Organic co-ordination compounds of transition metals

Calvin, G.

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of

Transition Metals

by

G. Calvin

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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 1956 and August 1959. 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 G.E. Coates; Chemistry and Industry, 1958, 160.

Contents

Summary

Several new organometallic compounds of nickel, palladium, platinum, copper and gold have been prepared. Most work has been carried out on palladium and all the derivatives prepared have basically a normal σ bond between the metal and carbon atoms.

They are for the first three metals, of the type

L_2MR_2, L_2MRX, DMR'_2 or $DMR'X$

where:-

L = Et_3P or Ph_3P

R = CH_3, Ph, C≡CPh, p-substituted Ph or mesityl.

D = a bidentate chelating group.

R' = CH_3

X = Cl, Br, CN or SCN.

In the case of copper and gold they are of the type LMR where:

L = Et_3P, R = CH_3, Ph or C≡CPh.

All the derivatives (except for those of copper) were prepared by the action of Grignard reagents or organolithium compounds on the complex metal halides, e.g.

$$(\text{Ligand})MX_2 + 2RLi \longrightarrow (\text{Ligand})MR_2 + 2LiX$$

The properties of the methyl derivatives have been studied in some detail and bis(triethylphosphine)dimethylpalladium has been found to decompose *via* a free radical

mechanism.

Infrared data have been obtained for most of the compounds isolated and a frequency (at about 500 cm^{-1}) is suggested for the Pd-CH_3 stretching. A deformation frequency for a methyl group bonded to palladium is also suggested, at 1160 cm^{-1}.

From the physical and chemical properties of the compounds prepared it has been possible to deduce the relative order of the strength of the donor atoms towards palladium as:

P $\rangle$ As $\rangle$ S $\rangle$ dienes

Present work

The present investigation was undertaken in order to prepare stable organic co-ordination complexes of the transition metals nickel, palladium, platinum, copper, silver and gold. The work described in this thesis is concerned mainly with derivatives of palladium as it was found, fortunately at an early stage, that Dr. J. Chatt was working on similar lines and in order to avoid duplication it was agreed to study palladium in detail in these laboratories and leave nickel and platinum to be studied by Dr. Chatt and co-workers at the Akers Research Laboratories of Imperial Chemical Industries.

From a study of the literature it was obvious that no great success could be hoped for in preparing organopalladium compounds by using the direct method of attack of a Grignard reagent on the metal halide. In all similar cases, apart from the remarkable platinum (IV) methyls, decomposition usually occurred. It was thought that stability could be introduced by having present co-ordinating groups, for example triethylphosphine, to give a general lowering of the energy of the molecule. No rules of guidance were available apart from the fact that phosphorus was known to

be one of the strongest donors towards palladium.

Thus the present investigation has been to find out which donor atoms are suitable for stabalizing compounds containing a metal-to-carbon bond, which organic groups it is possible to bond to the metal, and to study the physical and chemical properties of the compounds prepared.

INTRODUCTION

The transition metals occupy a very large section of the periodic table and it would have been impossible to study the preparation and properties of organic derivatives of more than a few of them in the time available for the present investigation. Consequently only six elements are considered in any detail. These are nickel, palladium, platinum, copper, silver and gold. The chemistry of some of these metals was already under investigation in these laboratories when the present work was started.

In this introduction a review is made of the organometallic compounds of the metals listed above where the metal-carbon bond is of the σ type (cyclopentadienyl derivatives are mentioned only briefly) and where the donor atoms are of the more common and straight forward nature e.g. tri-alkyl,-aryl phosphine, amine, acetylacetone and thiol type of donor.

Nickel

Apart from the cyclopentadienyl compounds of nickel, no organonickel compound has been isolated until very recently. Previously the only evidence for the existence of organonickel derivatives was in the behaviour of Grignard solutions to which nickel chloride has been added.[1] Weichselfelder and Thiede[1] observed that freshly prepared reaction mixtures consisting of nickel chloride suspended in an ether solution of phenylmagnesium bromide in two fold molar proportion absorb 2 moles of hydrogen per mole of nickel, giving a black pyrophoric precipitate. This precipitate was found to have a composition NiH_2 after drying in a stream of hydrogen. With this information the following reaction schemes seemed plausible:-

$$NiCl_2 + 2C_6H_5MgBr \longrightarrow (C_6H_5)_2Ni + MgCl_2 + MgBr_2 \qquad 1$$

$$(C_6H_5)_2Ni + 2H_2 \longrightarrow 2C_6H_6 + NiH_2 \qquad 2a$$

$$(C_6H_5)_2Ni + 2H_2 \longrightarrow C_6H_5C_6H_5 + NiH_4 \xrightarrow{\text{drying}} NiH_2 + H_2 \qquad 2b$$

$$(C_6H_5)_2Ni \longrightarrow C_6H_5C_6H_5 + Ni \xrightarrow{2H_2} NiH_4 \xrightarrow{\text{drying}} NiH_2 + H_2 \qquad 2c$$

A determination of the hydrogen content of the nickel hydride without removing it from the reaction mixture showed that NiH_4 never forms, thus eliminating 2b and 2c.

A mechanism in which the nickel is reduced directly to the metal without appearance of diphenylnickel would also necessitate the initial formation of NiH_4 with loss of hydrogen on drying and is thus eliminated. Thus it was considered that the correct mechanism is probably as represented by equation 1 and 2a, which provided circumstantial evidence for the existence in solution of diphenylnickel.

There is much evidence showing that diphenylnickel is very unstable. Thus when the reaction mixture (of Grignard solution and nickel chloride) is allowed to stand for one hour and then hydrolysed, essentially quantitative yields of diphenyl and nickel are obtained.[2] Weichselfelder and Thiede attempted to isolate the diphenylnickel, using a variety of techniques and reaction conditions, but without success. Weichselfelder and Kossodo showed that when the reaction mixture of nickel chloride and phenylmagnesium bromide was allowed to stand for increasing lengths of time before treatment with hydrogen, the absorption of hydrogen over the quantity required to produce NiH_2 decreased, becoming zero for a mixture which had stood four hours. The NiH_2 was assumed to have arisen from the uptake of hydrogen by highly

reactive nickel deposited on decomposition of the diphenylnickel.

Various unsaturated gaseous compounds are absorbed by reaction mixtures consisting of nickel chloride and a Grignard reagent, particularly phenyl Grignards. Among those to have been studied[1,3] are carbon monoxide, ethylene, and acetylene. In most cases it has been reported that the gases are absorbed in integral mole ratios to the nickel present, but little knowledge of probable organonickel intermediates is to be obtained from this work. Studies on "nickel hydride" have recently been repeated[3a] but no crystalline hydride could be obtained; the dark oily product always contained magnesium, halogens and organic matter in addition to nickel and hydrogen.

Cyclopentadienyl compounds

Bis cyclopentadienylnickel, $(C_5H_5)_2Ni$ was obtained both from cyclopentadienyllithium and hexamminenickel thiocyanate in liquid ammonia[4] and from cyclopentadienylmagnesium bromide and nickel (II) acetylacetonate.[5,6] It was purified by vacuum sublimation and condenses in deep green crystals. On standing in air it gradually decomposes,

and it does not, in contrast to its iron analogue, withstand Friedel-Craft acylation. The lower stability of the nickel relative to the iron compound is reflected in a difference of 24 Kcal./mole in the metal to ring binding energy.[5,6] This lower stability and greater reactivity of the nickel compound is associated with the presence of two unpaired electrons (paramagnetic, μ = 2.88 B.M.).

Bisindenylnickel, deep red-brown in colour has also been mentioned.[7] E.R. Lippincott and R.D. Nelson[8] have shown in a comparison study of $(C_5H_5)_2Fe$, $(C_5H_5)_2Ru$ and $(C_5H_5)_2Ni$, that, thermodynamically, $(C_5H_5)_2Ni$ is the least stable of the three compounds.

Biscyclopentadienylnickel (III) salts result from the oxidation of the neutral compound by benzoquinone, bromine or iodine. These are orange compounds, and like the similar cobalt (III) salts, the reineckate is sparingly soluble and the tetraphenylborate almost insoluble. The ion $(C_5H_5)_2Ni^{++}$ which might be expected to be stable, being isoelectronic with $(C_5H_5)_2Co^{+}$ and $(C_5H_5)_2Fe$, has not been detected.

Cyclopentadienyl carbonyls and related compounds

In the preparation of certain cyclopentadienyls by the interaction of cyclopentadienyl and metal carbonyls, mixed carbonyls have been observed in addition to the formation of biscyclopentadienyl derivatives. Cobalt, for instance forms $C_5H_5Co(CO)_2$ from $(C_5H_5)_2Co$ and CO at 90-150° and 200 atm. The compound is stable in air but readily undergoes thermal decomposition, b.p. 75°/22 mm.

Various other groups of similar character to the carbonyl group, e.g. NO, RNC, which form partial double bonds with transition metals, can be introduced into cyclopentadienyls. E.O. Fischer and R. Jira[9] prepared a volatile brown liquid C_5H_5NiNO, cyclopentadienylnitrosylnickel, b.p. 49°/27 mm. This compound has also been prepared by reaction of nitric oxide with biscyclopentadienylnickel.[10]

Structure of biscyclopentadienylnickel and related compounds

Fundamental points about these compounds are (i) the high symmetry of the C_5H_5 radical, which allows low energy orbitals extending round the ring and (ii) the possibility of forming bonds between some of these orbitals and those atomic orbitals of metals which have suitable

symmetry to combine with the cyclopentadienyl molecular orbitals without greatly disturbing the latter. Atomic orbitals of suitable symmetry involve d orbitals either alone or hybridized with s orbitals, and that is why the compounds are formed by transition metals.

The cyclopentadienyls, with their new and interesting structure, have been discussed by several workers.[11]

The structure of cyclopentadienylnitrosylnickel has been discussed by T.S. Piper, F.A. Cotton and G. Wilkinson.[10]

More recent work by J. Chatt and B.L. Shaw which has been carried out in conjunction with their investigation of alkyl and aryl platinum complexes[12,13] has shown that it is possible to isolate stable organo-nickel compounds by the action of lithium-alkyls and -aryls or similar Grignard reagents on complexes of the type $(PR_3)_2NiX_2$. The authors state that in a series platinum, palladium, nickel the stability of the organo-metallic complexes falls rapidly in the order Pt>Pd>Ni.

Platinum

Trimethylplatinum iodide

The first organoplatinum compound, and incidentally the first organometallic compound of a Group VIII metal, was prepared by Pope and Peachey in 1907.[14,15] The compound prepared was trimethylplatinum iodide, $(CH_3)_3PtI$, obtained by the action of anhydrous platinic chloride, (partly in ether solution but mainly as a dark red viscous liquid), obtained from chloroplatinic acid by heating at 200° at low pressure, on an ether-benzene solution of methylmagnesium iodide. A considerable excess of the Grignard reagent was used, about twice as much as indicated by the equation:-

$$PtCl_4 + 3CH_3MgI \longrightarrow (CH_3)_3PtI + 2MgCl_2 + MgI_2 \qquad 3$$

After standing for an hour and hydrolysing with ice-water, the product was extracted with benzene and crystallized from that solvent as a bright yellow crystalline powder. The product is freely soluble in hot benzene or chloroform and on evaporating the solution in benzene it separates in square, doubly refracting plates of a yellow-amber colour. The iodide is readily soluble in cold ethyl bromide or methyl iodide and it may be recrystallized, in hexagonal

plates belonging to the cubic system, from ethyl bromide. It is soluble in water and is very sparingly soluble in ether, alcohol, acetone or light petroleum. The substance is not attacked in the cold by bromine or iodine, nor by concentrated acids or alkalis; alkali sulphides produce no darkening in colour. Heating with concentrated nitric acid causes it to dissolve with the elimination of iodine and evaporation of the solution leaves behind a residue which explodes on further heating, giving a mixture of carbon and platinum. The action of concentrated sulphuric acid is similar, the iodide is slowly dissolved with elimination of iodine, the remainder being given off on evaporating and heating; a residue of platinum remains. Trimethylplatinum iodide has no definite melting point; heating in a melting point tube results in gradual decomposition which is complete below 250°. The substance catches fire on heating in a flame, and it burns with a smoky lurid flame, leaving a residue of metallic platinum.

Compounds of trimethylplatinum iodide

With trimethylplatinum iodide as a starting material Pope and Peachey (ib. id.) prepared a number of trimethylplatinum compounds. Diamminotrimethylplatinum iodide $(CH_3)_3PtI(NH_3)_2$, was prepared by heating

trimethylplatinum iodide with a mixture of benzene, alcohol, and concentrated ammonia on a water-bath and evaporating to dryness. White crystalline scales were deposited and the substance is slightly soluble in water, moderately so in benzene or ether, but dissolves very readily in alcohol, ethyl acetate or acetone. It is insoluble in chloroform or light petroleum and treatment with potassium hydroxide and heating produces evolution of ammonia.

Trimethylplatinum hydroxide, $(CH_3)_3PtOH$, was prepared by boiling trimethylplatinum iodide in moist acetone solution with freshly precipitated silver hydroxide. The conversion to hydroxide is enhanced by the addition of benzene, which dissolves the iodide and hydroxide and forms a separate layer of liquid floating on the acetone solution. After evaporation of the benzene solution the hydroxide separates in almost colourless transparent crystal plates. This crude material may be recrystallized from benzene; being deposited in massive square tablets which are colourless and transparent. The crystals contain solvent of crystallization. The substance burns explosively on heating, leaving a residue of carbon and platinum. The hydroxide is fairly soluble

in ether, alcohol, acetone, ethyl acetate, chloroform and, naturally, benzene and recrystallizes from the last three named with solvent of recrystallization, which is quickly lost in air. The substance is insoluble in water, alkalis, or light petroleum; it is not attacked in the cold by mineral acids but dissolves on warming with nitric acid. Concentrated sulphuric acid partly decomposes the hydroxide.

Trimethylplatinum sulphate, $\left[(CH_3)_3Pt\right]_2SO_4,2H_2O$, was prepared by boiling equivalent quantities of trimethylplatinum iodide and silver sulphate with a mixture of moist acetone and benzene under reflux for several hours. Filtration and evaporation of the solution produced the sulphate in small, colourless, rectangular plates. The salt is readily soluble in water, alcohol, or acetone, but it is insoluble in benzene, light petroleum ether or chloroform. The compound can be recrystallized from water but the crystals retain water of crystallization which is retained at 100^{o}.

Trimethylplatinum nitrate, $(CH3)_3PtNO_3$, was prepared by treating an aqueous solution of trimethylplatinum sulphate with an equivalent amount of barium nitrate and evaporating after filtration. On crystallizing from the

pure aqueous solution, colourless crystalline plates are obtained which are very deliquescent.

This ready solubility of trimethylplatinum sulphate and nitrate in water makes these two compounds suitable sources from which less soluble salts may be prepared.

Use is made of the sulphate or nitrate in aqueous solution, to prepare trimethylplatinum chloride by precipitating the aqueous solution with potassium chloride or by dissolving the hydroxide in alcohol and evaporating to dryness after adding hydrochloric acid. The chloride is insoluble in water, dissolves sparingly in acetone, alcohol or ethyl acetate but is moderately soluble in benzene or chloroform. Colourless crystals of the cubic system are obtained on recrystallizing from chloroform. They contain no solvent of crystallization.

By adding potassium cyanide to a solution of trimethylplatinum nitrate or sulphate, a white flocculent precipitate is thrown down, partially soluble in excess of precipitant. The substance is insoluble in water and too sparingly soluble in organic solvents to be purified. The substance was not obtained in crystalline form and was not analysed. Boiling with caustic soda gave

evolution of ammonia but no acidic hydrolytic product was obtained.

Potassium trimethylplatinic platinocyanide, $K(Me_3Pt)Pt(CN)_4$, was obtained by adding potassium platinocyanide to an aqueous solution of trimethylplatinum nitrate. A slimy, yellow precipitate was obtained and the compound was insoluble in water and the usual organic solvents with the exception of acetone and alcohol in which it dissolves freely. Evaporation of its solution in the latter two solvents gave an amorphous resinous film having a yellow-green colour.

None of the trimethylplatinum compounds prepared by Pope and Peachey (loc. cit.) was characterized by a melting point. They underwent decomposition without melting. No yields of products were given by the two workers. It is interesting that the halides and hydroxide are soluble in most organic solvents and quite insoluble in water, whereas the nitrate and sulphate are soluble in only a few polar organic media and are highly soluble in water.

A reinvestigation of the reaction (Equation 3) has been carried out[16,17,18,19] by Gilman and Lichtenwalter, who state that the reaction is more complicated than was

indicated by Pope and Peachey. Satisfactory conditions for optimum yields of trimethylplatinum iodide are described. Anhydrous platinic chloride was prepared by the method of Karasch and Ashford[20] and a 40% yield of trimethylplatinum iodide was obtained. The product was recrystallized from a mixture of chloroform and benzene.

The pyridine complexes of trimethylplatinum iodide

The tedious preparation and handling of anhydrous platinic chloride led Foss and Gibson[21] to look for a more convenient starting material. Success experienced with pyridinotrichlorogold as a source of dialkylgold compounds[22] led them to investigate the use of cis- and trans- dipyridinotetrachloroplatinum; the former separating quantitatively when sodium chloroplatinate is refluxed with pyridine in aqueous solution and the latter by oxidation of tetrapyridino-platinous chloride.[23,24] The trans-isomer with methylmagnesium iodide gave no alkylation product, dipyridinodi-iodoplatinum being the main product. The cis-isomer, suspended in an anhydrous mixture of benzene and ether reacted completely with the Grignard reagent in 2 hours at 0-15°, giving a compound of empirical formulea $pyMe_3PtI$ in 70% yield. This compound

was shown to be binuclear and may be represented by (1). It is sparingly soluble in water, alcohol, ether or acetone but was soluble in chloroform or benzene. It is stable to dilute acid or alkali but decomposed, liberating pyridine, in hot alkali. With pyridine it is converted into dipyridinotrimethyliodoplatinum, Me_3Ptpy_2I (2), which is identical with the complex prepared directly from trimethylplatinum iodide and excess pyridine.[25] Observations on depression of freezing point of (2) in benzene solution were interpreted in terms of an equilibrium:-

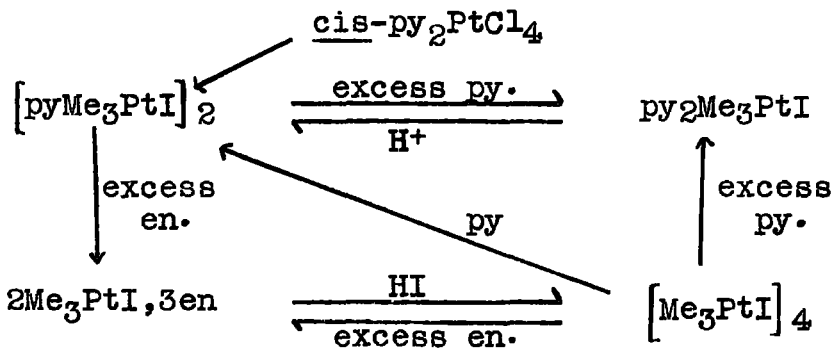
$$2py + pyMe_3Pt\begin{matrix}\diagup I \diagdown \\ \diagdown I \diagup\end{matrix}PtMe_3py \rightleftharpoons 2py_2Me_3PtI$$

(1) (2)

Shaking a benzene solution of (2) with dilute hydrochloric acid removed one molecule of coordinated pyridine with regeneration of the dimer (1). The stability of the dimer in aqueous dilute acid indicates that the second molecule of pyridine is more firmly held but it was displaced by addition of ethylenediamine to a chloroform solution of (1). This compound $2Me_3PtI,3en$, named by Lile and Menzies[25] sesquiethylenediaminotrimethylplatinic iodide, separates as colourless crystals quantitatively. The addition of

hydriodic acid to a hot aqueous solution of this ethylenediamine complex produces trimethylplatinum iodide $(Me_3PtI)_4$ in good yield. This latter compound may be converted into the dimer (1) with one equivalent of pyridine.

This interesting series of reactions may be represented:-



This is thus a good method of obtaining the trimethylplatinum iodide in good yield. Trimethylplatinum iodide has been prepared by the action of methylmagnesium iodide containing excess methyl iodide on platinum (II) complexes. A.D. Gel'man, and E.A. Gorushkina,[26] prepared trimethylplatinum iodide from Zeise's salt $K(C_2H_4)PtCl_3$, claiming incidentally that this proved the quadrivalency of the platinum atom in Zeise's salt. However, J. Chatt, and L.A. Duncanson,[27] pointed out that the Grignard reagent contained a large excess of methyl iodide and

suggested the following course for the reaction:-

$$K\left[(C_2H_4)PtCl_3\right] + 2CH_3MgI \longrightarrow C_2H_4 + (CH_3)_2Pt + KCl + MgCl_2 + MgI_2$$

$$(CH_3)_2Pt + CH_3I \longrightarrow (CH_3)_3PtI \qquad 4$$

Chatt and Duncanson (loc. cit.) supported this by preparing trimethylplatinum iodide using the same quantities of reagents, with Na_2PtCl_4 substituted for Zeise's salt.

Structure of Trimethylplatinum iodide and related compounds

Powder photographs[28] by E.G. Cox, and K.C. Webster, showed that trimethylplatinum chloride has a body centred cubic lattice, but although the symmetry was consistant with a tetrahedral disposition of the four groups around the platinum atom, in view of the strong tendency of platinum (IV) to demand six-co-ordination, the tetrahedral model is questionable. The question was answered by R.E. Rundle, and J.H. Sturdivant,[29] in a more complete analysis. This analysis indicates that the molecule is tetrameric and that the platinum atom is in fact six-co-ordinated.[30,31] The iodide is also tetrameric,[32] the platinum having an approximately octahedral disposition of bonds; the bonds to the methyl being normal single

covalent bonds and the three bonds to chlorine being of fractional order. The Pt - Cl distance is 2.48Å which is greater than the sum of the covalent radii of 2.30Å, which supports this view. The dipole moment of trimethylplatinum iodide, bromide and chloride have been measured in benzene solution and were found to be 1.1, 0.98, and 0.97 Debye units respectively.[33] Assuming the iodide and bromide are also tetrameric in solution all three compounds should have zero permanent dipole. In computing the above results however, no correction for atomic polarization was made. Atomic polarization in compounds such as these could easily account for a dipole moment of 1 Debye unit and these data are in accordance therefore with a tetrameric structure, since with a tetrahedral orientation a larger dipole might be expected.[30]

The evidence that the bromide and iodide of trimethylplatinum have tetrameric structure is indicative rather than conclusive. Similarity in dipole moment supports the idea and cryoscopically and ebullioscopically, trimethylplatinum iodide shows an association factor of about 4.4. However, trimethylplatinum iodide crystallizes in the monoclinic system[34,35] while trimethylplatinum

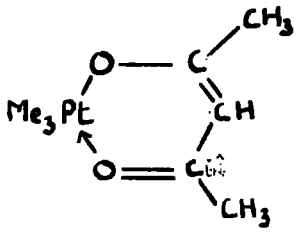
chloride forms isometric rhombohedra and assumption that the iodide and bromide are tetrameric must be made with reservation.

