analogy with the symmetrical compounds, 6 c.c. has been allowed for each phosphine-metal bond 7 c.c. for each metal halogen bond, 3.9 c.c. for $\underline{p}$-ClC_6H_4, 4.5 c.c. for $\underline{p}$-BrC_6H_4, and 1 c.c. for Ph.

Cyanogen has an atom polarisation of 8.34 c.c. and it seems reasonable to allow half of this plus 7 c.c. making a total of 11 c.c., for the metal-cyanide bond. The atom polarisation of methane is very small (0.08 c.c.[31]) and as the bending force constant of the metal methyl bond will be relatively large the bond will contribute little to the total atom polarisation. No allowance therefore has been made for the contribution of this bond.

The values are then

	AP	μ	μ (15% rule)
$(Et_3P)_2PdMeBr$	19 c.c.	4.02	4.04
$(Et_3P)_2PdMeCN$	23 c.c.	4.74	4.79
$(Et_3P)_2Pd(\underline{p}\text{-}BrC_6H_4)Br$	23.5 c.c.	1.66	1.73
$(Et_3P)_2Pd(\underline{p}\text{-}ClC_6H_4)Br$	22.9 c.c.	1.70	1.75
$(Et_3P)_2PdPhBr$	20 c.c.	3.55	3.56

Compounds of Gold

The solid organo gold compounds are colourless and monomeric (cryoscopically) in nitrobenzene but slightly associated in benzene.

Et_3PAuMe, and Et_3PAuPh were stored in sealed flasks at room temperature for several weeks before any signs of decomposition (the appearance of a purple colour due to metallic gold) were observed. Ph_3PAuPh, Ph_3PAuMe, and Ph_3PAuEt were kept for several months under similar conditions without any apparent change. Et_3PAuEt showed signs of considerable decomposition after storing for a day. Attempts to prepare Et_3PAuPr^n and Et_3PAuBu^n

resulted in the isolation of oils. The oil from the former preparation decomposed slowly over a few days but the oil from the latter appeared to be quite unchanged after two weeks.

With ethanolic hydrochloric acid at room temperature Et_3PAuMe was quantitatively converted to Et_3PAuCl, Et_3PAuEt effervesced vigorously and Ph_3PAuMe very slowly. The aryls were apparently unaffected. Et_3PAuEt also reacted with ethanol. This is rather surprising as all the compounds have been in contact with water at one stage in their preparation. Possibly the reason they do not react with water is their insolubility.

Et_3PAuMe, Et_3PAuPh, Ph_3PAuMe, Ph_3PAuPh, Ph_3PAuEt, and the oil from the attempted preparation of Et_3PAuBu^n (inadvertantly) were all in contact with the air for at least twelve hours without showing any signs of decomposition. Thus it appears that they are insensitive to atmospheric oxidation.

Et_3PAuMe and Et_3PAuPh melted without decomposition, Et_3PAuEt showed slight decomposition, Ph_3PAuMe decomposed on melting and Ph_3PAuPh began to darken about 30° below its melting point; this does not imply that the triphenylphosphine complexes have higher thermal stability since their melting points are much higher (about 100°C) than those of triethylphosphine complexes.

The reaction of Ph_2AsK and Ph_2PK with Et_3PAuCl produced solids which were practically insoluble in all solvents. It was considered that these were polymers and attempts to break up the polymers by reaction with phosphines were made. They were, however, unsuccessful. The compounds produced from the reaction of Ph_2PK with Et_3PAuCl was apparently unaffected, whilst an oil soluble in benzene was obtained from the other on mixing with a solution of dimethylphenylphosphine in benzene. A reaction between PhSNa and Et_3PAuCl produced a white crystalline solid, $Et_3PAuSPh$, which was slightly associated in benzene. Et_3PAuCl was then allowed to react with EtSNa in the hope that a dimer would result but the product was an evil smelling oil which decomposed when attempts were made to purify it by vacuum distillation.