Complexes of Trimethylplatinum

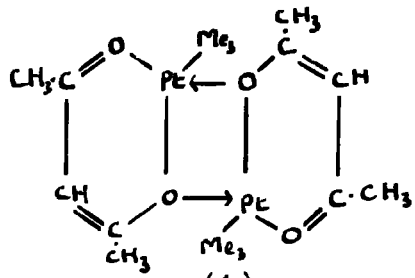
a. With oxygen containing compounds

Trimethylplatinum iodide forms many complexes in co-ordination with oxygen and nitrogen. It reacts with acetylacetone, dipropionylmethane, benzylacetone and, ethylacetoacetate to form dimerized chelate derivatives.[36,37]

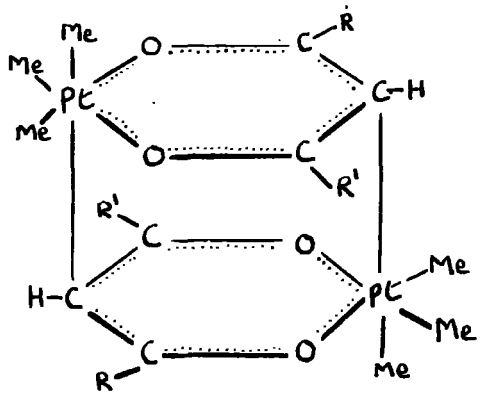
A 3% solution of trimethylplatinum acetylacetone shows a molecular weight nearly twice that required for the monomeric formulea (3). A structure such as (4) was postulated to account for dimerization, which is in keeping with the demand of platinum (IV) for six-co-ordination, but this must now be revised in view of the recent X-ray crystal structure analysis of trimethylplatinumdi-n-butyryl-methane and ethyl-(trimethylplatinum) acetoacetate by Hazell, Swallow and Truter.[38]



(3)



(4)



(5)

X-ray structure determinations by these workers show that the compounds are centrosymmetrical dimers in the solid state and that each platinum atom is octahedrally co-ordinated. The Pt-Pt distance is given as 4.5Å. In the two compounds studied it was found that the -CO-CH-CO- system acts as a tridentate group in which the central CH is co-ordinated to one platinum atom and the two oxygens are co-ordinated to the other as shown in figure 5.

For ethyl-(trimethylplatinum) acetoacetate (R = OEt, R' = Me) it has been established that the platinum to "active methylene" bond is the preferred bond in this type of compound and there is no reason to doubt

that the structure of the ester complex is essentially the same as that of the diketone compound.

When heated in a capillary tube trimethylplatinum acetylacetone decomposes at about 200° without melting; but in a dry tube or flask it sublimes, a little being deposited apparently unchanged on the cooler parts of the vessel. The vapour is decomposed by hot glass; platinum being deposited in a coherent form. A platinum mirror can be produced. The compound sublimed at 160° when heated in a vacuum produced by a water-pump in a test tube immersed in a sulphuric acid bath. The compound condensed above the acid level; decomposition of the solid on the hot glass below the acid level began at 160° and at 190° was rapid. Subsequent heating of the evacuated tube over a flame and finally at red heat after the platinum had been deposited, gave a strongly adherent mirror which was not stripped by boiling with water, nitric or hydrochloric acid. Thus trimethylplatinum acetylacetone is a volatile platinum compound.[36]

The <u>trimethylplatinum acetylacetone</u> was prepared by heating a solution of 3.7 g. of trimethylplatinum iodide and 3.03 g. of thallous acetylacetone in warm benzene under reflux. The thallium iodide was removed and the filtrate

was evaporated to dryness and the residue was recrystallized from hexane. 2.4 g. of trimethylplatinum acetylacetone were obtained. Recrystallized from hot benzene, the compound separates as long needles but as thick plates on slow evaporation of a cold benzene solution.[36]

The chelate derivatives of trimethylplatinum with acetylacetone, dipropionylmethane and ethyl acetoacetate are white crystalline substances being soluble in organic solvents.[37] The dipropionylmethane derivative decomposes at 190°, the benzoylacetone derivative at 187° and the ethyl acetoacetate melts with blackening and evolution of gas when placed suddenly, in a sealed tube, into a bath at 200°. The molecular association of the dipropionylmethane and ethyl acetoacetate in benzene is about 2.0, thus affording yet another example of the stable 6-covalent compounds of quadrivalent platinum. The mode of preparation of the trimethylplatinum derivatives of dipropionylmethane, of ethyl acetoacetate and of benzoylacetate was similar to that described by Menzies[36] for the acetylacetone compound. The reaction goes quite readily for dipropionylmethane and with ethyl acetoacetate, but more slowly with benzoylacetone.

Ethyl(trimethylplatinic) acetoacetate recrystallizes as hexagonal plates from ethyl ether, trimethylplatinum dipropionylmethane as thick needles from hexane but trimethylplatinum benzoylacetone was not obtained either pure or in large amounts. It recrystallizes from methyl alcohol in long prisms.

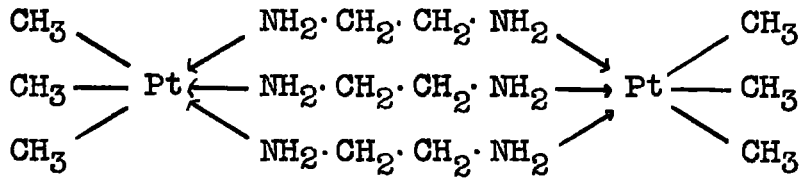
The trimethylplatinum compounds described[36,37] are all chelate compounds, soluble in organic solvents and when carefully heated in a tube, they sublime, giving a platinum mirror.

R.C. Menzies, H. Overton and E.R. Wiltshire,[39] obtained a colourless substance closely resembling Pope and Peachey's trimethylplatinum iodide[15] by dissolving trimethylplatinum acetylacetone in aqueous acetic acid and adding potassium iodide to the solution. The orange compound (Pope and Peachey) and the white compound prepared from trimethylplatinum acetylacetone crystallize from benzene in transparent hexagonal prisms, indistinguishable under the microscope except in colour. Both sets of crystals become opaque on standing in air; the opacity beginning at two opposite faces and gradually extending inwards. When recrystallized from toluene the crystals remain transparent.

b. With nitrogen containing compounds

The residues from molecular-weight determination of chelate trimethylplatinum compounds were evaporated to dryness, dissolved in 30% glacial acetic acid, and after filtration, treated with dilute hydrochloric acid. The precipitate obtained on boiling was filtered off, washed and dried. The compound when analysed agreed with trimethylplatinum chloride.

The stable 6-covalency of platinum evident in the diamminotrimethylplatinic iodide of Pope and Peachey[15] and in the stable association of trimethylplatinic acetylacetone into double molecules in benzene[37] was further confirmed[25] by the preparation of dipyridinotrimethylplatinum iodide, 2:2'dipyridyltrimethylplatinum iodide, monoethylene-diaminotrimethylplatinum iodide, and sesquiethylene-diaminotrimethylplatinum iodide. Ethylenediamine was the only base from which two compounds were obtained. All four compounds are colourless except that the second, made from orange trimethylplatinum iodide, is pale yellow. The first two are insoluble, the last two soluble in water, the mono compound more readily. A possible structure of the last compound is:-



which resembles that of iron enneacarbonyl.[40] Like trimethylplatinum acetylacetone, the above dipyridyl compound is insoluble in water but 2:2'-dipyridyltrimethylplatinum acetylacetone is soluble. The white trimethylplatinum iodide used in the preparation of the compounds prepared by Lile and Menzies was prepared by adding 5 g. of potassium iodide in 30 ml. of water to a solution in hot acetic acid of 1.65 g. of trimethylplatinum dipropionylmethane.[37]

Dipyridinotrimethylplatinum iodide was obtained by heating 0.13 ml. (excess) of pyridine with 0.1 g. of orange trimethylplatinum iodide in 10 ml. of benzene. The solution was evaporated and nucleated. Long colourless prisms were obtained, m.p. 168°. The compound decomposed explosively on heating.

2:2'-Dipyridyltrimethylplatinum iodide separated as colourless crystals (0.68 g. 95%) when the golden-yellow solution obtained from 0.212 g. (1 equivalent) of dipyridyl and 0.5 g. (1 equivalent) of colourless trimethylplatinum iodide in hot benzene, was boiled for

one minute, m.p. 273°, darkening slowly above 225°. From the acetone-water solution after estimation of iodide by the silver nitrate method, a bright yellow solid was obtained, soluble in alcohol, acetone and water. Long colourless needles were obtained, on crystallizing from boiling alcohol, which darkened above 220° and fused with decomposition at 246°. This is thought to be dipyridyltrimethylplatinic iodide.

Monoethylenediaminotrimethylplatinum iodide was obtained by refluxing 1 g. of orange trimethylplatinum iodide with 0.08 ml. (0.5 equivalent) of anhydrous ethylenediamine in 25 ml. of benzene for two hours. The white solid, m.p. 204°, was separated from the pale yellow solution and concentration of the filtrate to 1/3 volume gave dull orange crystals, m.p. 206°. Square plates and prisms were obtained on recrystallizing from water, m.p. 204°.

Sesquiethylenediaminotrimethylplatinum iodide was obtained (0.63 g.) as white needles (m.p. 273°, darkening above 230°) from 0.73 g. of orange trimethylplatinum iodide and excess of ethylenediamine dissolved in benzene. Water was added and after evaporation of the benzene the product was recrystallized from water.

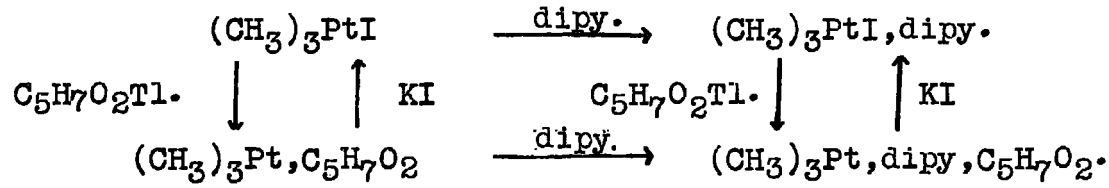
The sesqui-compound was obtained when 0.5 g. of the dipyridyl compound was dissolved in chloroform, and 0.08 ml. of ethylenediamine (1 equivalent) added to the hot solution, and the mixture heated under reflux. Colourless crystals were obtained. Free dipyridyl was detected by adding aqueous potassium mercuri-iodide solution to the clear mother liquor. The compound was recrystallized from water; m.p. 266°, darkening above 240°.

Dipyridyltrimethylplatinum acetylacetone was obtained as pale yellow hexagonal plates and prisms on allowing to evaporate at room temperature, the golden-yellow solution obtained by dissolving 0.17 g. of trimethylplatinum acetylacetone and 0.039 g. (0.5 equivalent) of dipyridyl in 10 ml. of benzene. Crystallized from hexane-benzene, this gave dull orange needles m.p. 143°, decomposition; darkening above 120°.

The same compound was also formed by heating dipyridyltrimethylplatinum iodide and thallous acetylacetone under reflux in benzene, filtering, and evaporating the solvent. Crystals and a brown sticky mass were obtained. This was stirred with benzene and alcohol and filtered from insoluble material. Orange needles m.p. 142° (decomposition darkening above 115°). The compound is

fairly soluble in water. The acetylacetone compound, when dissolved in water and a little acetic acid added followed by excess of potassium iodide, gave a white curdy precipitate. After washing and drying this darkened slightly above 230° and had a m.p. 268° (decomposition) and a mixed m.p. with dipyridyltrimethylplatinum iodide of 270°.

Thus the series of reactions carried out by Lile and Menzies may be summarized:-



Other methylplatinum compounds from similar reactions

Other methylplatinum compounds were isolated from the reaction between methylmagnesium iodide and anhydrous platinic chloride by H. Gilman, M. Lichtenwalter, and A.R. Benkeser,[17] This reaction is complex leading in part to the formation of trimethylplatinum iodide[15,19] dimethylplatinum diiodide and methylplatinum pentaiodide. Besides these compounds, two other platinum compounds were isolated which were not identified. These workers also prepared methylplatinum triiodide, hexamethyldiplatinum and

tetramethylplatinum.

Trimethylplatinum iodide was obtained, using a modification of the Pope and Peachey method, in 45% yield.

Hexamethyldiplatinum was obtained by the action of powdered potassium metal on trimethylplatinum iodide.

$$2(CH_3)_3PtI + 2K \longrightarrow (CH_3)_3Pt\cdot Pt(CH_3)_3 + 2KI \qquad 5$$

The yield was 60% after recrystallizing as colourless crystals from benzene-petroleum ether solution. Analysis was difficult owing to the compound exploding on heating, and cryoscopic molecular weight determination showed it to be undissociated in benzene.

Trimethylplatinum iodide (12 mg.) was produced when iodine (12.7 mg.) was added to a solution of hexamethyldiplatinum (20 mg.) in ether (10 mls.) and the solution refluxed for several hours during which time the iodine colour disappeared and a precipitate formed. This was filtered and the trimethylplatinum iodide recrystallized from benzene.

Tetramethylplatinum was obtained by the action of methylsodium on trimethylplatinum iodide in 46% yield

$$(CH_3)_3PtI + CH_3Na \longrightarrow (CH_3)_4Pt + NaI \qquad 6$$

The above reaction when carried out replacing methylsodium by methyllithium gave no reaction, unchanged

trimethylplatinum iodide was recovered after a reaction time of ten hours.

No reaction occurred when benzoyl chloride and tetramethylplatinum were refluxed together in benzene solution nor when tetramethylplatinum and iodine in chloroform solution were refluxed together.

Structure of tetramethylplatinum and hexamethyldiplatinum

R.E. Rundle and J.H. Sturdivant,[29] examined tetramethylplatinum and, on the basis of location of platinum atoms, concluded that this molecule is, like trimethylplatinum chloride, tetrameric. However in this case the bridging is effected by a methyl group. Although this is the only known example of an alkyl group functioning as a threeway bridge, in view of the existence of two-way methyl and ethyl bridges in aluminium alkyls[41] and the fact that the functioning of a methyl group as a three-way bridge may be readily explained on Rundle's theory of partial bonds,[42] the tetrameric structure of tetramethylplatinum seems reasonably certain. Tetramethylplatinum, when recrystallized from benzene, contains half a molecule of benzene as solvent of crystallization which is quickly lost through efflorescence. R.E. Rundle, and

J.H. Sturdivant,[43] showed that the presence of this benzene in the lattice in no way disturbs the tetrameric groups.

The facts that hexamethyldiplatinum is very soluble in benzene, in which it is monomeric, and that it forms trimethylplatinum iodide with iodine, suggest that there is present in the compound a Pt-Pt bond. While X-ray investigation of hexamethyldiplatinum is not conclusive it appears that the molecule is at least dimeric but not larger than $[(CH_3)_3Pt]_{12}$, although the possibility of continuous chains is not excluded.[44] Molecular weight determination in freezing benzene agrees with $(CH_3)_6Pt_2$.[16] It is possible that again there is methyl bridging, perhaps giving the platinum atoms six co-ordination, although as stated a direct Pt-Pt bond is also possible.

Other organoplatinum Compounds

No organoplatinum compound is formed by the action of the nascent ethyl radical, produced by electrolysis of $C_2H_5Na/Zn(C_2H_5)_2$-system on a platinum anode.[45]

In an earlier attempt to prepare an organoplatinum compound, Buckton[46] observed that diethylzinc reacted vigorously with platinic chloride with deposition of platinum black and evolution of gas. Frankland[47] found that the halide compounds of platinum reacted violently

with diethylzinc but the organic group did not unite with the platinum. When he heated platinous chloride in contact with the chloride of cacodyl, two equivalents of hydrogen in the cacodyl were replaced by a molecule of platinum producing a "chloride of cacoplatyl". This reaction he formulated:-

$$(C_2H_5)_2AsCl + PtCl_2 \longrightarrow (C_2H_5)AsCl(C_2H_3Pt") + 2HCl \qquad 7$$

Although the equation (7) balances, Frankland put forward no other evidence in support of the rather strange formulation of the product.

The formation of double salts from organoarsenic compounds and platinous, or platinic chloride is a general reaction.[48a,48i]

Organoantimony compounds react with platinic or platinous chloride with the formation of double salts.[48a,b]

A number of mixed carbonyl compounds of platinum are known.[49] Schutzenberger,[50] in 1868 passed chlorine and carbon monoxide over platinum sponge at 250°, and obtained a yellow sublimate from which three distinct compounds were isolated; $PtCl_2 \cdot CO$, $PtCl_2 \cdot 2CO$, $PtCl_2 \cdot 3CO$. These compounds dissolve unchanged in carbon tetrachloride but are decomposed by water.

$$PtCl_2 \cdot CO + H_2O \longrightarrow Pt + 2HCl + CO_2 \qquad 8$$

Pullinger[51] prepared platinum carbonyl dibromide $PtBr_2 \cdot CO$, by passing dry carbon dioxide over platinous bromide at 180°. Platinum carbonyl di-iodide was obtained by Mylius and Forster[52] by adding dilute hydriodic acid to a solution of platinum carbonyl dichloride in hydrochloric acid. Platinum carbonyl monosulphide, $PtS \cdot CO$, is thrown down as a brown precipitate when hydrogen sulphide is passed into a solution of platinum carbonyl dichloride in fairly concentrated hydrochloric acid.[52] A double salt of platinum carbonyl thiocyanate, $Pt(CNS)_2 \cdot CO$, with potassium thiocyanate is obtained by adding a solution of potassium thiocyanate to one of platinum carbonyl dichloride.

The carbonyl compounds of platinum are crystalline solids. They decompose on heating to give metallic platinum. Manchot[53] made use of the platinum chloride carbonyls in the separation of platinum from palladium.

Aryl platinum Compounds

The organo-metallic chemistry of platinum has been until recently almost entirely that of the methyl derivatives of platinum (IV). M. Lichtenwalter,[18,19] has reported work with other organic groups.

When platinum tetrachloride is added to phenylmagnesium

iodide, it is found that about ten equivalents of the Grignard reagent are required in order that the solution will give a positive colour test. An insoluble white complex was formed in the reaction which on hydrolysis generates an amorphous brown solid containing organic matter, platinum, and iodine which Lichtenwalter thought to be a mixture of phenylplatinum compounds, although no individual compounds could be isolated. This mixture was found to be slightly soluble in benzene, alcohol, and chloroform and very soluble in dioxan. Various fractions were obtained varying in platinum content from 30-48%.

Analysis of this red-brown powder gave Pt, 37.9 and 37.7% and, on dissolving a portion of the solid in hot concentrated nitric acid, the solution deposited, on cooling, white needles which had m.p. 229° after recrystallization from alcohol. These crystals gave no depression of m.p. when mixed with a known sample of 4,4'-dinitrodiphenyl. As the platinum-containing compound had been washed several times with benzene, in which diphenyl is very soluble, it appears unlikely that the nitro compound came from diphenyl contained in the material. The 4,4'-dinitrodiphenyl may have been formed by cleavage of the phenylplatinum bond with the formation of diphenyl which was subsequently nitrated,

or the phenyl groups may have been nitrated prior to cleavage.

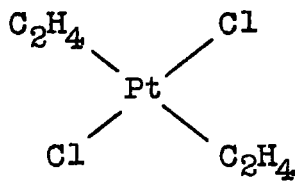
The amorphous nature of phenyl-platinum compounds together with lack of m.p.'s made it impossible to separate the components of the mixture into definite individual compounds. This mixture of products is analogous to the mixture obtained from methylmagnesium iodide and platinic chloride.

The reaction of α-naphthylmagnesium bromide with platinous bromide was said to result in the formation of di-α-naphthylplatinum, which was not obtained in a pure condition.

Olefin Co-ordination Compounds of Platinum

The olefin co-ordination compounds of platinum have been known for many years; Zeise's salt, $KPtCl_3C_2H_4$ having been described in 1830.[54] These complexes formed between platinous chloride and olefins have structures involving an unfamiliar type of covalent bond and their structure has only recently been elucidated. Though $K[C_2H_4PtCl_3]$ was known many years ago, $(C_2H_4)_2PtCl_2$ (6) was unknown, in spite of attempts by Gel'man[55] and Anderson,[56] to prepare it, until 1950 when Chatt and Wilkins were

successful.[57] These two authors[58] describe dichlorodiethyleneplatinum (6) as being rapidly precipitated in canary-yellow crystals by passing ethylene into a concentrated solution of dichlorodiethylene-$\mu\mu'$-dichlorodiplatinum (7) in acetone or in ethyl methylketone at about -70°.



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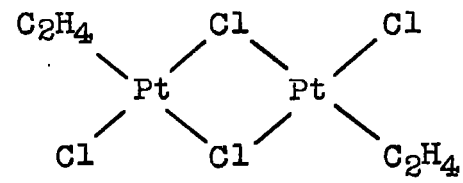


(7)

It is only slightly soluble in the ketone at this temperature but dissolves to a yellow solution at -50° and reverts, with evolution of ethylene, to the orange solution of (7) at room temperature. The yellow solid is thermally very unstable and was obtained, damped with acetone or ether, by pumping off the acetone-ethylene mother-liquor through a sintered-glass filter and washing the solid with acetone or ether at -70° in a closed system which excluded moisture. The yellow solid, in this state, reverts at -60° to orange (7) in an atmosphere of ethylene but is converted again on the surface into yellow (6) by cooling. At -70° (6) is sufficiently dissociated in acetone for one molecule of

ethylene to be lost, with dissolution of the solid to an orange solution, by passage of carbon dioxide through its acetone suspension.

The authors postulate that the presence of the ketone helps in the formation of (6), facilitating the entry of ethylene into (7) by opening the bridge, which is known to be split in boiling acetone.[59] They also suppose that the instability of (6) is best explained by trans-configuration.

The supposed cis-dichlorodiethyleneplatinum was obtained by dissolving the yellow isomer in cold acetone and allowing the solution to attain room temperature. Ethylene was evolved and after 48 hours the solution had become cherry-red and deposited a small quantity of almost white crystalline complex.

Since dichlorodiethyleneplatinum has been prepared, diolefins under the right conditions would be thought to give reasonably stable chelate complexes, but Gel'man[60] showed that butadiene and hexa-1:5-diene do not chelate but that double bonds react independently with different platinum atoms. Chatt and Wilkins[58] confirmed Gel'man's finding in the case of butadiene which gave $K_2\left[C_4H_6(PtCl_3)_2\right]$ with potassium chloroplatinite in 3% hydrochloric acid solution.

Kharasch and Ashford[20] describe a dipentene complex of empirical formulae $C_{10}H_{16}PtCl_6$ prepared by reaction of

dipentene with platinic chloride in glacial acetic acid. Chatt and Wilkins[58] repeated this preparation obtaining the known compound (α) but also attempted to prepare it by the action of dipentene with (7) in alcohol. The compound (7) (6.0 g) in 100 ml. alcohol was filtered, dipentene (2.65 g) added and the mixture evaporated at 15-20 mm. The residue (7.66 g) was extracted with 400 ml. hot alcohol, filtered, and cooled to -70°. The product, β-dipentene-platinous chloride, which separated recrystallized from 2:1-alcohol-acetone (yield 3.0 g), and decomposed at 171-172°.

Each of these compounds is formed without contamination by the other; and each isomer (0.3 g) was dissolved separately in chloroform (20 ml.) and shaken with cold aqueous potassium cyanide (0.3 g in 20 ml.). The chloroform was separated and the aqueous layer extracted twice with chloroform. The combined extracts were dried (Na_2SO_4) and brominated at -10° (ca. 0.4 g of bromine - slight excess). The chloroform was removed at 15-20 mm. and the residue was washed out with ethyl acetate (yields: from α-isomer 0.25 g; from β-isomer 0.3 g). Recrystallized once from ethyl acetate the products had m.p. (α) 122-123° and (β) 120-122°, not depressed when mixed with authentic dipentene tetrabromide.

β-Dipenteneplatinous iodide was obtained when the β-chloride reacted in the cold with sodium iodide in acetone. The precipitated sodium chloride was filtered off from the orange-brown solution, which by evaporation at 15-20 mm. gave a red crystalline iodide. This was purified by precipitation twice from chloroform solution with ether and had a decomposition point 122-124°. The iodide decomposed rapidly in boiling benzene. The α-chloride under similar treatment yielded a red oil, which decomposed rapidly at room temperature.

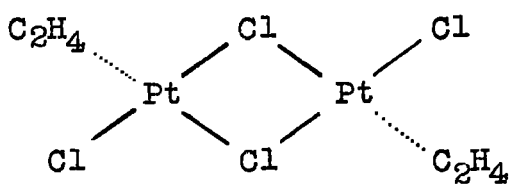
Other differences between the α- and β-compounds include m.p. (α, 148-149°; β, 171-172°) and solubility, α-being generally the less, and β- generally the more soluble.

Chatt and Duncanson[27] described a much improved method of preparation of ethylene platinous chloride $(C_2H_4PtCl_2)_2$ (dichlorodiethylene-μμ'-dichlorodiplatinum of Chatt and Wilkins.[58]) A solution of 15 g. of potassium chloroplatinite in dilute hydrochloric acid was shaken for 10 days in an atmosphere of ethylene and the colour changed from red-brown to golden-orange. On cooling in ice-water potassium ethylene trichloroplatinite monohydrate, $K[C_2H_4PtCl_3]H_2O$, crystallized. To obtain ethylene platinous chloride the solution was taken to dryness over sulphuric acid and sodium hydroxide

pellets and the residual mixture was extrated with alcohol containing concentrated hydrochloric acid to dissolve the yellow trichloroplatinite. The orange solution was filtered and taken to dryness under reduced pressure and this gave almost pure ethylene platinous chloride (10 g) as a rose coloured powder, decomposition about 165°.

Propylene platinous chloride was prepared as above except that the absorption of propylene by potassium chloroplatinite in 3% hydrochloric acid required three weeks. Potassium propylene trichloroplatinite monohydrate $K\left[C_3H_6PtCl_3\right]$, H_2O was isolated from the residue remaining after evaporation of the solution obtained after shaking.

Chatt and Duncanson (loc. cit.) propose structure (8) for ethylene platinous chloride. In propylene platinous chloride the propylene exists with its double bond, and this disposes



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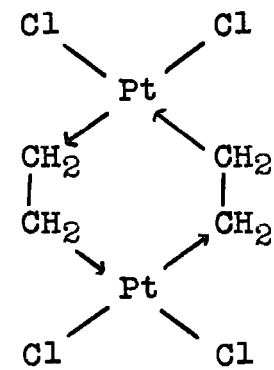


(9)

of such structures as (9) which was preferred by Gel'man.[55] Thus Chatt and Duncanson considered ethylene platinous chloride to have structure (8) (halogen bridged) as originally suggested by Pfeiffer.[61]

Some reactions of platinum olefin compounds

J.H. Flynn and H.M. Hulbert[62] investigated the reduction of ethylene platinous chloride with hydrogen and deuterium, in order to elucidate the role of metal catalysis in the heterogeneous reduction of olefins. J.S. Anderson[63] had previously reported that solid ethylene platinous chloride is quantitatively reduced by hydrogen at room temperature according to the equation:-

$$(PtCl_2C_2H_4)_2 + 4H_2 \longrightarrow 2Pt + 4HCl + 2C_2H_6 \qquad 9$$

Flynn and Hulbert found that the reaction in toluene solution took place at an appreciable rate at -40° and that it was autocatalysed by platinum and inhibited by olefins. Evidence was found for homogeneous reduction of diethylene platinous chloride in presence of ethylene below -10° in acetone solution; the reaction having an activation energy of 2Kcal. The authors conclude that the parallelism of these reactions to the heterogeneous reduction of olefins by metals suggests that the catalytic activity of metals may be due to the properties of small groups of metal atoms rather than to

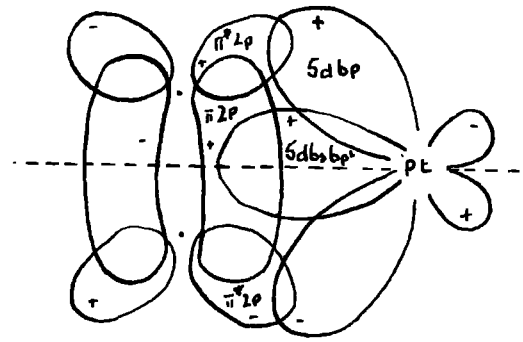
macroscopic properties peculiar to crystal lattice structure.

The same authors[62] postulate the formation of a mixed ethylene-propylene platinous chloride complex. It was concluded that $PtCl_2(C_2H_4)$ - (C_3H_6) may be formed at low temperatures and that it decomposes into the propylene complex mainly.

The reduction of solid ethylene platinous chloride with deuterium at -22° resulted in the formation of all ethanes from C_2H_6 to C_2D_6. The results indicated that the deuterium did not add unsymmetrically to the carbon double bond. Bromination of ethylene platinous chloride at room temperature resulted in the formation of $PtCl_2Br_2C_2H_4$, while at 61° ethylene dibromide was formed.

Bonding in the olefin compounds

Because olefins are among the most trans-directing ligands[64] Chatt and Duncanson consider that they bond to the metal by a σ and a π type of bond. Initially an ethylidene structure was proposed for $C_2H_4PtCl_3$[65] but a second structure also satisfying the above requirements, but with no hydrogen ion migration, was proposed by M.J.S. Dewar.[66] In platinous complexes the σ type of bond would be formed by overlap of a $5d6s6p^2$ hybrid orbital of the platinum atom



Orbitals used in the combination of ethylene with platinum.[27]

with the $\overline{\pi}$ orbital of the olefin, and the $\overline{\pi}$ type of bond by overlap of a filled 5d orbital of the metal atom with the anti-bonding $\overline{\pi}$ molecular orbital of the olefin. Hybridization of the 5d orbital with the vacant 6p orbital of the platinum atom would strengthen the $\overline{\pi}$ type of bond, giving a dp-hybrid more suitably shaped than the unhybridized 5d orbital to provide a large overlap with the antibonding orbitals of the olefin.[27]

Infra-red spectra showed that in the complexes of olefins with platinous chloride the olefin retains its double bond in the compounds and is symmetrically co-ordinated to the platinum. Dipole moment calculation by Chatt and Duncanson gave (tentatively) the C_2H_4 - Pt bond about 1/3 double-bond character.

These authors consider the platinum in olefin complexes to be divalent and not quadrivalent as proposed by Gel'man.[67,68] Ethylene platinous chloride in dry acetone was immediately oxidized by a dry acetone solution of permanganate at room temperature. On reduction by hydrogen it gives ethane, platinum and hydrogen chloride.[62] The bridge is broken by p-toluidine giving p-toluidine-ethylene platinous chloride, $C_7H_7NH_2 \cdot PtCl_2 \cdot C_2H_4$.

By analogy to the reaction of excess bromine with stilbene platinous bromide, $\left[(C_6H_5)_2C_2H_2\right]_2Pt_2Br_4$, which yielded stilbene dibromide,[20] Chatt and Duncanson attempted to chlorinate ethylene platinous chloride. Production of ethylidene dichloride would have been indicative of the ethylidene structure. The theoretical quantity of chlorine, according to the equations:-

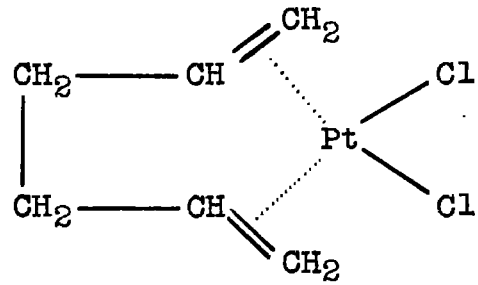
$$(C_2H_4)_2\ Pt_2Cl_4 + 2Cl_2 \longrightarrow 2C_2H_4Cl_2 + 2\ PtCl_2 \qquad 10$$

$$(C_2H_4)_2\ Pt_2Cl_4 + 2Cl_2 \longrightarrow (C_2H_4)_2\ Pt_2\ Cl_8, \qquad 11$$

added to a chloroform solution of the ethylene complex, gave no precipitate of platinous chloride; thus equation 11 appears to be the course of reaction. When twice the amount of chlorine required by the equation was added to a nitro-benzene solution of ethylene platinous chloride, and the solution boiled, ethylene dichloride was obtained and

characterized by conversion into ethylene bis(phenyl sulphide).

Some olefin complexes of platinum (II) have been obtained in which one olefin molecule appears to occupy two co-ordinate positions. Compound (10) is monomeric in



(10)

bromoform and its dipole moment, 6D, is consistent with the cis-structure.[69] A similar monomeric and polar (μ = 7D) compound PtI_2,C_8H_8 has been prepared from cyclo-octatetraene.[70]

Diene-platinum complexes

More recently J. Chatt, L.M. Vallarino and L.M. Venanzi[71] have prepared a number of chelate complexes of the type [diene PtX_2] (X = halogen). Of the dienes used the stabilities of the complexes are in the order cyclooocta-1:5-diene $\approx$ dicyclopentadiene $>$ dipentene $>$ hexa-1:5-diene and the stabilities of the dihalides decrease in the order Cl $>$ Br $>$ I. The dithiocyanate is not of the same type and has the formulea [diene$Pt(SCN)_2$Ptdiene]$(SCN)_2$. With anhydrous

sodium carbonate in alcohol the dihalides gave crystalline, stable alkoxy-halides (diene OR)$_2$Pt$_2$X$_2$. The dicyclopentadiene methoxy-chloride $\left[(C_{10}H_{12}OMe)_2Pt_2Cl_2\right]$ was easily prepared; its chlorine atoms are readily replaced by I^-, SCN^-, and SEt^-, but the methoxy-group is very firmly bound. p-Toluidine splits the halogen bridge to give monomeric $\left[C_{10}H_{12}OMe,C_7H_9NPtCl_2\right]$ although the corresponding iodide does not react with p-toluidine. The methoxy-group can be replaced by boiling concentrated hydrochloric acid to reform $\left[C_{10}H_{12}PtCl_2\right]$.

A few peculiar cycloocta-1:5-diene derivatives approximating to $\left[C_8H_{12}Pt(OR)_2\right]_n$ (R = Me and H) were discovered but were not investigated.

Recent work on organo-platinum compounds

Recently J. Chatt and B.L. Shaw[12] have described the preparation of several methyl platinum compounds and have suggested a reason for the instability of the alkyls and aryls of transition metals in general. They described the preparation and properties of a series of platinous methyls stabilized by tertiary phosphines or a chelating disulphide or diphosphine. The types trans - $(PR_3)_2PtMeX$ and cis - $(PR_3)_2PtMe_2$ [X = halogen] were found to be the

most stable and both are prepared by action of methyl-lithium or methylmagnesium halide on cis- or trans-$(PR_3)_2PtX_2$. The less stable cis-$(PEt_3)_2PtMeCl$ was prepared by the action of hydrogen chloride on the cis- dimethyl compound but trans-$(PR_3)_2PtMe_2$ was obtained in small quantity with considerable difficulty.

In general a mixture of mono- and di-methyls is obtained by the reaction of either cis- or trans-$(PR_3)_2PtX_2$ with the appropriate Grignard reagent MeMgX. These products are not easily separable and since use of theoretical quantities of Grignard reagent leaves some starting material a large excess of Grignard reagent was usually used.

A general equation may be written:-

$$(1+m+n)(PR_3)_2PtCl_2 \xrightarrow[20^\circ/1hr.]{MeMgX} 1 \text{ trans-}(PR_3)_2PtMeX + m \text{ cis-}(PR_3)_2PtMe_2 + n \text{ cis } (PR_3)_2PtMeX$$

The ratio 1:m:n depends upon the configuration of the starting material and the halogen X. All attempts to isolate trans-$(PR_3)_2PtMe_2$ from the reaction mixture failed.

The highest proportion of trans-monomethyl is produced by use of starting material of trans-configuration and of iodo-Grignard reagent. Thus trans-$(PEt_3)_2PtCl_2$ and MeMgI in large excess gave a 90% yield of trans-$(PEt_3)_2PtMeI$.

The use of a higher reaction temperature (80°) did not give the dimethyl compound. The use of starting material of cis configuration or of the lighter halogens increases the proportion of dimethyl but even the reaction of cis-$(PEt_3)_2PtCl_2$ with a large excess of methylmagnesium chloride did not give the pure dimethyl. This is best obtained by the use of methyllithium. cis-$(PEt_3)_2PtMe_2$ was obtained in 80% yield by reaction of the cis-dichloride with a 10% excess of methyllithium and the dimethyl $C_2H_4(PEt_2)_2PtMe_2$ and $C_2H_4(SEt)_2PtMe_2$ were prepared similarly.

The monomethyls, when present in large proportion, were removed from cis-$(PEt_3)_2PtMe_2$ by treating the mixture in ethanol with thiourea which forms easily separable complexes with monomethyls, leaving the dimethyls.

Preparation of cis-$(PEt_3)_2PtMeCl$. This is thought to be an intermediate in the formation of cis-$(PEt_3)_2PtMe_2$ from cis-$(PEt_3)_2PtCl_2$ by the Grignard or methyllithium procedures, but it could be isolated only in very small yield from the reaction mixture, and was isolated in similar quantity from some preparations of trans-$(PEt_3)_2PtMeCl$ from trans-$(PEt_3)_2PtCl_2$.

The cleavage of cis-$(PEt_3)_2PtMe_2$ by dry hydrogen chloride in ether at room temperature was found to be the best method.

cis-$(PEt_3)_2PtMeCl$ is stable in benzene solution but the addition of a trace of free phosphine caused rapid and almost complete isomerization. In contrast, trans-$(PEt_3)_2PtMeCl$ after keeping in presence of free phosphine for two weeks was almost unchanged and no cis-$(PEt_3)_2PtMeCl$ was isolated from solution.

Attempted preparation of trans-$(PEt_3)_2PtMe_2$

trans-$(PEt_3)_2PtX_2$ (X = Cl or Br) reacts with the corresponding methylmagnesium halide at 20° much more slowly than does the cis-isomer to give the monomethyl as the major product. At higher temperature (80°) the second halogen is partially replaced, but only the cis-dimethyl was isolated. Similarly from the reaction of methyllithium (2.2 mols at 20°) the only dimethyl isolated had a cis-configuration.

Repeated distillation of cis-$(PEt_3)_2PtMe_2$ (m.p. 81-82°) at 12 mm/130° gave a product of low m.p. but identical analysis. This product had a low dipole moment and was probably a mixture of cis- and trans- $(PEt_3)_2PtMe_2$. A very small quantity of pure trans-isomer was isolated by chromatography.

Platinous methyls stabilized by tri-n-propylphosphine and by triphenylphosphine were also prepared.

Melting points and dipole moments of the platinum

methyls (including three new platinum (IV) methyls) are given in the paper,[12] in which the reactions of the platinum methyls are described; they are summarized as follows:-

1. Replacement of halogen

The halogen atoms of the monomethyl derivatives are readily replaced by treatment with an appropriate salt. Thus $(PEt_3)_2PtMeCl$ is converted almost quantitatively into the corresponding bromide and iodide by treatment with the corresponding alkali metal salt in acetone. Similarly trans-$(PEt_3)_2PtMeI$ is converted into the thiocyanate by treatment with potassium thiocyanate, and in smaller yield, into the nitrate by treatment with silver nitrate in aqueous methanol.

2. Cleavage of the methyl group from the metal

The methyl groups are rapidly removed from the metal at room temperature by reaction with iodine, magnesium iodide or hydrogen chloride in ether solution and from the dimethyl by cis-$(PEt_3)_2PtCl_2$ in boiling benzene, e.g.

cis-$(PEt_3)_2PtMe_2 \xrightarrow{I_2}$ trans-$(PEt_3)_2PtMeI$ + MeI
(c.f. the diphenyl compound)

cis-$(PPh_3)_2PtMe_2 \xrightarrow{MgI_2}$ trans-$(PPh_3)_2PtMeI$ + MeMgI

cis-$(PEt_3)_2PtMe_2 \xrightarrow{HCl}$ cis-$(PEt_3)_2PtMeCl$ + CH_4

3. Addition Reaction

a. Methyl iodide (c.f. Equation 4)

The monomethyl derivatives react with methyl iodide in a sealed tube at 100° to produce platinic compounds, e.g. $(PEt_3)_2PtMe_2I_2$, m.p. 101-103° and $(PPr^n_3)_2PtMe_2I_2$ m.p. 128°. The methyl iodide can be removed from the former compound in three hours at 80° and 0.01 mm. pressure, or slowly in boiling solvents. It was shown not to be held as solvent of crystallization because the product could not be obtained from a solution of the monomethyl compound in methyl iodide at room temperature. When the components are heated in a sealed tube at 100° for 20 hours cleavage of the methyl groups occurs.

$$(PEt_3)_2PtMe_2I_2 \longrightarrow (PEt_3)_2PtI_2 + C_2H_6$$

Iodine does not react with $(PEt_3)_2PtMe_2I_2$ in cold benzene but on boiling for fifteen minutes the methyl groups are eliminated.

Methyl iodide did not react with trans-$(PEt_3)_2PtI_2$ and with cis-$(PEt_3)_2PtMe_2$ gave a mixture of products.

b. Chlorine

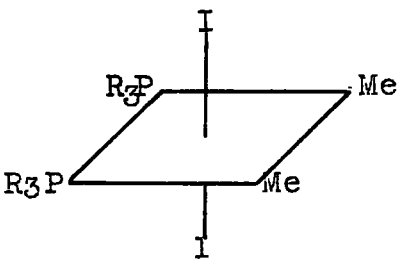
cis-$(PEt_3)_2PtMe_2$ reacts with two equivalents of chlorine to give $(PEt_3)_2PtMe_2Cl_2$.

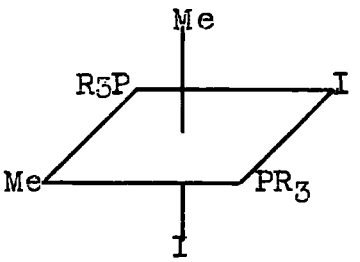
c. Iodine

As shown above and in contrast to chlorine, iodine causes cleavage of cis-$(PEt_3)_2PtMe_2$.

Configuration of the complex platinic dimethyls

From a comparison of estimated and observed dipole moments of the six sterioisomers of $(PEt_3)_2PtMe_2I_2$ and $(PEt_3)_2PtMe_2Cl_2$ the structure is postulated as being one of the following.





Estimated 5-6 D 6 D

Found 5.8 D

Later work by Chatt and Shaw[13] describes the preparation and properties of a series of alkyl and aryl derivatives of platinum. In the alkyl series L_2PtR_2 and L_2PtRX, complexes were prepared where L = PMe_3, PEt_3, PPh_3; R = Me, Et, Pr^n, Bu^n and X = Cl, I and SCN. Some benzyl derivatives were also prepared, cis-$(PEt_3)_2Pt(CH_2 \cdot Ph)_2$, trans-$(PEt_3)_2Pt(CH_2 \cdot Ph)Cl$ and trans-$(AsEt_3)_2Pt(CH_2 \cdot Ph)Cl$.

The authors state that the higher alkyl homologues and the benzyls of type cis-$(PR_3)_2PtR_2$ and trans-$(PR_3)_2PtRCl$ are less stable than the corresponding Pt-methyl derivatives.