Stability of Gold Complexes

Chatt and Shaw[29] suggested that decomposition of the organometallic compounds of palladium and platinum took place by the promotion of an electron from an occupied, non-bonding d orbital of the metal to the lowest vacant antibonding orbital, and that lowering of the energy of the non-bonding d orbitals by π bonding with suitable ligands, thus increasing the energy gap between the *d* orbitals and the lowest energy, vacant antibonding orbital would confer stability upon the complex.

In the case of gold(I) it is convenient to regard the bonding as taking place along the Z axis.[36] The non-bonding *d* orbitals with highest energy would thus be the d_{xz} and d_{yz} due chiefly to the repulsion of the electrons in the bonds. These however are particularly suitable for π bonding with the vacant *d* orbitals of the phosphorus atom and such bonding probably provides the reason for the stability of the complexes.

Dipole Moments

The compounds Et_3PAuX where X is Cl, Br, and I have similar dipole moments. (μ = 8.4, 8.32 and 8.36 D). Although the 'separated charges' which go to make up the dipole will probably be larger in Et_3PAuCl than in Et_3 PAuI their distance apart will be smaller due to the difference in size of the halogen atoms. Another factor affecting the moment is the amount of π bonding which takes place between the filled d orbitals of the metal atom and the vacant d orbitals of the phosphorus atom. This will be greater, and tend to decrease the overall compound moment more, in Et_3PAuI than it will in Et_3PAuCl.

The dipole moments of the organic derivatives are smaller than those of the halogen derivatives and in the order PhC≡C (6.55 D) Ph (6.2 D) Me (5.5 D) in agreement with the trend in electronegativity.

The methyl compound has a dipole moment of 5.5 D. If the moment of the C-H bond is 0.4 D[*] and that of the Au-C

[*] (The moment of the C-H bond was at first considered to be 0.4 D with the C atom at the negative end of the dipole. This view, chiefly based upon the observed dipole moment of toluene was substantiated by Malone who pointed out that if differences in electronegativity values (derived by Pauling)[33] for pairs of atoms were expressed in Debye units they were numerically equally to observed bond moments in many cases. This approximation held for bonds involving carbon atoms only if the value of 0.4 D with the C atom negative, was used.

More recently theoretical calculations have shown that the moment is in the reverse direction and Gent[34] in his review concluded that the value was 0.4 D with H negative.

Other workers have arrived at various figures and as yet there appears to be no value which meets with unanimous agreement).

bond also 0.4 D* then the moment due to the phosphine metal portion of the molecule is 4.7 D. If the moment is considered due to the charges on the phosphorus and gold atoms then the amount of charge transfer is 0.4 of an electronic charge. (Assuming that the phosphorus gold bond length is 2.5 Å [35]).

These figures will be subject to modification as the charge transfer from the phosphine to the metal will be affected by the other substituent in the molecule. Charge transfer is likely to be greater and probably the moment of the Et_3P-Au portion of the molecule higher with the strongly electronegative chlorine atom as substituent than with the less strongly electronegative Ph-C≡C- grouping.

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* The electronegativity value for Au(I) is subject to considerable doubt as quite widely different figures have been arrived at by various workers. Pritchard and Skinner[32] after reviewing these figures suggested that a value of 2.1 is probably the best one to take.

As the electronegativity of C is 2.5 on this scale, and as a number of bond moments have been found to be numerically equal to the electronegativity difference between the bonded atoms, the assumption that the Au-C bond has a dipole moment of 0.4 D with the carbon atom at the negative end of the dipole, appears to be fairly reasonable.

Although triphenylphosphine is normally a weaker donor than triethylphosphine little change in moment is observed when one is substituted for the other.