Aryl derivatives of the type cis- and trans-L_2PtAr_2 and cis- and trans-L_2PtArX were obtained and it was found that complexes derived from phenyl and p-substituted phenyl groups appeared to be similar in their properties and only the phenyls were investigated in detail. m-substituted phenyls were not investigated but o-substituted phenyls gave especially stable complexes and were therefore examined more closely than the other substituted aromatic derivatives.

In general it was found that the Pt-aryl derivatives were more easily prepared and purified, and were more stable than the aliphatic. The authors suggest that one might expect the aryl groups to form bonds of partial double bond character to a platinum atom and evidence from dipole moments is put forward to support this view. This double bonding might account for the greater stability of the Pt-aryl complexes and could be due to two causes:
1. increased M-C bond strength due to the addition of a certain amount of π-bonding between the metal and carbon atoms and 2. increased splitting of the 5d-energy levels

leading to stabilization.

It was easier to obtain the Pt-diaryl derivatives by the reaction

$$L_2PtCl_2 + 2RMgX \longrightarrow L_2PtR_2 + 2MgXCl \qquad 12$$

than the Pt-monoaryl derivatives by the reaction

$$L_2PtCl_2 + RMgX \longrightarrow L_2PtRX + MgCl_2 \qquad 13$$

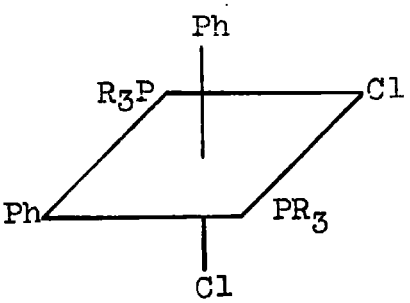
Reaction (12) occurs most readily with cis-L_2PtCl_2 (at 20°) to give a cis product. With trans-L_2PtCl_2 the reaction is more sluggish needing a higher temperature (80°) and the product was a mixture of cis- and trans- isomers. Aryl-lithiums react similarly but much more readily than Grignard reagents and give better yields of the cis-isomer from both cis- and trans- L_2PtCl_2.

cis- and trans- L_2PtAr_2 are cleaved to the corresponding monoalkyl complexes, $L_2PtArCl$, by dry hydrogen chloride in ether and this is the best method of preparing the cis-monoaryl derivatives, e.g. cis $(PEt_3)_2PtPhCl$, from which the trans-isomers are best obtained by isomerization using a trace of free phosphine. The trans-diaryl complexes were not readily obtained in sufficient quantity to serve as raw materials for the preparation of the trans-monoaryl complexes.

As only the complexes having at least one anionic ligand such as Cl in $(PR_3)_2PtCl_2$ and $(PR_3)_2PtRCl$, are isomerized

rapidly to the equilibrium mixture of cis- and trans- isomers by a trace of free phosphine and as the diaryls $(PEt_3)_2PtPh_2$ are not isomerised, this points to isomerization through an ionic intermediate, e.g. $[(PR_3)_3PtR]Cl$, rather than by the intramolecular rearrangement of a 5 or 6 co-ordinated intermediate, e.g. $(PR_3)_3PtRCl$.

In contrast to cis-$(PEt_3)_2PtMe_2$, which loses a methyl group by reaction with one molecule of iodine, both cis- and trans-$(PEt_3)_2PtPh_2$ add iodine to give the same stable Pt(IV) derivative $(PEt_3)_2PtPh_2I_2$. Chlorine behaved similarly and these are the first isolateable aryl derivatives of Pt(IV) ever described. The dipole moments of the two compounds are 4.95 D and 4.25 D respectively and comparison with the estimated dipole moments of the isomers of $(PEt_3)_2PtPh_2Cl_2$ leads to the conclusion that it has a structure



The Pt-o-substituted phenyl derivatives are especially stable, and the view is put forward that the o-groups hinder the attack of reagents at the platinum atom, and so the reactions of cleavage and decomposition are much slower than those of the phenyl and p-substituted phenyl complexes.

Attempts to prepare a dimesityl complex $(PEt_3)_2Pt(mesityl)_2$ failed but the monomesityl complex cis-$(PEt_3)_2Pt(mesityl)Br$ was easily obtained. A model showed that there was room for the two mesityl groups and there is probably a kinetic difficulty preventing introduction of the second group.

The ethynyl derivatives, trans-$L_2Pt(C{\equiv}CR)_2$ were obtained by reaction (12) from $RC{\equiv}CMgX$ in ether but were most readily prepared by the reaction of $RC{\equiv}CNa$ with L_2PtCl_2 in liquid ammonia. They are described as beautifully crystalline substances whose stabilities increase in the order of R's H < Me < Ph. The substituted ethynyls have very strong bonds in the infrared spectrum at ca 2100 cm^{-1} and in $(PEt_3)_2Pt(C{\equiv}CH)_2$ at 1958 cm^{-1} indicating that these organic radicals have retained their triple bonds in the complex.

Attempts to prepare styryl and cyclopentadienyl derivatives failed.

The new organometallic complexes prepared are listed,

together with their melting points and dipole moments.

Dipole moments

The chelate complexes $C_2H_4(PEt_2)_2PtPh_2$ and $C_2H_4(PEt_2)_2PtMe_2$ have moments which are about 1.2D greater than those of the corresponding complexes of monophosphine e.g. $(PEt_3)_2PtPh_2$. The authors postulate that this difference is due to the rather smaller P-Pt-P bond angles which must occur in the chelate complex. The dipole moments of complexes containing the strongly dipolar P-Pt-P bonds would be very sensitive to changes in the angle between the bond.

In the phenyl and methyl complexes it might be expected that the difference in the moments of the Pt-CH_3 and the Pt-Ph bonds would be about 0.35D, the dipole moment of toluene. The observed differences are all greater than this and the phenyl group appears to carry an appreciably greater negative charge, relative to the methyl group, than would be expected on the basis of their difference in electronegativity.

In a comparison of the moments of cis-$(PEt_3)_2PtPh_2$ (7.2 D) and $C_2H_4(PEt_2)_2PtPh_2$ (D = 8.4) with those of their Pt-methyl analogues (5.55 D and 6.7 D respectively) the differences are about 1.7 D in each case instead of the

0.5 D expected on the basis of the dipole moment of toluene. The authors suggest that this unexpectedly large difference between the moments of the corresponding cis-diaryl and cis-dialkyl complexes might be due to distortion of the P-Pt-P bond angle and would require the angle to be smaller in the diaryl than in the dialkyl complexes. This would then be a steric effect of the more bulky aryl groups.

Acetylenic Compounds

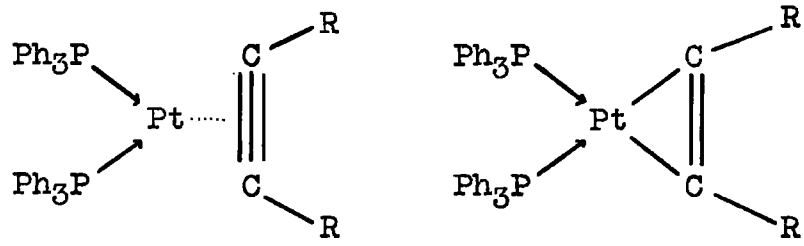
Attempts by Chatt and Duncanson[27] to prepare acetylene complexes of platinous chloride using simple acetylenes such as $CH_3 \cdot C \equiv C \cdot CH_3$ and Ph - C ≡ C - Ph were not successful.

However, later work[72] has produced a series of stable acetylene complexes of general formulea $Pt(PPh_3)_2ac$ (where ac = acetylenic substance). The compounds were prepared by reduction of an alcoholic suspension of cis- $(PPh_3)PtCl_2$ in presence of the acetylene and purified by crystallizing from benzene or chloroform by addition of ethanol. One acetylene displaces another from its complex in solution at room temperature,

$$C_2H_2 \langle \text{ Alk-C} \equiv \text{CH} \langle C_2Alk_2 \langle \text{ Ph C} \equiv \text{CH} \langle C_2Ph_2$$

The compounds showed no sign of a triple bond in the infrared spectrum but absorbed in the region 1700 cms^{-1}. Possible

structures put forward were:-



Palladium

Organopalladium compounds have been postulated as intermediates in the catalytic hydrogenation of aryl halides.[73] This assumption is based on varying yields of diphenyl obtained in catalytic hydrogenation of bromobenzene under varying conditions.

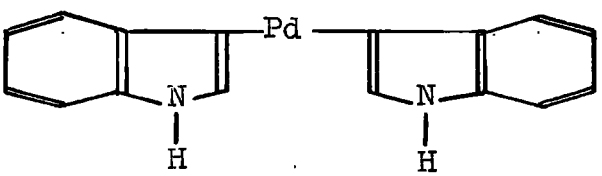
Palladium chloride, $PdCl_2$, forms a complex with trimethylethylene.[74] This complex forms stable orange crystals decomposing at 85-90°, which correspond to the formula $PdCl_2, C_5H_{10}$.

Palladium forms a halogen carbonyl complex of composition $PdCl_2 \cdot CO$, which is the least stable of all such compounds formed by the platinum metals. This compound was obtained by the action of carbon monoxide, saturated with the vapour of methyl alcohol on palladium chloride at 0°.[75] This complex is decomposed by water.

$$PdCl_2 \cdot CO + H_2O \longrightarrow Pd + CO_2 + 2HCl \qquad 14$$

M. Lichtenwalter[19] added phenylmagnesium iodide (0.0163 moles) to palladous chloride (0.00566 moles). This produced a black deposit of metallic palladium after a vigorous reaction. Diphenyl (0.85 g.) m.p. 68-69° was isolated (98% yield). No other organic material was isolated.

Compounds of palladium with indole[76] and pyrrole[77] have been prepared and formulated with palladium - carbon bonds. For the pyrrole compound the analysis does not, in fact, correspond to the formulas proposed. The indole derivative was prepared by adding a cold, saturated aqueous solution of indole to a 5 per cent aqueous solution of palladous chloride. After a few hours a dark precipitate appeared for which formulea (11) was proposed.



(11)

In an attempt to repeat this work,[78] it was found that immediately on mixing the solutions a rusty-red precipitate formed of composition $C_8H_6PdCl_2$. The assumption of a

palladium - carbon link by Delavigne is quite arbitrary since at least four other possibilities exist:-

1. a bond to nitrogen.
2. an amine-type donor bond.
3. an olefin-type donor bond as in platinum olefin complexes.
4. a sandwich type bond as in bis-cyclopentadienyl compounds.

Thus this indole-palladium compound cannot be regarded as an organopalladium compound.

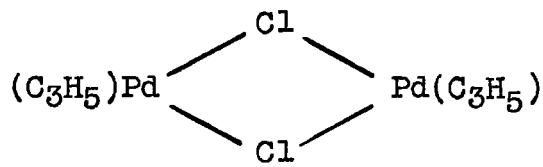
More recently J. Smidt and W. Hafner[79] have found that allyl alcohol reacts vigorously with $PdCl_2$ at about 50°. Propene is evolved and a small part of the palladium salt is reduced to the metal but most is transformed into a compound which forms large yellow crystals on cooling.

From the tarry products remaining when the solution is evaporated an easily polymerizing liquid can be isolated (b.p. 72°/9 mm.), which is an unsaturated cyclic alcohol $C_6H_{10}O_2$.

The yellow palladium compound is diamagnetic, has a formulea $C_6H_{10}Pd_2Cl_2$ and dissolves in acetone, chloroform, ethyl acetate, benzene, aqueous solutions of hydrogen halides, alkyl halides, ammonia and dilute alkali. It decomposes at about 145° to palladium and allyl chloride.

These facts are consistent with a bis-allyldipalladium

dichloride. The allyl anions should be considered as two-valent ligands



Solubility in HX or KX is thought to be due to bridge splitting. The dipole moment is 2.08 ± 0.04 D; attributed to solvation upsetting the symmetry. The compound isolated is compared with $C_4H_7Co(CO)_3$[80].

Palladium-olefin compounds

Palladium forms co-ordination complexes with olefins, of the type $(PdCl_2 \cdot CH_2 = CH_2)_2$ and $(PdCl_2 \cdot C_6H_5CH = CH_2)_2$.[81]

The first strictly organometallic derivatives of palladium were prepared by J. Chatt, L.M. Vallarino and L.M. Venanzi.[82] These were compounds of the type [diene PdX_2], [(diene OR)$_2Pd_2X_2$], and [(diene OR), p-toluidine PdCl]. Their properties indicate that they have similar structures to their platinous analogues, but in general the compounds are more deeply coloured, more easily formed, more reactive and less stable.

Stable diene derivatives were obtained from the cyclic diolefins cycloocta-1:5-diene and dicyclopentadiene but not from dipentene, which reduced palladous salts to the

metal. The cyclooctadiene complex with palladous chloride is exceptionally stable. It is rapidly formed by shaking an aqueous solution of ammonium chloropalladite with the diene; this is in marked contrast to the mono-olefin complexes of palladium (II) which are formed in anhydrous media, and are decomposed by water.[83]

Copper

Alkyl copper compounds

Methylcopper, MeCu, is obtained when methyllithium reacts with copper iodide at -15°. The yellow solid which separates decomposes in boiling ether with the formation of metallic copper, methane and ethane. It explodes violently when allowed to dry in the air at room temperature. A similar product is obtained from cupric nitrate and tetramethyllead. Addition of a second molecule of methyllithium causes the yellow methylcopper to dissolve to a clear almost colourless solution, which gives a positive colour test using Michler's ketone.[84] This solution may contain Li^+CuMe_2. Methylcopper can be detected in a reaction between methyl chloride and copper at 350°, since the gas deposits copper and then removes a lead mirror. At 250° the half-life of the methylcopper is 0.002 seconds.[85]

Ethylcopper is apparently much less stable and attempts to isolate it have led to the formation of ethane and ethylene, doubtless by interaction through the intermediate formation of ethyl radicals.

Aryl copper compounds

Phenylcopper, PhCu separates as a grey powder from the solution resulting from the addition of cuprous iodide to phenylmagnesium bromide. It decomposes vigorously at 80°, forming copper and diphenyl but slowly decomposes even at room temperature. It is insoluble in most organic solvents but dissolves in pyridine. On hydrolysis, benzene and cuprous oxide are formed, with benzoyl chloride it forms benzophenone, but it is not sufficiently reactive to combine with phenyl cyanide.[86] Gilman, Jones and Wood[84] have prepared phenylcopper from cuprous iodide and phenyllithium and shown it to undergo 1,4 addition to the conjugated system C=C-C=O in contrast to the 1,2 addition characteristic of phenyllithium, thus showing a similarity with other organic derivatives of complex-forming metals which also undergo 1,4 addition.

Acetylenic copper compounds

Raphael[87] states that compounds containing a free ethynyl group (e.g. Ph - C ≡ C - H) undergo characteristic metathesis

with ammonical cuprous salt solutions with the formation of the corresponding insoluble cuprous acetylide. The parent acetylene may be readily regenerated from the cuprous derivative by treatment with dilute mineral acid or, better, aqueous sodium cyanide solution.

The copper acetylides are relatively insoluble in both aqueous and organic media and they are unaffected by the action of alkyl halides. Their structures are as yet unknown. Carbonyl compounds usually react sluggishly under laboratory conditions, an exception being formaldehyde which undergoes smooth condensation with mono-substituted acetylenes to form the corresponding primary alcohol.

W. Reppe,[88] in Germany, found that acetylene, under pressure, will react with carbonyl compounds in presence of copper acetylide to produce acetylenic carbonols and glycols.

In 1870, C. Glaser,[89] observed that oxidation with air of an ammonical solution of the copper derivative of phenylacetylene resulted in a smooth coupling reaction to yield diphenyldiacetylene. The modern refinement of this process entails shaking the initial ethynyl compound at room temperature with an aqueous cuprous chloride-ammonium chloride solution.

Coupling may also be effected by oxidation of the copper

acetylide with cupric chloride,[90] hydrogen peroxide[91] and potassium ferricyanide.[92]

Cyclopentadienyl-copper complexes

Cyclopentadienyltriethylphosphinecopper (I) $C_5H_5CuP(C_2H_5)_3$, has been made by adding triethylphosphine to a suspension of copper (I) oxide in cyclopentadiene and petroleum ether.[93] It may be recrystallized from petroleum ether or sublimed at 60° in vacuum as diamagnetic white needles melting at 127-128°.

Silver

Alkyl silver compounds

Methylsilver[94] is precipitated when alcoholic silver nitrate is added to alcoholic tetramethyllead at -10 to -60°,

$$AgNO_3 + Me_4Pb \longrightarrow Me_3PbNO_3 + MeAg \qquad 15$$

It is remarkable in that it decomposes to silver and ethane and may be a polymer or a salt $Ag^+AgMe_2^-$.

Isobutenylsilver is obtained by the action of ethanolic silver nitrate on isobutenyltriethyllead. It is an orange solid which affords isobutenyl radicals on decomposition.[95]

Aryl silver compounds

Phenylsilver, PhAg, has been prepared in an impure state when silver chloride or bromide is added to a cooled

solution of phenylmagnesium bromide. It is obtained as a brown or grey powder and decomposes even at -18° to silver and diphenyl, sometimes exploding at room temperature. It is insoluble in most organic solvents.[96]

A double compound of phenylsilver and silver nitrate, $(PhAg)_2AgNO_3$, of unknown constitution has been prepared as a canary-yellow powder by the action of alcoholic silver nitrate on ethyltriphenyllead, ethyltriphenyltin, or triphenylbismuth. It is unstable and slowly decomposes at room temperature.[97]

Acetylenic silver compounds

Monosubstituted acetylenes form silver salts, which are generally sparingly soluble. The usual reagent for this purpose is ammonical silver nitrate although relatively high concentrations of alkyne are needed for a positive response. A 5% solution of silver nitrate in 95% ethanol gives a quantitative precipitation of even traces of 1-alkynes as the silver acetylide-silver nitrate complex.[98]

$$R{\cdot}C{\equiv}CH + 2AgNO_3 \longrightarrow R\,C{\equiv}C{\cdot}Ag{\cdot}AgNO_3 + HNO_3 \qquad 16$$

The parent acetylene may be regenerated from the silver complex by treatment with aqueous sodium cyanide or ammonium thiocyanate.[99]

Gold

There is no evidence for the existance of auric compounds other than four-covalent derivatives of Au^{-} in which the four (dsp^2) bonds lie in a plane. All organo-gold compounds are of this type, no aurous organic compounds are known.

Trialkylgold compounds

Trimethylgold[100] has not been isolated as it is very unstable, but is formed when methyllithium is added to auric bromide in ether at -65°. On warming the reaction mixture to about -40 to -35° a gold mirror is deposited; decomposition is rapid at +35° and mainly ethane with some methane is evolved. The solution of trimethylgold almost certainly contains the co-ordination compound $Me_3A\bar{u}\ \dot{O}Et_2$ and since nitrogen is a stronger donor than oxygen much more stable complexes may be obtained by the addition of amines. In this way the following have been isolated, trimethylgold-benzylamine, m.p. 51.5-53°, trimethylgold-α-aminopyridine, and bistrimethylgold-ethylenediamine, $(Me_3A\bar{u}\cdot\dot{N}H_2CH_2-)_2$. The last explodes violently when warmed, and affords dimethylgold chloride in very good yield with ethereal hydrogen chloride.

Trimethylgold is not decomposed by phenol or trichloracetic acid at -65°, but reacts readily with thiols e.g.

$$2Me_3Au\cdot\overset{+}{O}Et_2 + 2PhSH = (Me_2Au\cdot S\cdot Ph)_2 + 2Et_2O + 2CH_4 \quad 17$$

Dialkylgold derivatives

Dimethyliodogold $(Me_2AuI)_2$, m.p. 78.5°, is formed by the action of methylmagnesium iodide on a cooled suspension of dipyridinodichlorogold chloride (from $pyAuCl_3$) in pyridine.[101] The compound forms colourless crystals, melting to a dark red liquid which detonates violently. It is insoluble in water and dissolves in most organic solvents though sparingly in ethanol. Addition of alkali to an ethanolic solution causes the gold to be deposited as a brilliant coherent film. It is dimeric in benzene the gold showing characteristic four-covalency.

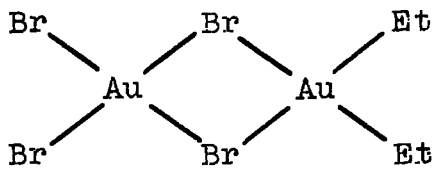
Co-ordination compounds have been obtained with nitrogen, oxygen and sulphur as donor atoms. Thus ethylenediamine gives two compounds and an appreciably volatile acetylacetoneate, m.p. 84°, is formed from thallous acetylacetoneate.[31] Treatment of the acetylacetoneate with hydrobromic acid affords dimethylbromogold, m.p. 68-69° (decomp), and with bromine, the deep red methyldibromogold results.

Diethylbromogold[102] is prepared in a similar way to the dimethyl compound and has a similar dimeric, structure.[103]

Ethyldibromogold,[102] prepared from diethylbromogold and bromine in carbon tetrachloride, is markedly less stable than the diethyl compound and decomposes quantitatively at 80-85° according to the equation:

$$2(EtAuBr_2) \longrightarrow 2EtBr + 2AuBr \qquad 18$$

It does not form a co-ordination compound with ethylene-diamine but disproportionates to $(Auen_2)Br_3$ and $(Et_2Auen)Br$: this suggests but does not prove the unsymmetrical structure:-

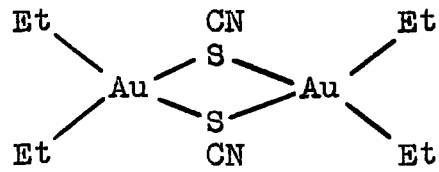


The above structure is supported by the high dipole moment of 5.5 D of the propyl compound.

Diethylcyanogold,[104] $(Et_2Au\ CN)_4$, prepared from the bromide and silver cyanide, has a square structure; the gold atom being at the corner of the square with linear -CN groupings between.[31] The structure has been confirmed by X-ray analysis of the di-n-propyl compound.[105] These compounds readily decompose on standing, with separation

of R_2 (e.g. n-butane from diethylcyanogold), first to a polymer $(RAuCN)_n$ and finally to aurous cyanide.

The thiocyanate[106] from diethylbromogold and an excess of silver thiocyanate, is dimeric and has a probable structure



The bridge is not broken by amines; in purified solvents it decomposes to butane and aurous thiocyanate.

Reaction in acetone between diethylbromogold and silver sulphate gives bis(tetra-ethylsulphatodigold), $(Et_4Au_2SO_4)_2$ which is soluble in organic solvents and water in which it ionizes to $\left[Et_2Au(OH_2)_2\right]_2SO_4$.[107] Derivatives of various dibasic acids are formed from the sulphate and the sodium salts of the dibasic acids in aqueous solution. Chelating diamines react with the sulphate giving salts.[108]

Arylgold compounds[109]

These have not been well characterized. Auric chloride chlorinates benzene and is itself reduced to aurous chloride, but the reaction seems to be stopped by addition of oxygen compounds (e.g. ether or ethyl acetate) possibly by co-ordination to the auric chloride. If the reaction is

stopped when a precipitate first begins to appear, aryldichlorogold derivatives can be isolated as pale yellow crystalline substances. Phenyldichlorogold, $PhAuCl_2$, is slightly soluble in water and in ether, insoluble in benzene and light petroleum and easily soluble in alcohol and salt solution in which it probably forms $Na^+ \left[(PhAuCl_3)\right]^-$

Attempts to prepare arylgold compounds by the Grignard method have not been successful.

Organic derivatives of nickel and cobalt

Since this introduction was typed J. Chatt and B.L. Shaw[110] have published their work on nickel and cobalt.

The nickel complexes were obtained by treatment of complexes of the type $(PR_3')_2NiX_2$ (where R' = Et n-Pr or Ph and X = halogen) with a Grignard reagent, or an aryllithium or with a sodio-derivative of an acetylene (in liquid ammonia). They are of types trans-$(PR_3')_2NiRX$ and trans-$(PR_3')_2NiR_2$ where R is an organic radical. Stable complexes were obtained with R=-C≡CH, -C≡C·Me, -C≡C·Ph and with R= an o-substituted aryl group such as o-tolyl, o-bromophenyl, o-methoxyphenyl, mesityl, 3-bromomesityl, 2-biphenylyl, α-phenanthryl; the corresponding complexes

with R= phenyl or a m- or p-substituted aryl group are much less stable and were not isolated in a pure condition.

Complexes with aliphatic radicals, R, are least stable and were not isolated.

The compounds isolated are stable in air indefinitely and some have appreciable volatility e.g. trans-$(PEt_3)_2Ni(mesityl)Br$ sublimes slowly at 150°/1 atm. without decomposition. They are diamagnetic and have a trans-planar arrangement of ligands.

A number of very stable aryl-nickel derivatives containing chelating diphosphines were also prepared, e.g. $(R'_2P\cdot CH_2\cdot CH_2\cdot PR'_2)NiRBr$ with R'=Et or Ph, and R = mesityl, α-maphthyl or 2-phenylyl and a methylnickel complex may also have formed but was too unstable to be isolated in a pure state.

Cobalt yielded planar complexes of the type trans-$(PPhEt_2)_2CoR_2$ where the aryl groups R carry particularly bulky ortho substituents, e.g. R=mesityl, 2-biphenylyl or 1-(2-methyl)naphthyl.

These complexes are paramagnetic (μsolid = 2.5-2.7 Bohr magnetous at 25°) and have very small or zero dipole moments. They are less stable than their nickel analogues but appear to keep indefinitely at room temperature in air.

Substituted ethynyl complexes of cobalt $(PR_3)_2Co(C{\equiv}CR)_2$ are not stable.

A representative selection of these complexes together with their melting points and dipole moments is given in the paper.

The authors consider that the stability of these nickel and cobalt complexes depends upon a combination of steric and electronic effects.

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EXPERIMENTAL

Contents

1. Preparation and purification of starting materials.

Contents

Note

The author wishes to express his thanks to the following for the preparation of the samples listed.

Professor G.E. Coates	Development of the method of preparation of o-bromophenylarsonic-acid.
	1,2-Bis(diphenylphosphino)ethane-dichloropalladium.
	1,2-Di(ethylthio)ethane.
	Cyclo-octa-1,5-dienedichloropalladium
Dr. R.G. Hayter	p-Bromobenzotrifluoride.
Mr. J.M.F. Braddock	2,2'-Dibromobiphenyl.
Mr. P.S. Dixon	Tri-n-butylphosphine.
	Triethylphosphinemonochlorogold.
Mr. J. Hutchinson	1,2-Di(methylthio)ethane.
	1,2-Di(methylthio)ethanedichloro-palladium.
Mr. J. Livingstone	Diphenylphosphine.
Mr. C. Parkin	1,2-Bis(diphenylphosphino)ethane.

1. Solvents

a. Ether

This was bought as "Anhydrous Methylated Ether", distilled over sodium, from J.F. MacFarlen and Co. Ltd. It was dried over sodium wire (at least twelve hours) and transferred to a distillation set where it was distilled from sodium-potassium alloy in a closed system under nitrogen. The ether so distilled gave no sign of reaction with lithium aluminium hydride.

Most of the ether used was simply stood over sodium wire for 24 hours and then more sodium wire was added.

b. Tetrahydrofurane, THF

This was bought from Badische Anilin and Soda Fabrik A.G., Ludwigshafen-a-Rhein, and was transferred to one-gallon bottles in which it remained in contact with solid potassium hydroxide. When required it was decanted from the alkali and boiled (with reflux) with potassium metal until addition of a little benzophenone resulted in a permanent blue or purple colour; then it was distilled.

2. Organolithium compounds[1,2]

a. Methyl-lithium[3]

This was prepared in three ways starting from:-

1. Methyl iodide

2. Methyl bromide and

3. A mixture of methyl bromide and methyl chloride (gas).

$$CH_3X + 2Li \longrightarrow CH_3Li + LiX$$

All three were made from lithium in the form of shot suspended in ether, and the organic halide dissolved in ether or bubbled into the reaction mixture as gas. All three reactions were carried out at about -10° (internal).

The shot was prepared as follows:-

The apparatus (Diagram IV) was purged with argon and petroleum oil, fraction 210-220°, was added until the oil was level with the two indentations. 3-4 drops of oleic acid were added followed by lumps of lithium metal (excess of 2 g. mols.). The oil was then warmed by means of the gas ring and the suspension was stirred gently. The stirrer was made of glass with tantalum wire loops. As the oil neared its boiling point the lithium softened and finally melted and as this gradually took place the stirring was increased to rapid until all the lithium had broken up.

Heating was stopped but stirring was continued to prevent the shot coalesing. When cold the oil was drained off and the shot washed twice with ether against a counter-current of argon or nitrogen and then washed through the 10 mm tap into the reaction vessel (Diagram I).

1. From methyl iodide

A 500 ml. flask fitted with a condenser, stirrer and dropping funnel (Diagram I) was purged with nitrogen and, against a counter current of nitrogen, the lithium shot was washed into the flask with ether; the condenser being temporarily removed. The flask was then cooled to -10° with an ice-salt bath and from the dropping funnel a solution of methyl iodide (1 mol.) in ether was slowly added with good stirring.

When all the organic halide had been added the reaction mixture was stirred at room temperature for 15 minutes and the solution was transferred to a graduated dropping funnel by means of an adapter (Diagram II).

2. From methyl bromide

An identical procedure was used and it was found more important here that the flask be kept at -10°.

3. From methyl bromide and methyl chloride

The flask was adapted so that methyl chloride gas could be passed into the ether solution and an identical procedure to the above was followed.

The flask containing the ether suspension of the lithium shot was cooled (-10^{o}) and from the dropping funnel a solution of methyl bromide (0.2 mols.) in ether was added slowly to initiate the reaction (about 2-3 minutes). A steady stream of methyl chloride was then passed into the ether solution in the flask with continued slow addition of methyl bromide. When the amount of lithium present in the flask was small the addition of the halides was stopped and the reaction mixture was stirred at room temperature for 15 minutes. Later preparations dispensed with the use of the bromide as the reaction was found to start perfectly well with the chloride alone.

Yield

High yields, 85-95% were regularly obtained using these procedures.

Yields were calculated by taking a 2 ml. aliquot of the lithium solution, hydrolysing and titrating against normal hydrochloric acid using bromocresol green as indicator.

b. n-Butyl-lithium[4,5]

i. To lithium shot (10.0 g. 1.45 g. atom.) in pentane (250 mls.) in a 2 litre flask cooled in an ice bath was added slowly and with good stirring, a solution of n-butyl chloride (185.2 g., 2 moles) in pentane (200 mls.). When reaction set in a further quantity of lithium shot (10.0 g.) in pentane (250 mls.) was added. A further dilution of the n-butyl chloride solution with pentane (300 mls.) and a steady slow addition gave a good reflux rate. More lithium shot (10.0 g.) was added in pentane (750 mls.).

When all the alkyl halide solution had been added the flask was allowed to attain room temperature and inorganic salts were allowed to settle overnight. The n-butyl-lithium solution was blown over into a storage vessel. (Diagram III).

Yield Solution strength 0.75N.

ii. Lithium (10.0 g., 1.45 g. atom) was converted into shot, washed with ether and pentane and transferred to a litre three-necked flask in pentane (200 mls.) n-Butyl chloride (64.9 g., 0.7 moles) in pentane (240 mls.) was added slowly with good stirring and the flask was warmed on a water bath and gentle refluxing was maintained