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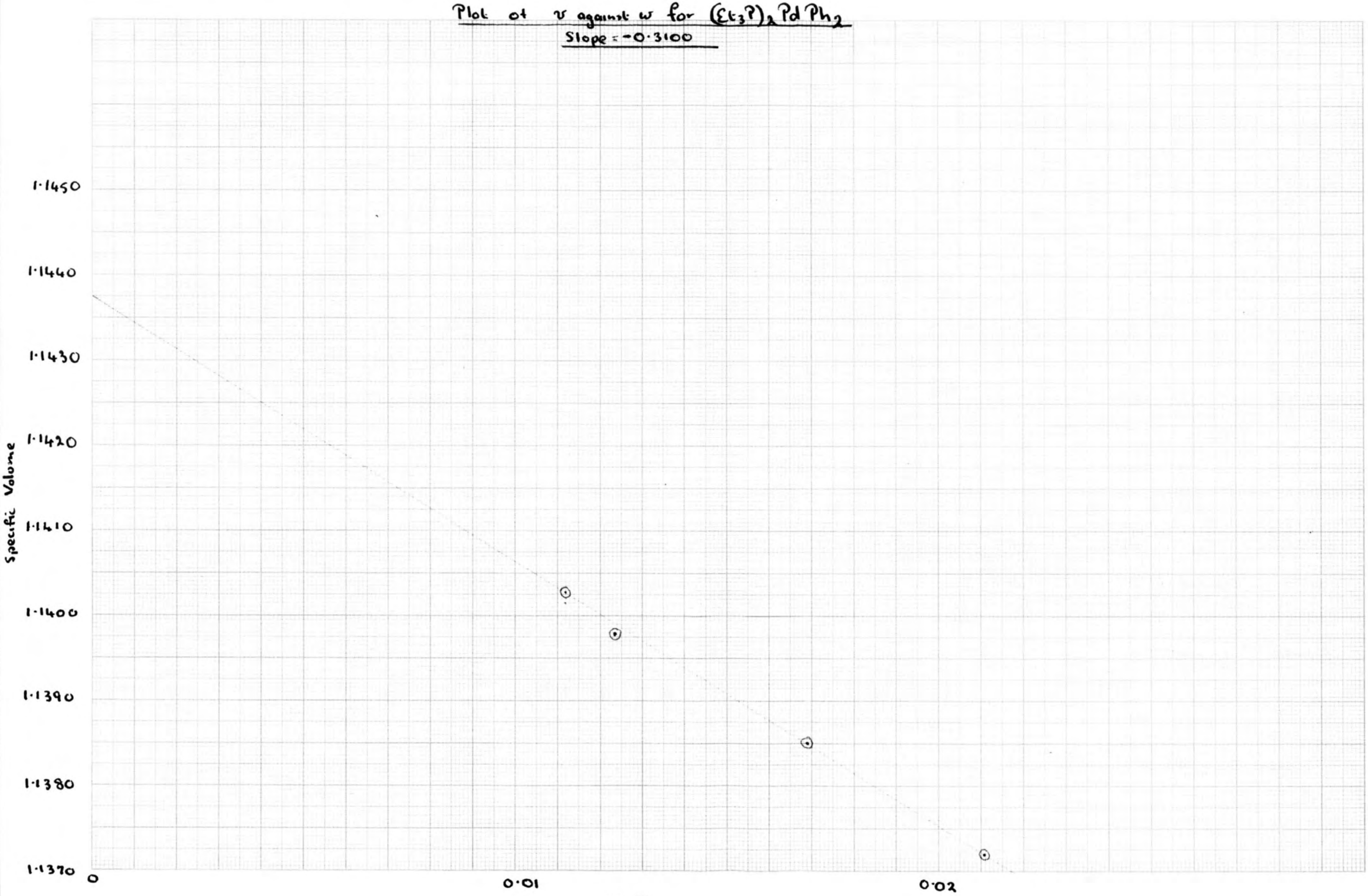