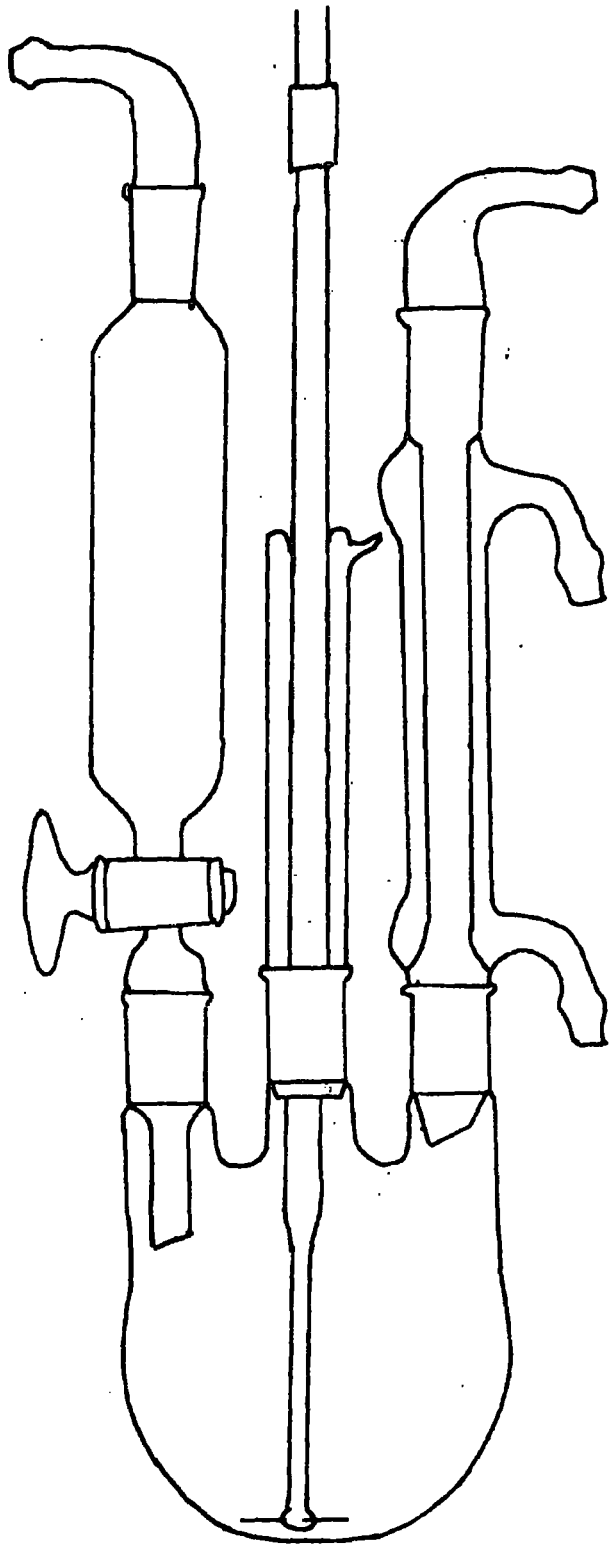


Fig. I

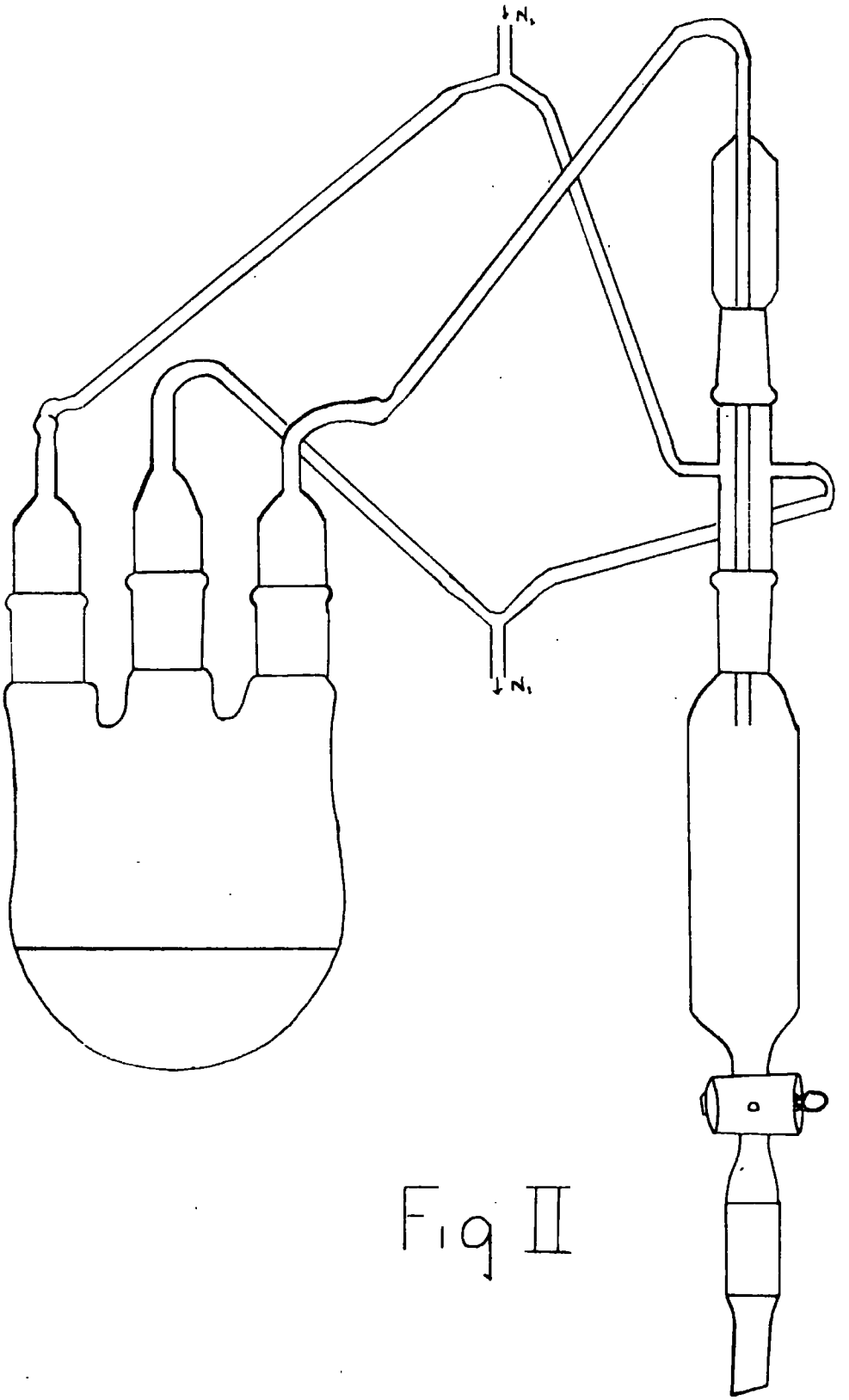


Fig II

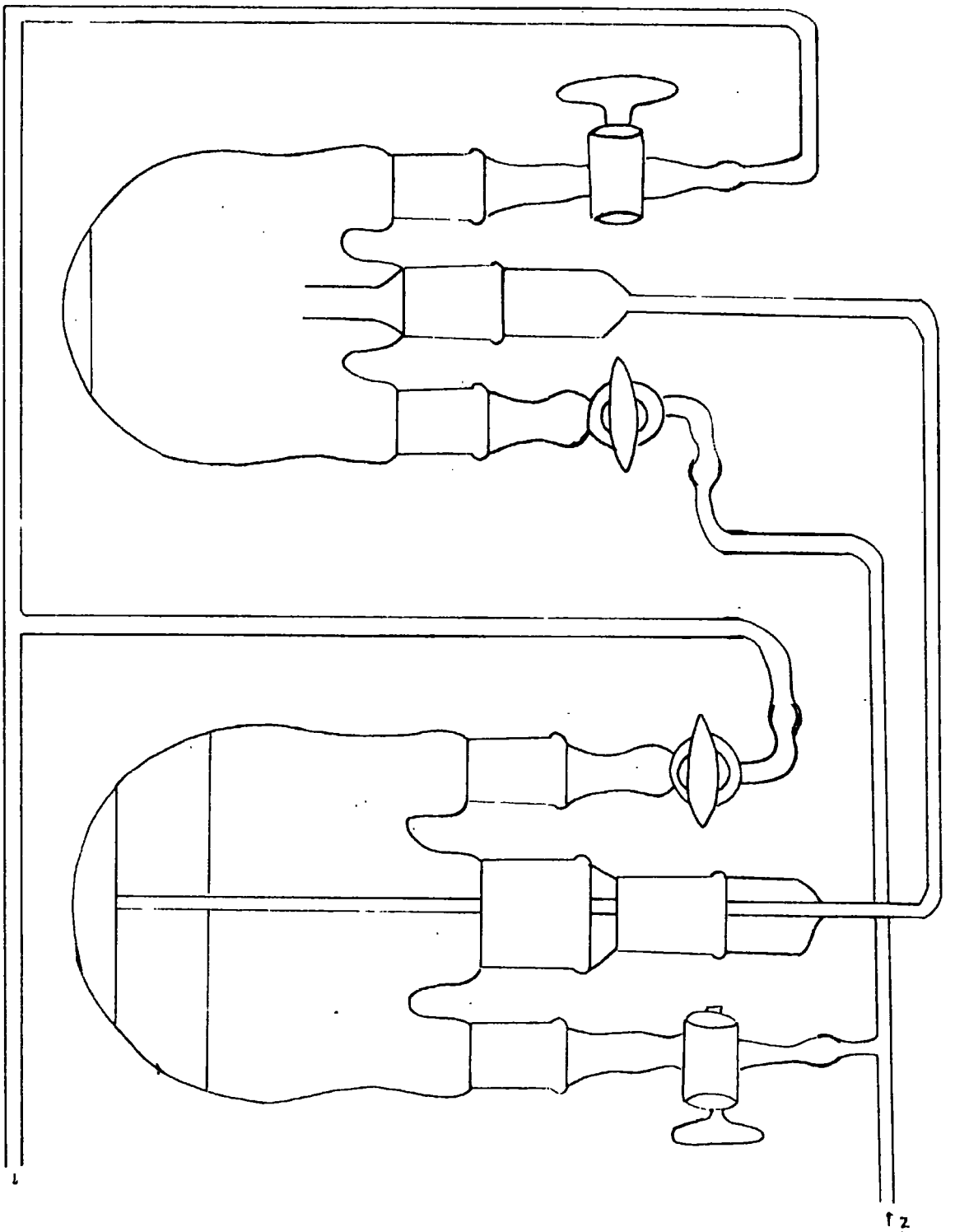


Fig III

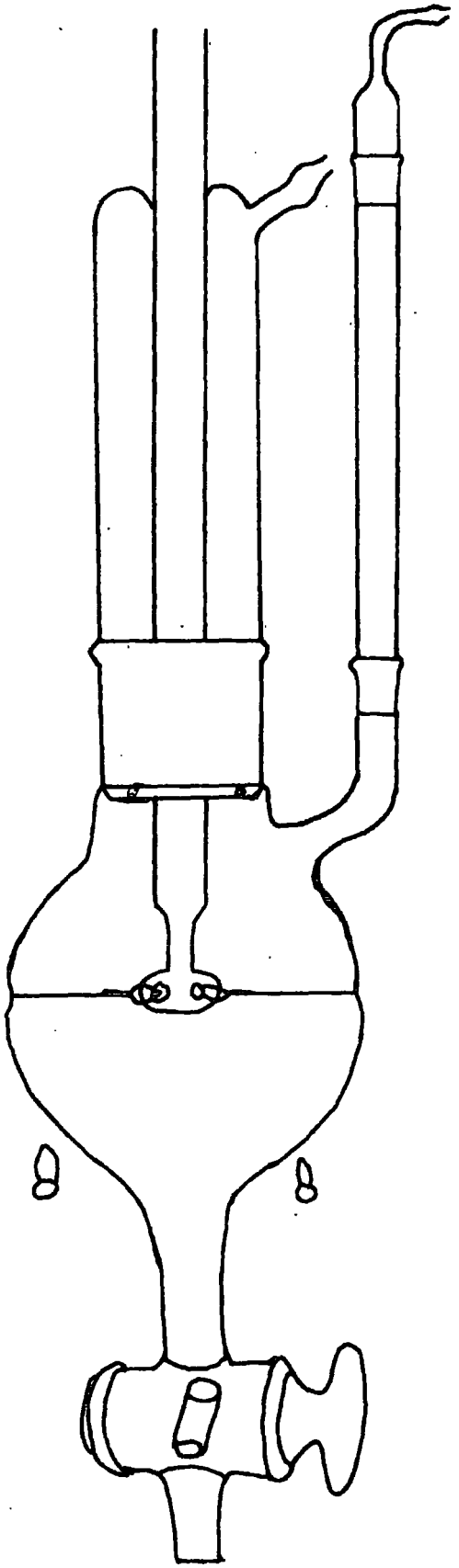


Fig IV

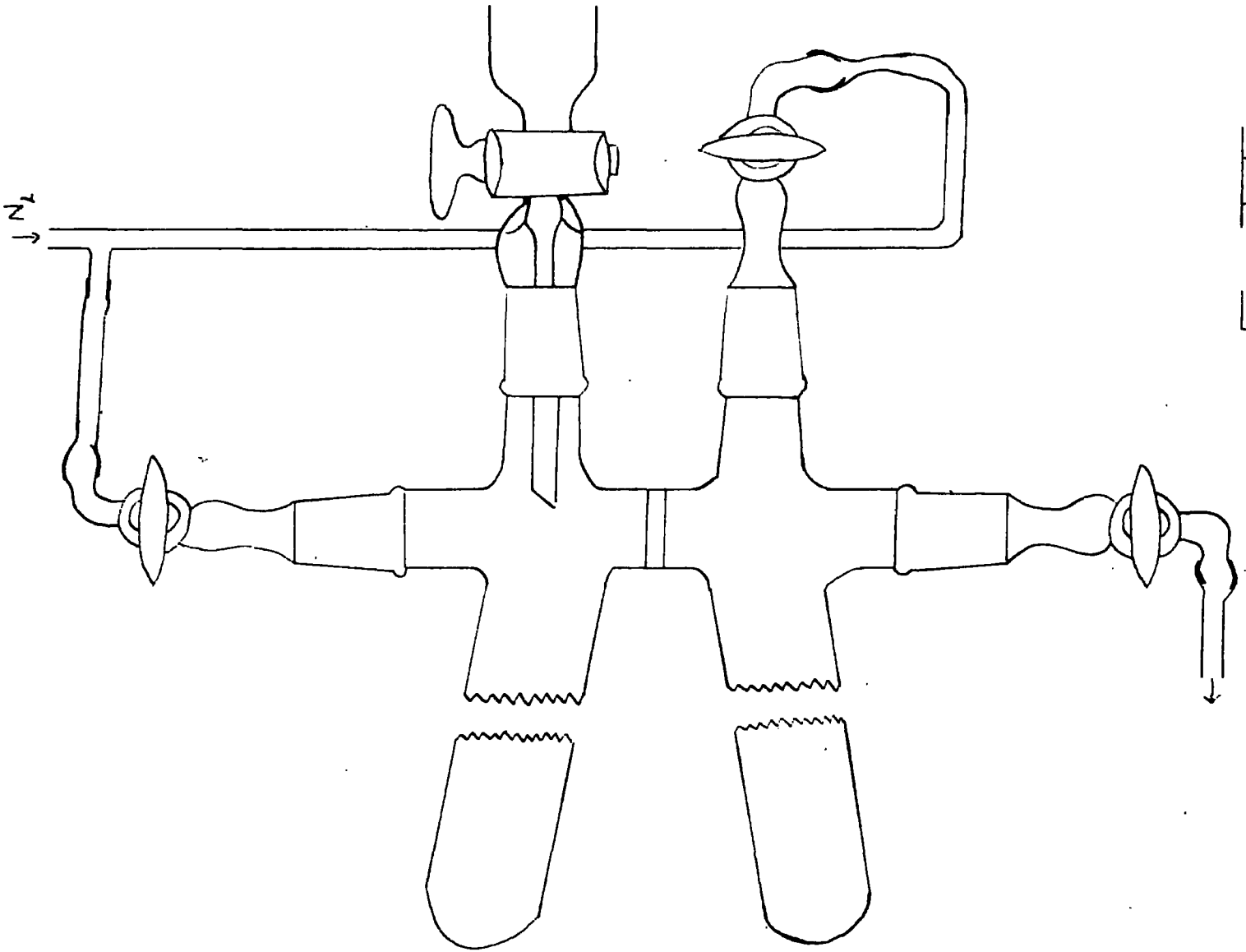


Fig 7

throughout addition of the halide solution. The solution was refluxed (one hour) after the addition. Inorganic salts were allowed to settle overnight and the clear n-butyl-lithium solution was decanted off.

Yield Solution strength 1.04N.

c. Phenyl-lithium[1]

1. From bromobenzene

To a dry, nitrogen filled, 250 ml. three-necked flask was added lithium shot (1.4 g., 0.2 g. atom.), prepared as described previously, in ether (80 mls.). At room temperature and with good stirring was added bromobenzene (15.7 g., 0.1 moles) in ether (20 mls.) at such a rate as to maintain steady reflux. After addition of the halide solution the reaction mixture was refluxed for 30 minutes.

Yield 90-95%.

2. From diphenylmercury[6]

Diphenylmercury[7,8] was prepared according to the equations:-

$$2PhMgBr + HgCl_2 \longrightarrow Ph_2Hg + MgCl_2 + MgBr_2$$

$$4PhHgCl + N_2H_4 \longrightarrow 2Ph_2Hg + 2Hg + N_2 + 4HCl$$

Phenylmagnesium bromide (1.15 moles) was prepared in a 2 litre flask from magnesium (28 g.) and bromobenzene (181 g., 1.15 moles) in ether (300 mls.). After addition of the bromobenzene the solution was refluxed (1 hour) and the addition of a small excess of bromobenzene eliminated any magnesium remaining.

A Soxhlet extractor containing mercuric chloride (135.7 g., 0.5 moles) was fitted to the flask containing the Grignard solution to which dry benzene (500 mls.) was now added to facilitate solution of Ph_2Hg. The Grignard solution was boiled and the mercuric chloride was slowly extracted until the soxhlet was empty. The flask was then adapted for distillation and distillate was collected at 46° for 45 minutes. Distillation was then stopped and the reaction mixture was heated and stirred for a further two hours after which time the excess Grignard was hydrolysed using ammonium chloride/ammonia solution. Hydrochloric acid was then added to pH 6 and the reaction mixture was filtered through a No.3 glass sinter and the white solid (I) remaining on the filter was washed with water, alcohol, benzene and petroleum ether.

The filtrate was transferred to a separating funnel and phases were separated. The organic phase was

evaporated and a white solid (II) was obtained.

Solid I (0.43 moles PhHgCl) was placed in a 1 litre flask with alcohol and an excess of a 60% solution of hydrazine was added with sodium carbonate (25 g.).[9] The reaction mixture was then heated on a water bath for four hours during which time a deposit of mercury appeared. The white solid in the flask was collected on a filter and dried at 80°, while the filtrate was evaporated giving more white solid. These two solids were combined, recrystallized from toluene and washed with petroleum ether, m.p. 120-122°.
Yield 50 g., 30%.

The solid (II) recrystallized from benzene, had m.p. 140°.

To a three-necked flask, purged with nitrogen and fitted with a stirrer, condenser and dropping funnel, was added lithium shot (2 g., 0.29 g. atom.), and diphenylmercury (18.4 g., 0.052 moles) was added in small portions (~1 g. each) at intervals so as to maintain a steady reflux rate. Reaction set in after about 20 minutes and the solution rapidly turned black. Addition was complete in one hour and stirring was continued for 30 minutes.
Yield 90%* (Hydrolysis and titration against NHCl)

* On standing overnight the PhLi decayed quite quickly to 30%.

This method gives a product which does not contain halide ions.

d. 4-Dimethylaminophenyl-lithium

To lithium shot (1.0 g., excess of 0.14 g. atom) in ether (50 mls.) was added (15 minutes) a solution in ether (50 mls) of p-bromodimethylaniline (14 g., 0.07 moles). The solution was refluxed (20 minutes) when addition was complete. Yield 90%.

e. 2,2'-Dilithio-biphenyl[10]

To a rapidly stirred solution of 2,2'-dibromobiphenyl (13.4 g., 0.043 moles) in ether (50 mls.) was added n-butyl-lithium (0.086 moles) in ether (47 mls.) at room temperature. The solution was then refluxed (2.5 hours) and then stirred at room temperature (90 minutes).

3. Grignard Reagents [11]

a. Methylmagnesium bromide

This was prepared under standard Grignard conditions from methyl bromide in ether solution and magnesium in ether.

b. Ethylmagnesium bromide

c. Phenylmagnesium bromide

At all stages during the preparation of these Grignard reagents, from the alkyl- or aryl-halide and magnesium in ether solution an atmosphere of nitrogen was maintained in

the reaction vessels.

d. Phenylethynylmagnesium bromide[12]

Ethylmagnesium bromide (0.0225 moles) was prepared from ethyl bromide (2.73 g., 0.025 moles) and magnesium (0.51 g., 0.025 moles) in ether (70 mls.). A 90% yield was assumed.

To the cold Grignard solution, phenylacetylene (2.3 g., 0.0225 moles) in ether (10 mls.) was added, slowly with stirring. After addition of the hydrocarbon, the solution was refluxed (30 minutes).

e. Styrylmagnesium bromide[13]

Magnesium (3 g., excess of 0.05 moles) was placed in a 250 ml. flask fitted with a stirrer, dropping funnel and condenser and ether (20 mls.) was added. A crystal of iodine, ethyl bromide (0.5 ml.) and ω-bromostyrene* (1.5 ml.) were added. Reaction set in after 60 seconds and, with disappearence of the iodine colour, the stirrer was started and more ether (20 mls.) was added. ω-Bromostyrene (9.1 g., 0.05 moles) in ether (35 mls.) was added (60 minutes) with stirring and refluxing. The reaction mixture was refluxed (15 minutes) after addition of the halide. Yield 78% based on carbonation to cinnamic acid.

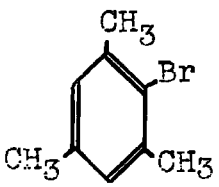
* The ω-bromostyrene was distilled before use at 84°/4mm.

f. p-Trifluoromethylphenylmagnesium bromide[14]

$$p\text{-}CF_3C_6H_4Br + Mg \longrightarrow p\text{-}CF_3C_6H_4MgBr$$

p-Trifluoromethylphenylmagnesium bromide (0.022 moles) in ether (43 mls.) was made from p-bromobenzotrifluoride (4.95 g., 0.022 moles) in ether (22 mls.) and magnesium (1.1 g., 0.045 moles) in ether (22 mls.). After addition of the bromide the mixture was stirred (10 minutes) and the final solution was red-brown in colour.

g. Mesitylmagnesium bromide[15]



$$+ Mg \longrightarrow (CH_3)_3C_6H_2MgBr$$

Magnesium (1.95 g., 0.08 g. atom) was placed in a 250 ml. three-necked flask with ether(20 mls.) and a solution in ether (55 mls.) of bromomesitylene* (11.0 g., 0.055 moles) and ethylene bromide (3.75 g., 0.02 moles) was added at such a rate as to keep a vigorous reflux rate. The reaction mixture was stirred (30 minutes) under reflux after addition of the bromide solution.

*Bromomesitylene was prepared as described in Organic Syntheses[16], b.p. 102-115°/17 mm.

Yield (Bromomesitylene) 42%. A fairly large low boiling fraction 80-100°/17 mm was obtained and this was set aside

for re-bromination.

h. The attempted preparation of p-trifluoromethylphenylmagnesium chloride

$$p\text{-}CF_3C_6H_4Cl + Mg \longrightarrow p\text{-}CF_3C_6H_4MgCl$$

To a 500 ml. three-necked flask was added magnesium (3.64 g., 0.15 mole) ethylene bromide (9.4 g., 0.05 mole) and THF (10 mls.). A vigorous reaction set in almost immediately and p-chlorobenzotrifluoride (18.0 g., 0.1 mole) in THF (30 mls.) was added slowly with good stirring with the internal temperature maintained at 45-50° by heat of reaction. The initial reaction was so vigorous that more THF (10 mls.) was added during addition of the first 2-3 mls. of the chloride solution. The Grignard solution was refluxed for one hour and after cooling, transferred into a 500 ml. three-necked flask containing lumps of solid CO_2. On warming to room temperature the reaction mixture was hydrolysed with 2N sulphuric acid (95 mls.) and after an ether extraction the ether phase was in turn extracted with alkali. On acidification no solid appeared and after an ether extraction and evaporation of the ether no solid came down.

The above procedure was repeated but instead of carbonating, an aliquot of the Grignard solution was

titrated against normal hydrochloric acid after hydrolysis.

To a 250 ml. flask, dried and purged, was added magnesium (4.0 g., excess of 0.15 moles) and a few mls. of a solution in THF (30 mls.) of $CF_3C_6H_4Cl$ (18.0 g., 0.10 moles) and ethylene dibromide. Reaction set in immediately and on stirring, vigorous reaction occurred. The remainder of the solution was added (25 minutes) dropwise and the addition rate was fast enough to maintain steady reflux. Stirring under reflux for one hour followed and the resulting solution was dark brown. An aliquot was taken for titration against NHCl.

Yield 5%.

Carbonation with solid CO_2 and hydrolysis (1N sulphuric acid) followed and the aqueous phase was extracted with ether to give an orange-brown solution and an orange-brown solid (I) which was collected on a filter. The ether phase was evaporated and a light brown solid (II) was obtained.

Both I and II were insoluble in alkali but II recrystallized from benzene m.p. 220-221°.

m.p. p-$CF_3C_6H_4COOH$ 213-214°.[17]

4. Donor substances

a. Phosphines[18]

i. Triethylphosphine

$$EtBr + Mg \longrightarrow EtMgBr$$

$$PX_3 + 3EtMgBr \longrightarrow PEt_3 + 3MgXBr$$

Ethylmagnesium bromide (5.66 moles) was made from ethyl bromide (562 g., 5.16 moles), ethyl iodide (78 g., 0.50 moles) and magnesium (139 g., 5.7 moles) in ether (1.5 litres).

The flask (5 litre) was then cooled (-10^{o}) and phosphorus tribromide (406.9 g., 1.5 moles) in ether (2 litres) was added (120 minutes). The reaction mixture was stirred for 30 minutes to complete the reaction.

Water was then added followed by a solution containing ammonium chloride (0.166 moles) and disodium hydrogen phosphate (0.166 moles) in water (20 mls.). Ether which distilled over was collected and when ether ceased to come off the reaction mixture was boiled and distillate collected until only one phase came over.

The ether phase was fractionated under nitrogen and the fraction $123-127^{o}$ was collected.

Yield 123 g., 68%.

ii. Diethylchlorophosphine[19,20]

$$Et_4Pb + 3PCl_3 \longrightarrow 3EtPCl_2 + PbCl_2 + EtCl$$

$$3EtPCl_2 + Et_4Pb \longrightarrow 3Et_2PCl + PbCl_2 + EtCl$$

A mixture of phosphorus trichloride (204 g., 1.75 moles, 153 mls.) and tetraethyl-lead (170 g., 0.525 moles, 102 mls.) was heated in a 500 ml. three-necked flask on an isomantle under reflux at 110° for 44 hours. A thermometer was placed in the flask so that its bulb was in the boiling liquid. After about one to two hours heating a thick white precipitate of lead chloride appeared. The crude ethyldichlorophosphine was distilled into a 500 ml. flask, b.p. 111-113°.

Yield 160 g., 1.23 moles, 70%.

The ethyldichlorophosphine prepared above was then heated at 140-145° for 38 hours with tetraethyl-lead (120 g., 0.37 moles, 72 mls.). A precipitate of lead chloride again appeared. The product was distilled from the reaction flask with a boiling range 128-130°. Refractionation of the distillate gave a fraction, 130-133°. A fraction 120-130° was rejected.

Yield 84 g., 0.675 moles, 55%; (based on PCl_3) 39%.

iii. Attempted preparation of di-n-butylchloro-phosphine[21,22,23]

$$2POCl_3 + 6BuMgBr \longrightarrow 2Bu_3PO + 3MgCl_2 + 3MgBr_2$$

$$Bu_3PO + PCl_5 \longrightarrow Bu_3PCl_2 + POCl_3$$

$$\downarrow$$

$$Bu_2PCl + BuCl$$

This preparation was carried out by first preparing tri-n-butyl phosphine oxide.[21] n-Butylmagnesium bromide was made from n-butyl bromide (616 g., 4.5 moles) and magnesium (110 g., 4.6 moles) in ether (1 litre). At 0° a solution in ether (750 mls.) of phosphorus oxychloride, $POCl_3$ (184 g., 1.2 moles) was added (four hours). The flask was allowed to reach room temperature and the contents were refluxed (two hours). The colour test for Grignard reagent after this time was positive. During refluxing ether (1 litre) was distilled off while the distillation temperature rose from 35 to 42°. The distillate was returned to the flask and the reaction mixture was hydrolysed using an aqueous solution (1000 mls.) of ammonium chloride (224 g., 4.2 moles). More water (750 mls.) was added and the phases were separated. The aqueous phase was washed with ether (2 x 500 mls.) and the ether

phase was washed with 4N caustic soda solution (2 x 250 mls.). The ether phase was concentrated on a water bath and fractionated.[22] A fraction 156-165°/8 mm. was collected. G.M. Kosolapoff[22] gives 185-186°/18 mm.

Yield 217 g., 83%.

The conversion to the chloride was carried out as described by G.M. Kosolapoff[23].

Into a distillation set under nitrogen was placed tri-n-butyl phosphine oxide (21.8 g., 0.1 moles) and phosphorus pentachloride (25 g., 25% excess of 0.1 moles). An immediate reaction occurred with vigorous effervescence and a red liquid remained, which was heated to 190-200° without resulting in any further visible reaction but a liquid b.p. 80° distilled over. The flask was cooled slightly and the pressure was reduced. A volatile liquid condensed in the traps. The temperature was raised and the pressure lowered and a fraction came over at 150°/10 mm. which continued to 160°/10 mm. and this gave way to a liquid at 164-170°/7.5 mm. which tended to solidify. This was obviously starting material. No Bu_2PCl fraction, 120-125°/15 mm.[23,24] was detected.

Yield 15 g. (i.e. almost all the initial oxide has been recovered).

The reaction was repeated on the same scale using a 50% excess of phosphorus pentachloride. No fraction apart from the low boiling one at 80-100°/760 mm. and one at 180°/7 mm. was obtained.

Conclusion

This general method of preparing dialkylchlorophosphines is not applicable in this case. A reaction is taking place as is indicated by the appearance of the low boiling fraction at 80-100°/760 mm. This consists of n-butyl chloride, b.p. 78°/760 mm. and phosphorus oxychloride, b.p. 105°/760 mm.

iv. Tri-n-butylphosphine

$$\underline{n}\text{-BuBr} + Mg \longrightarrow \underline{n}\text{-BuMgBr}$$

$$PBr_3 + 3\underline{n}\text{-BuMgBr} \longrightarrow \underline{n}\text{-}Bu_3P + 3MgBr_2$$

This was prepared by a procedure identical to the one described for triethylphosphine.

v. 1,2-Bis(diphenylphosphino)ethane

$$Ph_2PH + K \longrightarrow Ph_2PK + \tfrac{1}{2}H_2$$

$$2Ph_2PK + C_2H_4Cl_2 \longrightarrow Ph_2PCH_2CH_2PPh_2 + 2KCl$$

Diphenylphosphine (20 mls. 21.4 g., 0.115 moles) was added to about 350 mls. of ethylene glycol dimethyl ether in a 500 ml. three-necked flask. Potassium wire (5.0 g., theoretical 4.5 g.) was added and the flask attached to a

gas bubbler. An orange colour developed at once, and gas evolution practically ceased after 1½ hours. The reaction mixture became slightly warm but cooled again as the rate of gas evolution diminished.

The red solution of the potassium salt was decanted from a small amount of excess potassium, into a 1000 ml. three-necked flask fitted with a stirrer and well flushed with nitrogen. The solution was cooled in an acetone - CO_2 bath, and the salt crystallized when the temperature fell to about -40°. When the temperature of the solution was -60°, ethylene dichloride (5 mls., theoretical 4.55 mls.) in ethylene glycol dimethyl ether (100 mls.) was slowly added from a dropping funnel whose end reached beneath the surface of the reaction mixture. The reaction mixture was allowed to warm up and gradually became a pale cream colour. It was, after three hours stirring, poured into cold water (1 litre) with stirring. The precipitate was separated, washed with water, and recrystallized from a mixture of ethanol (50 mls.), benzene (50 mls.) and isopropanol (10 mls.).

The filtered aqueous phase was extracted with two lots (30 mls. each) of chloroform, the chloroform extracts being combined with the mother-liquor from the crystallization, concentrated by evaporation under reduced pressure

and allowed to crystallize.

Yield 5 g., m.p. 142-143°, 66%.

The product was recrystallized from n-propanol (about 120 mls.).

b. Arsines

i. Dimethyliodoarsine (Cacodyliodide)[25]

A solution in water (4 litres) of cacodylic acid (544 g., 3.94 moles), potassium iodide (1125 g., 6.77 moles) and concentrated sulphuric acid (205 mls.) was saturated with SO_2. The iodide, which collected as an oily layer at the bottom of the beaker (5 litre) was separated off from the aqueous phase, washed with a little water, dried over magnesi sulphate and distilled. B.p. 154-157°.

Yield 580 g., 63%.

ii. o-Bromophenyldimethylarsine

I. o-Bromophenylarsonic acid

1. From o-bromoaniline[26]

$$o\text{-}BrC_6H_4NH_2 + HNO_2 + HCl \longrightarrow o\text{-}BrC_6H_4N_2Cl + 2H_2O$$

$$o\text{-}BrC_6H_4N_2Cl + Na_3AsO_3 \longrightarrow o\text{-}BrC_6H_4AsO_3Na_2 + N_2 + NaC$$

o-Bromoaniline (200 g., 1.16 moles) was added to a mixture of water (700 mls.) and concentrated hydrochloric acid (250 mls.) and the resulting suspension of amine hydrochloride heated until it dissolved. The solution was

then cooled rapidly, and, keeping the temperature below 7^{o}, it was diazotized by the slow addition, with good stirring, of a solution of sodium nitrite (82 g.) in water (250 mls.). Care was taken to prevent the sodium nitrite solution from running down the side of the reaction vessel; it was made to drop directly into the reaction mixture. Diazotization was continued until starch-iodide paper showed an immediate blue colour.

Anhydrous sodium carbonate (650 g.) was dissolved in hot water (2.0 litres), and technical arsenious oxide (400 g., 4.05 g. atom As) was stirred with the soda solution until dissolved. The oxide went into solution very slowly and the temperature was kept at about 70^{o}. The resulting solution was filtered into a 2-gallon polythene bucket fitted with a stainless steel paddle stirrer and a thermometer, and was cooled below 10^{o} by an ice bath. Immediately before addition of the diazo solution, a solution of cupric chloride (12 g.) in water (50 mls.) to which concentrated ammonia had been added until the precipitate just dissolved, was added to the arsenite solution.