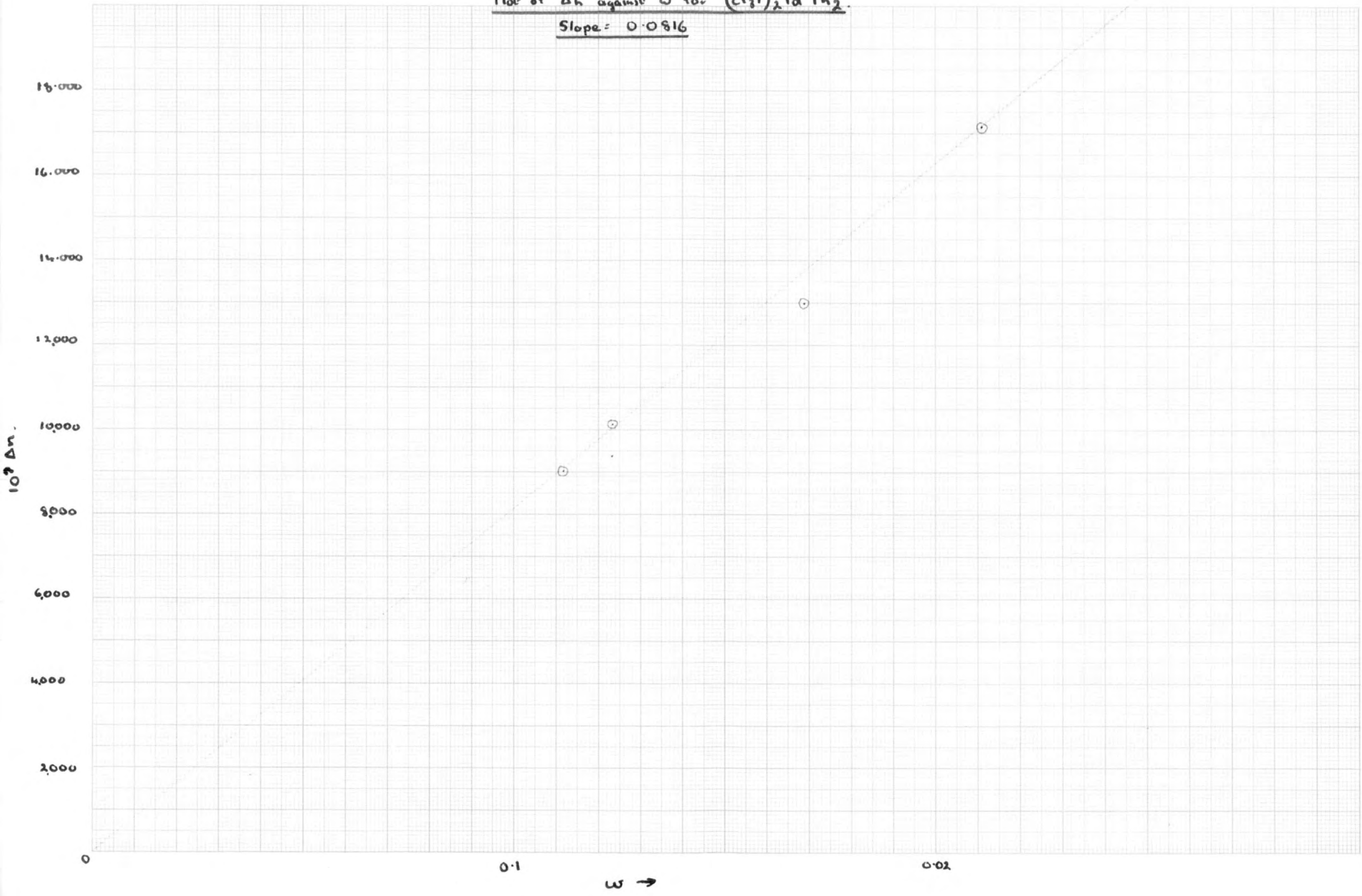
Plot of v against w for $(Et_3P)_2PdPh_2$