With continuous stirring the diazo solution was slowly run into the arsenite solution; excessive foaming being controlled by the occasional addition of a few mls. of

benzene. When addition was complete the reaction mixture was stirred for one hour and then allowed to stand overnight.

On the next day, charcoal and super-cel were added to the reaction mixture which was then filtered through super-cel in a Büchner funnel. The filtrate (volume about 5 litres) was warmed to 60-70°, more charcoal was added, and it was again filtered. The clear light coloured filtrate was transferred to an evaporating basin on a water bath, and, with good stirring, glacial acetic acid (100 mls.) was cautiously added, producing evolution of CO_2, followed by concentrated hydrochloric acid (300 mls.). The pH was now between 8 and 9. The solution was then evaporated, by heating in a 5 litre three-necked flask under reduced pressure with an air leak into the liquid, to about 1.5 litres. Solid had by this time begun to precipitate and further addition of concentrated hydrochloric acid to pH 4 gave a heavy precipitate of arsenious oxide (solution acid to bromocresol green). Charcoal was added and the suspension was allowed to cool. The precipitate was filtered off and the straw coloured filtrate was heated to 60-70° and acidified to Congo red. The suspension of arsonic acid was allowed to cool and was then collected on a No.3 sintered disc, washed with water and dissolved in

sodium bicarbonate solution. This leaves behind any arsenious oxide, which was filtered off. The filtrate was heated to 60-70°, acidified to Congo red and the suspension of arsonic acid allowed to cool overnight after which the acid was collected on a No.3 sintered disc, washed with water and dried at 110°. A white, finely crystalline powder was obtained.

Yield 102 g., 0.36 moles, 31%.

2. From o-aminophenylarsonic acid[27]

o-Aminophenylarsonic acid (196 g., 0.905 moles) was dissolved in concentrated hydrochloric acid (275 mls.) and water (275 mls.) and the solution was cooled to below 5°. It was then diazotized by the slow addition, with good stirring, of a solution of sodium nitrite (65.4 g.) in water (150 mls.). The temperature was kept below 5° (thermometer actually in the liquid) and was at 1-2° for most of the diazotization.

Cuprous bromide, made by reducing a solution of $CuSO_4$, $5H_2O$(186 g.) in water (500 mls.) and KBr (98 g.) in water (230 mls.), with SO_2 collecting on a filter and washing with water, was dissolved in hydrobromic acid (300 mls. of a 48% solution) and to this solution, cooled

slightly initially, was added the diazo, solution, slowly and with good stirring (stainless steel paddle). After stirring for one hour after addition of the diazo solution, the precipitated acid was collected on a filter, washed with water and dissolved in sodium bicarbonate, filtered and the filtrate warmed to 60-70°. Acidification to Congo red by addition of concentrated hydrochloric acid gave a precipitate of the arsonic acid which was allowed to cool, collected on a filter, washed with water and dried at 110°.

Yield 97 g., 0.345 moles, 35%.

Total amount of o-bromophenylarsonic acid was 199 g., 0.708 moles.

II o-Bromophenyldichloroarsine[28]

$$o\text{-}BrC_6H_4AsO_3H_2 + SO_2 + 2HCl \longrightarrow o\text{-}BrC_6H_4AsCl_2 + H_2SO_4 + H_2O$$

o-Bromophenylarsonic acid (199 g., 0.708 moles) was suspended in concentrated hydrochloric acid (1.70 litres) and a concentrated solution in water of potassium iodide (1.5 g.) was added. The suspension was then saturated with SO_2 and after two hours, by which time a thick curdy precipitate had appeared, the reaction mixture was heated on a water bath. The precipitate then turned into a light brown oil. After decanting off the liquid the oil was solidified by

cooling and washed with a little water after which it was again melted and transferred to a 500 ml. flask containing glass wool. Distillation gave a purple liquid (from which settled out yellow crystals). B.p. 110-125°/0.5 mm.

Yield 177 g., 0.589 moles, 83%.

On dissolving this solid in ether in a subsequent reaction 17.7 g did not dissolve but remained behind as a white unidentified crystalline solid.

Actual Yield 159.3 g., 0.528 moles, 75%.

III. o-Bromophenyldimethylarsine[28]

$$o\text{-}BrC_6H_4AsCl_2 + 2CH_3MgI \longrightarrow o\text{-}BrC_6H_4AsMe_2 + MgCl_2 + MgI_2$$

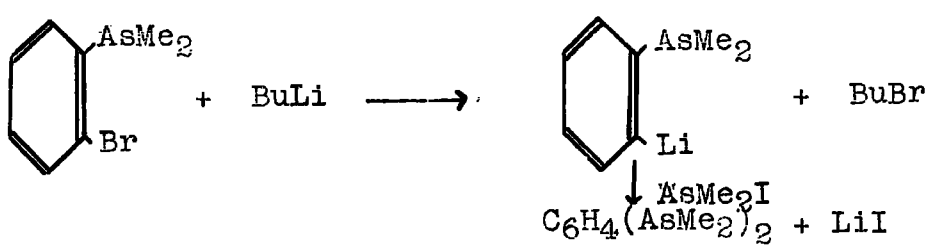
Methylmagnesium iodide (1.46 moles) was made from magnesium (1.50 moles) and methyl iodide (1.46 moles, 208 g., 92 mls.) in ether (800 mls.) in a 5 litre flask. The solution was refluxed (30 minutes) after addition of the methyl iodide (in 250 mls. ether).

The solution was then cooled (-8° external) in an ice-salt bath and, slowly with good stirring, the solution in ether (800 mls.) of o-bromophenyldichloroarsine (159.3 g., 0.528 moles) was added (180 minutes). After addition of the dichloroarsine the flask was allowed to attain room temperature and the reaction mixture was refluxed (15 minutes), after which time it was hydrolysed with a solution of ammonium chloride (200 g.) in water (1 litre). The ether phase was

then clear and almost colourless and the aqueous phase was colourless with a little white solid present. The two phases were decanted under nitrogen into a 5 litre, nitrogen purged separating funnel, through a glass wool filter. The phases were separated and the ether layer dried over magnesium sulphate and decanted into a 2 litre flask which had been flushed with nitrogen. Ether was distilled off through a wide, helices-packed column, a little distillate being allowed to run down the column to provide some reflux, and the concentrated solution was transferred under nitrogen to a 500 ml. three-necked flask containing glass wool, and ether was boiled off at atmospheric pressure. Fractionation gave a clear colourless liquid. B.p. 84-94°/1.5 mm.

Yield 119 g., 0.456 moles, 86.5% (Based on o-bromophenylarsonic acid).

iii. o-Phenylenebis(dimethylarsine)[28]



n-Butyl-lithium (0.41 moles) in pentane (258 ml.) was placed in a litre three-necked flask. o-Bromophenyl-

dimethylarsine (102 g., 0.39 moles) in ether (200 mls.) was added (70 minutes) and the mixture was boiled for one hour. After cooling in an ice bath, iododimethylarsine (0.39 moles, 90.5 g.) in ether (100 mls.) was added (30 minutes). The mixture was refluxed (30 minutes).

After cooling in a water bath, water (200 mls.) was added and phases were separated. More water (100 mls.) was added and two clear (aqueous colourless; organic light yellow) phases were obtained.

The ether and pentane were distilled off, and the resulting liquid was pumped at 12 mm. to remove n-butyl bromide.

A fractionation was carried out and a fraction b.p. 142-150°/12-13 mm was collected.

Yield 73 g., 66%.

iv. o-Diethylphosphinephenyldimethylarsine[28]

$$o\text{-}BrC_6H_4AsMe_2 + n\text{-}BuLi \longrightarrow o\text{-}LiC_6H_4AsMe_2 + BuBr$$

$$o\text{-}LiC_6H_4AsMe_2 + Et_2PCl \longrightarrow o\text{-}Et_2PC_6H_4AsMe_2 + LiCl$$

n-Butyl-lithium (0.33 moles) in pentane (311 mls.) was placed in a 2 litre nitrogen purged three-necked flask and o-bromophenyldimethylarsine (86 g., 0.33 moles)

in ether (140 mls.) was added slowly (one hour) with good stirring. A colour test was negative and more n-butyl-lithium (0.005 moles) was added. The solution was then stirred (one hour) at room temperature.

After cooling in an ice bath a solution of diethylchlorophosphine (41.3 g., 0.33 moles) in ether (100 mls.) was added slowly with good stirring. The colour of the solution before addition of the phosphine was yellow and this colour lightened and intensified during addition of the phosphine. The reaction mixture was refluxed (15 minutes) and hydrolysed with water (200 mls.) and after transferring the two phases to a separating funnel under nitrogen, they were separated. The ether phase was dried ($MgSO_4$), the aqueous phase extracted with ether, and the ether phases were combined and concentrated. The concentrated solution was transferred to a 250 ml. flask containing glass wool and the liquid was fractionated using a vacuum jacketed column. A fraction 90-120°/0.5-0.6 mm. was collected, and the liquid boiling at 30-90°/0.6 mm. was refractionated.

Yield 41 g., 0.152 moles, 46%.

c. Sulphides

i. 1,2-Di(methylthio)ethane

$$CH_3OH + Na \longrightarrow CH_3ONa + \tfrac{1}{2}H_2$$

$$CH_3ONa + CH_3SH \longrightarrow CH_3SNa + CH_3OH$$

$$2CH_3SNa + C_2H_4Br_2 \longrightarrow CH_3SCH_2CH_2SCH_3 + 2NaBr$$

Sodium methoxide was made by adding sodium (24.0 g., 1.04 mole) to methanol (430 mls.) in a litre three-necked flask, which was cooled under a tap during addition of the sodium. After addition of the sodium, a dropping funnel, condenser and stirrer were fitted and in an atmosphere of nitrogen, the flask was cooled in an ice/salt bath. Methane thiol (50 g., 1.04 moles) in methanol (30 mls.) was then added from the dropping funnel with good stirring.

After addition of the thiol, ethylene dibromide (45.0 mls., 0.52 moles) in methanol (30 mls.) was added and on warming precipitation of sodium bromide was complete.

The methanol was distilled off while the contents of the flask were stirred vigorously, and the remainder of the reaction mixture was mixed with water (350 mls.) and 40-60° petroleum ether (100 mls.). Two layers formed and the aqueous phase was discarded. The product was distilled and a fraction b.p. 181-183° was collected.

Yield 47.9 g., 0.392 moles, 76%.

ii. 1,2-Di(ethylthio)ethane

This was prepared by a procedure identical to that described for the methyl analogue.

5. Metal halides

a. Nickel bromide[29]

To a hydrobromic acid solution (128 g., 0.4 moles, 48% w/w), nickel carbonate was added (47.2 g., 0.4 moles). The resulting solution was filtered and an excess of ammonia was added. This precipitated $NiBr_2 \cdot 6NH_3$ as a light blue powder, which was then heated in a furnace at 150-200° and the ammonia was pumped off at 0.05 mm. The yellow-brown nickel bromide was obtained after several hours heating.

Yield 70 g., 80%.

b. Potassium chloroplatinite[30]

This was obtained in two ways, each requiring the preparation of potassium hexachloroplatinate, K_2PtCl_6.

a. Platinum residues

The residues were evaporated to near dryness with aqua regia several times and then the nitric acid was boiled off and the solution filtered. Addition of potassium chloride to a slightly diluted solution produced precipitation of

K_2PtCl_6 which was collected on a filter, washed, dried, and weighed.

b. Platinous chloride

Platinous chloride (2.43 g) was placed in a beaker, aqua regia was added, and the mixture was warmed. The solid went into solution as hexachloroplatinic acid, H_2PtCl_6, and after boiling off nitric oxide and diluting to 50 mls, potassium chloride (1.6 g.) was added to precipitate the potassium salt.

Yield 4.3 g., 86%.

The hexachloride (11.1 g., 0.023 moles) was placed in a 100 ml. beaker and water (70 mls.) was added. Reduction to the tetrachloride was carried out using SO_2. 0.6 ml. portions of a saturated solution of SO_2 in water were added to the beaker, which was maintained at 80°, at intervals of 2-3 minutes. The odour of SO_2 was allowed to disappear before the next addition. This produced a deep red solution of potassium chloroplatinite (0.023 moles).

c. Palladium dibromide

This was prepared from palladium residues.

The residues were evaporated to near dryness and concentrated hydrochloric and nitric acids were added and the mixture was twice taken to dryness. Hydrochloric acid

was added while nitric oxide was boiled off and Palladium (II) chloride was thus obtained in dark red solution. Sodium carbonate was added to the filtered solution until the solution was faintly acidic. Sodium formate was added and the solution was warmed on a water bath until CO_2 ceased to be evolved. The now black suspension was cooled, filtered, washed, dried and ignited at 550°. The ignited metal was weighed, placed in a beaker and an equivalent of hydrobromic acid solution was added and sufficient nitric acid to cause solution of the palladium as $PdBr_2$.

d. Sodium chloropalladite

This was supplied by Johnson, Matthey and Co. Ltd., London and was dissolved in water and filtered before use.

6. Co-ordinated metal halides

a. Nickel

i. Bis(triethylphosphine)dibromonickel[31]

$$NiBr_2 + 2Et_3P \longrightarrow (Et_3P)_2NiBr_2$$

To an ice cold solution of anhydrous nickel bromide (11 g., 0.05 moles) in ethanol (60 mls.), triethylphosphine (11.8 g., 14.7 ml. 0.1 moles) was added with stirring. The dark red-blue crystals precipitated were filtered, washed

with a little cold ethanol, and dried by pumping at 0.05 m.m.

Yield 16.5 g., 70%. m.p. 106-107°.

b. Platinum

i. Cis- and trans- bis(triethylphosphine)-dichloroplatinum[32]

To the solution of potassium chloroplatinite (0.023 moles) obtained from platinum residues and platinous chloride in a 250 ml. flask under nitrogen, triethylphosphine (0.046 moles, 6.8 mls.) was added with stirring. After prolonged standing, precipitation of crude $(Et_3P)_2PtCl_2$ was complete.

Yield 8.7 g., 75%.

A further quantity of dichloride (8.5 g., 89%) was obtained from sodium chloroplatinite and triethylphosphine under similar conditions.

Separation of the isomers was effected owing to the fact that the cis- isomer is completely insoluble in light petroleum (40-60°)[33]

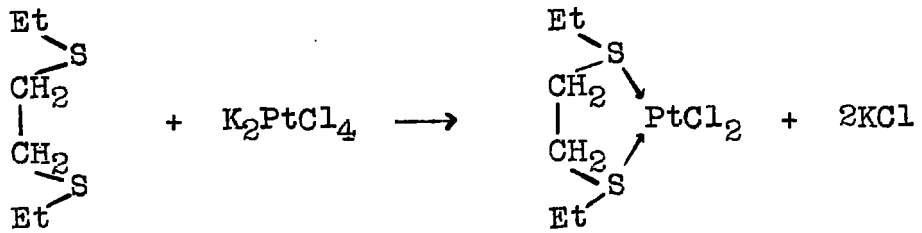
The crude product (17.2 g.) was placed on a sintered disc of an extraction apparatus with light petroleum in the pot. By refluxing the petroleum through the disc, the trans-isomer was extracted. This gave a yellow solution of the trans-isomer in the pot and left the white cis-compound

on the disc.

The sintered disc contained cis-$(Et_3P)_2PtCl_2$ (7.3 g.) and on evaporating the petroleum solution, trans-$(Et_3P)_2PtCl_2$ (8.9 g.) was obtained.

Both isomers were recrystallized from alcohol m.p. cis 192-193°; trans 142-143°.

ii. 1,2-Di(ethylthio)ethanedichloroplatinum[34]



Hexachloroplatinic acid, $H_2PtCl_6,6H_2O$ (15 g., 0.029 moles was dissolved in water (140 mls.) and with stirring, potassium chloride (4.8 g.) in water (45 ml.) was added. K_2PtCl_6 was precipitated and the solution was diluted with an equal volume of alcohol and was allowed to stand (25 minutes). Reduction was carried out to the tetrachloride using SO_2 as described previously. The red solution of the tetrachloride was filtered under gravity into a 250 ml. flask, the total water volume being about 100 mls. The flask was heated under reflux to 100°

on an isomantle and 1,2-di(ethylthio)ethane, $C_2H_4(EtS)_2$, (4.4 g., 0.029 moles) was added slowly with good stirring. When addition was complete, heating was stopped but stirring was continued to room temperature. When cool, the precipitate was filtered, dried at 110° extracted and recrystallized from acetone.

Yield 10 g., 83%, m.p. 186-187°.

c. Palladium

1. With phosphines

i. Bis(triethylphosphine)dichloropalladium[35]

$$Na_2PdCl_4 + 2Et_3P \longrightarrow (Et_3P)_2PdCl_2 + 2NaCl$$

To a solution of sodium chloropalladite, $Na_2PdCl_4,3H_2O$ (17.42 g., 0.05 moles) in water (500 mls.) triethylphosphine (11.8 g., 0.1 moles) was added from a dropping funnel with stirring. The yellow precipitate which formed was collected on a filter and a dilute solution of the chloride was added to the filtrate which produced a further precipitate.

Precipitates were combined and recrystallized from alcohol; a little ligand being added.

Yield 16.5 g., 80% m.p. 139°.

ii. Bis(triethylphosphine)dibromopalladium

a. The solution of palladium bromide ($PdBr_2$) obtained from palladium residues was filtered into a 500 ml. flask

under nitrogen and with stirring triethylphosphine (2 mols.) was added in a small amount of alcohol. A yellow precipitate immediately formed and the solid was collected on a filter, washed with water and dried. Recrystallized from alcohol m.p. 134-135°.

Yield Almost quantitative.

b. From sodium chloropalladite as described for the dichloride but in presence of a slight excess of Br'(sodium bromide). The darker yellow coloured product was recrystallized from acetone containing lithium bromide to ensure complete conversion to the dibromide.

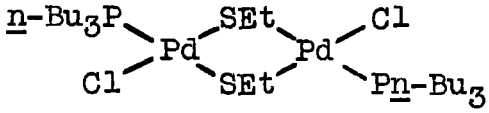
iii. Bis(triphenylphosphine)dichloropalladium[36]

$$Na_2PdCl_4 3H_2O + 2Ph_3P \longrightarrow (Ph_3P)_2PdCl_2 + 2NaCl + 3H_2O$$

To the chloride (34.8 g., 0.1 mole) in water (200 mls.) in a 500 ml. three-necked flask was added, with good stirring, a solution in ethanol and ether of triphenylphosphine (52.5 g., 0.2 mole). A yellow precipitate formed immediately and when addition was complete the precipitate was separated by filtration and washed with water and ethanol. A small amount was recrystallized from toluene, m.p. 260°.

Yield Almost quantitative.

iv. Bis(tri-n-butylphosphine)-$\mu\mu'$-bis(ethanethio)-dichlorodipalladium,



$$2.5\,n\text{-}Bu_3P + Na_2PdCl_4 3H_2O \longrightarrow \underset{I}{(n\text{-}Bu_3P)_2PdCl_2} + 2NaCl + 3H_2O$$

$$(n\text{-}Bu_3P)_2PdCl_2 + Na_2PdCl_4 3H_2O \longrightarrow \underset{II}{(n\text{-}Bu_3P)ClPdCl_2PdCl(Pn\text{-}Bu_3)} + 2NaCl + 3H_2O$$

$$(n\text{-}Bu_3P)_2Pd_2Cl_4 + 2EtSH \longrightarrow \underset{III}{(n\text{-}Bu_3P)ClPd(EtS)_2PdCl(Pn\text{-}Bu_3)} + 2HCl$$

a. Bis(tri-n-butylphosphine)dichloropalladium (I) was prepared as described for the triethylphosphine derivative.[35] Yield 86.3 g., almost quantitative, m.p. 66°.

b. The bulk of material was not recrystallized but was used immediately for the preparation of dichlorobis(tri-n-butylphosphine)-$\mu\mu'$dichlorodipalladium (II)[37].

A solution of sodium chloropalladite (51.6 g., 0.15 moles) in water (100 mls.) was diluted with alcohol (75 mls.) and then added to a solution of bis(tri-n-butylphosphine)dichloropalladium (86.3 g., 0.148 moles) in alcohol (140 mls.). The mixture was boiled under reflux for one hour and a trace of palladium was removed by filtration. On cooling the tetrachloride (II) crystallized out; was separated by filtration, washed with water and recrystallized from alcohol,

m.p. 143°.

Yield 86.6 g., 76%, m.p. 145° [37].

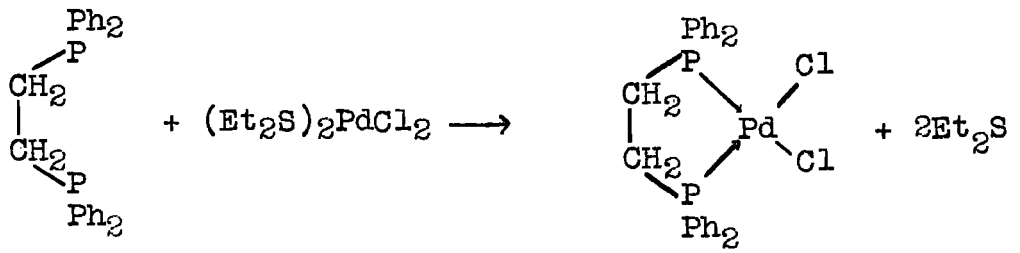
c. Bis(tri-n-butylphosphine)-μμ'-bis(ethanethio)-dichlorodipalladium (III) was prepared by a method similar to that used by Chatt and Mann.[38]

Ethanethiol (21.2 g., 25.3 mls., 0.342 moles) was dissolved in alcohol (750 mls.) in a 2-litre flask and a concentrated solution of the tetrachloride (II) (86.6 g., 0.114 moles) in benzene was added. The intense red colour of the benzene solution immediately disappeared in the ethanolic solution and a yellow colour appeared. After addition of all the benzene solution the reaction mixture was stirred for a further 30 minutes and after this time solvents were pumped off and a yellow solid which was precipitated was collected on a filter and recrystallized from alcohol.

Yield 77 g., 0.095 moles., 83%, m.p. 111-112°

Chatt and Mann[38] report 115-116°.

v. 1,2-Bis(diphenylphosphino)ethane



1,2-Bis(diphenylphosphino)ethane (13 g.) in chloroform (100 mls.) and bis(diethylsulphide)dichloropalladium (1 mol.) in chloroform (100 mls.) were slowly added at about equivalent rates to chloroform (50 mls.) which was stirred.