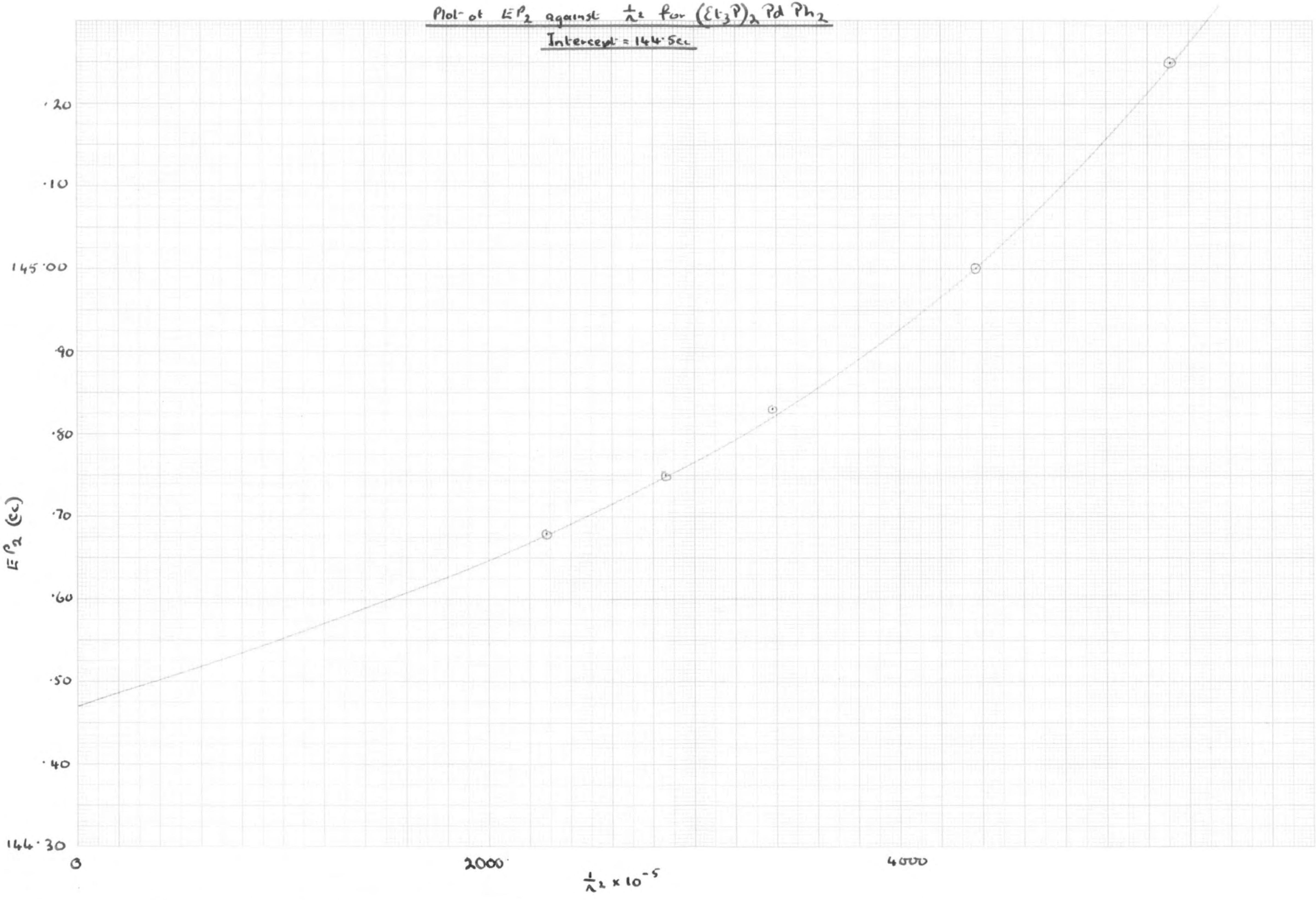
Slope = −0·3100



Plot of Δn against ω for $(Et_3P)_2PdPh_2$.

Slope: 0·0816





Plot of Δc against w for $(Et_3P)_2PdPh_2$

Slope = 5·95