The precipitate which formed was collected, washed with chloroform and dried.

Yield 18.6 g., 97%, decomposition above 330°, without melting.

2. With arsines

i. Dibromo-ortho-phenylenebisdimethylarsine-palladium[39]

Sodium chloropalladite (54.8 g., 0.1 mole) was dissolved in water (150 mls.) and filtered. Hydrobromic acid (10 mls. of 48% w/w; 10% excess of 0.1 mole) was added. This solution was added to a solution of o-phenylene bis-dimethylarsine (28.6 g., 0.1 mole, 20.6 mls.) in ethanol (40 mls.). To the brown precipitate which formed was added a mixture of ethanol (40 mls.) and hydrobromic acid solution (20 mls.) and the flask was heated to boiling under reflux (90 minutes).

The resulting mixture was filtered and the orange compound was washed with water and alcohol and pumped dry. The aqueous washings and filtrate were combined and

concentrated.

Yield 44 g., 80%, m.p. 310-312° decomposition.

ii. Dibromo-o-diethylphosphinephenyldimethylarsine-palladium[39]

The phosphine-arsine (14.1 g., 0.052 moles) in hot ethanol (10 mls.) was mixed with a solution of sodium chloropalladite (18.2 g., 0.052 moles) in water (minimum amount) to which sodium bromide (20.6 g., 0.02 moles) had been added. This produced a dark red-brown solid which was then heated under reflux with a mixture of hydrobromic acid (82 g., 48% w/w solution) and ethanol (40 mls.) for seven hours. More hydrobromic acid solution (10 mls.) and alcohol (10 mls.) were added during refluxing. After that time the yellow solid was collected on a filter, washed with water and recrystallized from alcohol.

Yield Greater than 17.6 g., 0.0328moles, 63%, m.p. 308° decomposition.

3. With sulphides

$$C_2H_4(RS)_2 + Na_2PdCl_4 \longrightarrow C_2H_4(RS)_2PdCl_2 + 2NaCl$$

R = Me or Et.

i. 1,2-Di(methylthio)ethanedichloropalladium[40]

To a solution of sodium chloropalladite (34.8 g., 0.1 mole) in water (200 mls.) was added 1,2-di(methylthio)-ethane (12.2 g., 0.1 mole) in methanol (40 mls.) with good stirring. The yellow precipitate which formed immediately was collected on a filter, washed with water and recrystallized from water.

Yield Almost quantitative, m.p. 234-5°.

ii. 1,2-Di(ethylthio)ethanedichloropalladium[41]

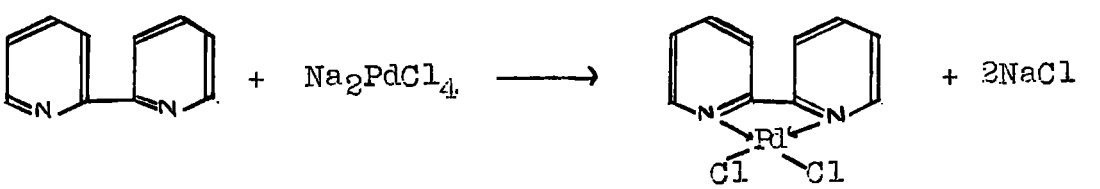
To a 10% solution of sodium chloropalladite (17.4 g., 0.05 moles) in water was added, with stirring, 1,2-di-(ethylthio)ethane (7.5 g., 0.05 moles). The orange-yellow precipitate which formed immediately was collected and washed with water.

The filtrate was concentrated and a second crop of crystals obtained. Precipitates were combined and recrystallized from alcohol.

Yield 13.2 g., 81%, m.p. 180-182°.

4. With nitrogen-containing donors

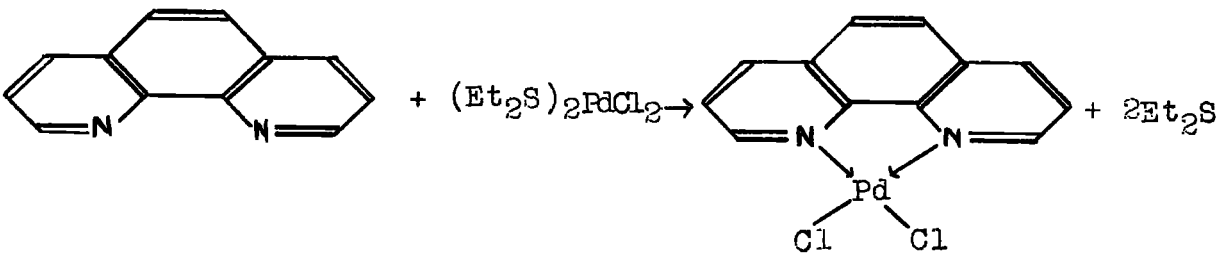
i. Dipyridyldichloropalladium[42]



To a solution of sodium chloropalladite (5 g., 0.014 moles) in water (60 mls.), α,α'dipyridyl (2.03 g., 0.014 moles) in alcohol (20 mls.) was added (15 minutes) dropwise from a dropping funnel with stirring. The orange-yellow precipitate which formed was collected on a filter, washed with water, alcohol and acetone, and dried at 85°.

Yield 4.2 g., 90%, m.p. above 300°.

ii. Phenanthrolinedichloropalladium



Solutions of phenantholine monohydrate (5.0 g., 0.25 moles) and bis(diethylsulphide)dichloropalladium (9.0 g., 0.025 moles) in chloroform (200 mls.) were run at equivalent rates into a beaker containing chloroform (200 mls.) which was stirred. The intense colour of the thio-palladium compound quickly disappeared and a salmon coloured precipitate formed. The precipitated material was collected, washed several times with chloroform and dried at 12 mm.

Yield 8.7 g., 97%, m.p. above 330°

5. With dienes

i. Cyclo-Octa-1,5-dienedichloropalladium[43]

$$C_8H_{12} + Na_2PdCl_4 \longrightarrow C_8H_{12}PdCl_2 + 2NaCl$$

Sodium chloropalladite (30 g., 0.087 mole) in water (100 mls.) was, after filtration, added with stirring to methanol (1 litre) to which cyclo-octa-1,5-diene (25 mls.) in methanol (75 mls.) was added at about the same rate. The colour changed to yellow rapidly and a yellow precipitate appeared very quickly.

The reaction mixture was allowed to stand about one hour, the precipitate collected, washed with methanol then with a mixture of benzene-light petroleum. It was dried at 120°.

Yield 26 g. Decomposed without melting at about 225°.

d. Gold

i. Triethylphosphinemonochlorogold[44]

$$H_2O + HAuCl_4 + 2Et_3P \longrightarrow Et_3PAuCl + 3HCl + Et_3PO$$

Brown gold chloride (57.7 g., 0.15 moles) was dissolved in water (150 mls.) and ethanol (150 mls.) was added. To this solution cooled in an ice-salt bath, under nitrogen was added triethylphosphine (43.5 mls., 0.3 moles) in ethanol (300 mls.) dropwise with stirring.

When all the triethylphosphine had been added the ice

bath was removed and the mixture stirred for a further 30 minutes. The mixture was at first very bright yellow but after about 15 minutes this yellow colour slowly disappeared and a faint dirty brown colour remained. Addition of hydrazine (1 ml. in 25 ml. water) did not affect this colour.

The ice bath was then replaced and water (750 mls.) was added slowly. The solution became pale yellow in colour and greyish white crystals of triethylphosphinemonochlorogold were precipitated.

The precipitate was collected, washed with water and dried.

Crude yield 44 g.

On allowing the solution to stand overnight a further 13 g. of monochloride were obtained and after two days still more material was precipitated.

Yield 53 g., 100%.

2. Analysis for Metals.

1. Nickel[45]

Bis(triethylphosphine)di(phenylethynyl)nickel, $(Et_3P)_2Ni(C{\equiv}C\text{-}Ph)_2$, (0.1 g.) was decomposed with concentrated and then fuming nitric acid and the solution boiled. Concentrated hydrochloric acid was added and nitric oxide removed by boiling. The solution was diluted to 60 mls. with water, filtered, neutralized with ammonium hydroxide and a little sodium acetate was added. 15 mls. of a 1% solution of dimethylglyoxime in 95% alcohol were added to the hot solution and after it had stood for one hour the red precipitate was collected and dried to constant weight.

Found: Ni, 11.6%.

$C_{28}H_{40}P_2Ni$ requires Ni, 11.8%.

2. Platinum[46]

Platinum, in for example bis(triethylphosphine)dichloroplatinum, $(Et_3P)_2PtCl_2$, was estimated as metal.

The dichloride (0.25 g.) was weighed accurately into a 10 ml. beaker and concentrated nitric acid (2 ml.), followed by a little fuming nitric acid was added. The solution was boiled and became clear. Concentrated hydrochloric acid was added and nitric oxide was boiled off. After it had been diluted to about 150 mls. in a 500 ml. round bottomed flask the solution was neutralized with

ammonia and ammonium acetate (10 mls.) was added. Formic acid (10 ml.) was added and the solution was warmed to 80° on a water bath. Platinum was precipitated and boiling was continued for six hours. The metal was collected on a No.40 filter paper which was dried at 100° and ignited in a weighed silica crucible.

Found: Pt, 38.6%.

$C_{12}H_{30}Cl_2PtP_2$ requires Pt, 38.8%.

3. Palladium[47]

Palladium was estimated as its dimethylglyoxime derivative $(C_4H_7O_2N_2)_2Pd$. Bis(triethylphosphine)dichloropalladium $(Et_3P)_2PdCl_2$, was used in developing the method.

The dichloride (about 0.1 g.) was weighed accurately and transferred into a 10 ml. beaker which was covered with a watch glass. A few drops of nitric acid were added and the beaker was warmed. More nitric acid was added and a clear solution was obtained on boiling. Hydrochloric acid was added dropwise to cause solution of the palladium as chloride and nitric oxide was boiled off. When a clear, brown solution was obtained the contents of the beaker were diluted and transferred to a 400 ml. beaker with 200 ml. water (any residue at this stage was filtered off onto a glass sinter, treated with fuming nitric acid and

aqua regia, and finally washed with water). The solution was neutralized with solid Na_2CO_3 (care) and acidified to 0.2N acid with HCl. A 1% solution of dimethylglyoxime in 95% ethanol was added, 0.25 ml. for every 1 mg. of palladium present. After it had stood for one hour the yellow precipitate was collected in a No.3 sintered crucible, washed well with hot water and dried at 110° to constant weight.

Found: Pd, 25.5%

$C_{12}H_{30}P_2PdCl_2$ requires Pd, 25.8%.

4. Copper

The copper in $Et_3P \longrightarrow CuC{\equiv}CPh$ was determined in solution by the standard thiosulphate technique.

A weighed sample (0.4-0.5 g.) was placed in a beaker, decomposed with nitric acid, and the beaker was warmed after the initial decomposition. When the decomposition was complete the contents of the beaker were transferred into a 250 ml. conical flask. The pH was adjusted to neutral with caustic soda and 7 mls. of 6N acetic acid were added followed by 3 g. of analar potassium iodide. The liberated iodine was titrated against standard thiosulphate.

$$Cu^{++} \equiv I \equiv S_2O_3$$

Found: Cu, 22.2%; 23.0%.

$C_{14}H_{20}PCu$ requires Cu, 22.5%.

5. Gold

This was estimated as metal.

Triethylphosphinemonophenylgold Et_3PAuPh (0.2591 g.) was weighed accurately and placed in a silica crucible, and a silica lid was placed over the top. With a low bunsen flame the crucible was warmed gently for 15 minutes. Signs of decomposition were seen and the heating was gradually increased until after 25 minutes the bunsen was at its maximum temperature and decomposition and evolution of volatile matter was soon complete. A residue of metallic gold remained and the crucible and contents were weighed. Weight of gold remaining was 0.1307 g.

Found: Au, 50.43%.

$C_{12}H_{20}PAu$ requires Au, 50.24%.

3. Preparation of the organometallic compounds.

Contents

Gold

Nickel

1. The preparation of bis(triethylphosphine)di(phenylethynyl)nickel

$$(Et_3P)_2NiBr_2 + 2PhC \equiv CMgBr \longrightarrow (Et_3P)_2Ni\ (C \equiv CPh)_2 + 2MgBr_2$$

The dibromide (20.5 g., 0.045 moles) was placed, with ether (200 mls.) in a nitrogen-purged 500 ml. flask which was cooled (-52°). Phenylethynylmagnesium bromide (0.09 moles) in ether (100 mls.) was added during 30 minutes. The reaction mixture was allowed to attain room temperature and was stirred (60 minutes) at that temperature. The flask was then cooled (0°) and a dilute solution in water (100 mls.) of ammonium chloride was added.

Isolation of the product

The contents of the flask were filtered under nitrogen and the two liquid phases were separated. A yellow-brown solid on the disc was washed with ether (120 mls.) and benzene (3 x 50 mls.).

i. The ether phase

This was dark red in colour and solid matter present was collected on a filter, washed with ether, and washings and filtrate were combined and concentrated.

An orange-yellow compound was separated, washed with n-hexane (4 x 20 mls.), recrystallized from cyclohexane and then alcohol m.p. 138-139° (decomposition).

Analysis Found: C, 66.8%; H, 8.3%.

ii. The benzene phase

The benzene was pumped off at 8 mm. and the orange-yellow needles produced were washed with n-hexane. The solid was recrystallized from cyclohexane. m.p. 132-134° (decomposition).

Analysis Found: C, 66.5%; H, 7.9%; Ni, 11.6%.

$C_{28}H_{40}P_2Ni$ requires C, 67.6%; H, 8.1%; Ni, 11.8%.

Yield 8.5 g. (38%) recrystallized once from cyclohexane.

2. The reaction between $(Et_3P)_2NiBr_2$ and styrylmagnesium bromide

The dibromide (16.0 g., 0.035 moles) was placed with ether (200 mls.) in a 500 ml. flask which was cooled (-60°). Styrylmagnesium bromide (0.075 moles) in ether (100 mls.) was added (60 minutes).

The flask was then allowed to attain room temperature where stirring was continued (30 minutes). The flask was cooled (0°) and water (100 mls.) was added.

Isolation of the product

The contents of the flask were filtered and a solid

remained on the filter but this decomposed to a green coloured material.

The ether phase, after separation and evaporation, gave a light coloured compound which was washed with n-hexane and recrystallized from acetone, m.p. 147-148°.
1 g. 13%, based on the Grignard reagent.

Analysis Found: C, 92.0%; H, 6.8%.
$C_{16}H_{14}$, distyryl, requires C, 93.06%; H, 6.84%. m.p. 147-148°.

Conclusion

It was concluded that any reaction product underwent decomposition during working up processes.

Platinum

1. The preparation of bis(triethylphosphine)diphenylplatinum

$$(Et_3P)_2PtCl_2 + 2PhLi \longrightarrow (Et_3P)_2PtPh_2 + 2LiCl$$

The cis-dichloride (5 g., 0.01 moles) was placed in a 500 ml. flask with ether (150 mls.) and the flask was cooled (-60°). Phenyl-lithium (0.02 moles) in ether (20 mls.) was added (30 minutes) and stirring was continued (15 minutes) at -60°. The flask was then allowed to attain room temperature and a thick white colour developed near room temperature. A colour test at this stage was negative. The flask was cooled (0°) and water (100 mls.) was added after

which the ether phase became clear.

Isolation of the product

The contents of the flask were filtered and the liquid phases were separated. The ether phase was evaporated and a white solid was obtained (3.7 g., 63%) which was twice recrystallized from alcohol as white needles m.p. 148-149° and from acetoneas hexagonal plates m.p. 147-148°,(decomposition

Analysis Found C, 49.3%; H, 7.0% (from alcohol);
C, 49.3%; H, 6.9%; Pt, 32.7% (from acetone).
$C_{24}H_{40}P_2Pd$ requires C, 49.3%; H, 6.8%; Pt, 33.3%.

Structure Measurement of $\Delta\epsilon/f$ (change in dielectric constant with mole fraction) gave a large value, which indicates a cis configuration.

Very recently[48] the geometrical isomers cis- and trans-$(Et_3P)_2PtPh_2$ have been prepared. The m.p. given for the cis compound (154°) compares favourably with the cis compound prepared above (m.p. 148-149°).

2. The preparation of 1,2-di(ethylthio)ethanediphenyl-platinum

$$C_2H_4(EtS)_2PtCl_2 + 2PhLi \longrightarrow C_2H_4(EtS)_2PtPh_2 + 2LiCl$$

The dichloride (8.4 g., 0.02 moles) was placed in a 500 ml. flask with ether (200 mls.) and the flask was cooled (-60°). Phenyl-lithium (0.04 moles) in ether was

added (30 minutes). A colour test was positive but on reaching room temperature was negative. The flask was cooled (0°) and water (100 mls.) was added to the now dense white suspension in the flask.

Isolation of the product

The reaction mixture was filtered, a white solid was obtained and the two liquid phases were separated.

The solid (9.7 g.) was pumped dry and was found to be soluble in acetone, chloroform readily, and alcohol, benzene, ethyl acetate and cyclohexane less so. Recrystallized from cyclohexane, m.p. 124-125°.

Analysis Found: C, 42.9% H, 4.7%; Pt, 38.7%.

$C_{18}H_{24}S_2Pt$ requires C, 43.3%; H, 4.8%; Pt, 39.1%.

Yield 54%.

The ether phase gave a yellow solid, (2.5 g.) m.p. 112-114°, on evaporation. This solid was soluble in the usual organic solvents and was partially purified by recrystallization from alcohol, m.p. 123-124°. It was thus thought to be impure 1,2-di(ethylthio)ethanediphenylplatinum.

Palladium

i. With phosphines as donors

1. Preparation of bis(triethylphosphine)bromo(methyl)-palladium

$(Et_3P)_2PdBr_2 + CH_3MgBr \longrightarrow (Et_3P)_2Pd(CH_3)Br + MgBr_2$

The dibromide (10.0 g., 0.02 moles) was placed in a 500 ml. flask with ether (200 mls.) and the flask was cooled (-65°). Methylmagnesium bromide (0.045 moles) was added (30 minutes) in ether (40 mls.). After stirring (15 minutes) at -65° the flask was allowed to attain room temperature and stirring was continued for 30 minutes. The flask was cooled (0°) and water (100 mls.) was added.

The colour of the contents of the flask turned from yellow to white as the flask warmed up to room temperature.

Isolation of the product

After filtering the reaction mixture and separating the phases, the ether phase was evaporated and a white solid came out (9.5 g.) which was readily soluble in acetone, alcohol, cyclohexane, benzene, ether, n-hexane, and methylcyclohexane. 2 g. of the impure solid were recrystallized by cooling from n-hexane; m.p. 73-74°.

Analysis Found: C, 35.0%; H, 7.4%; Pd, 24.7%; 24.6%.
$C_{13}H_{33}BrP_2Pd$ requires C, 35.6%; H, 7.6%; Pd, 24.4%.

Yield 6.7 g., 78%.

Structure The dipole moment is 4.0 D and the compound isolated is therefore trans-$(Et_3P)_2Pd(CH_3)Br$.

Exchange and replacement reactions of $(Et_3P)_2Pd(CH_3)Br$

1. Iodine

$$(Et_3P)_2Pd(CH_3)Br + I_2 \longrightarrow (Et_3P)_2PdI_2 + CH_3Br$$

The monomethyl compound (0.6194 g., 1.41 mmoles) was dissolved in acetone (5 mls.) and iodine (0.343 g.) in acetone (5 mls.) was added. The solution was allowed to stand for three days after which time the solvent was pumped off and an orange material was isolated, 0.7664 g. m.p. 92-94°. Recrystallized from methanol m.p. 130°; mixed m.p. with authentic $(Et_3P)_2PdI_2$ 128-130°.

2. Potassium cyanide

$$(Et_3P)_2Pd(CH_3)Br + KCN \longrightarrow (Et_3P)_2Pd(CH_3)CN + KBr$$

To a solution of the monomethyl compound (0.6649 g., 1.52mmoles) in methanol (5 mls.) was added a concentrated solution of KCN (0.099 g.) in methanol. On evaporating the solvent it was found difficult to dry the residue completely. Water was added and a white solid precipitated which was filtered off and dried in the air. It crystallized, after prolonged standing, from methanol and water, m.p. 42-44° no decomposition.

Analysis Found: C, 39.5%; H, 8.3%.

$C_{14}H_{33}P_2Pd^N$ requires C, 43.8%; H, 8.65%.

Repeat preparation

About 1 g. of the monomethyl compound was dissolved in methanol and an excess of KCN was added. After sixteen hours the reaction product was precipitated by adding water and standing the beaker containing the suspended, white oily product in ice water. After about one hour and after prolonged scratching the oil solidified and the white solid was separated and recrystallized, after drying, from n-hexane, m.p. 78°, (softening 5° lower).

Analysis Found: C, 43.7%; H, 8.5%.

An infrared spectrum gave good confirmation of the formation of the cyanide (absorption at 2127 $cm.^{-1}$ and 2117 $cm.^{-1}$).

Structure The dipole moment is 4.75 D and the compound therefore trans.

3. Sodium iodide

$$(Et_3P)_2Pd(CH_3)Br + NaI \longrightarrow (Et_3P)_2Pd(CH_3)I + NaBr$$

A concentrated solution in alcohol of sodium iodide (1.7 g.) was added to the monomethyl compound (0.4996 g., 1.14 mmoles) in alcohol (5 mls.). The solution developed an immediate yellow colour and a yellow residue remained on pumping off the solvent. Washing with water and recrystallization from methanol and water gave a solid,

orange in colour as needles m.p. 80-86°.

Analysis Found: C, 29.7%; H, 6.2%.

$C_{13}H_{33}P_2PdI$ requires C, 32.21%; H, 6.86%.

Only partial conversion to the iodide has occurred.

4. Methyl iodide

The monomethyl compound (0.6688 g., 1.53 mmoles) in methanol (5 mls.) and a solution in methanol (1 ml.) of methyl iodide (4 mls.) were mixed together. No change took place and after one hour the solvent was removed and the residue (0.6516 g.) was recrystallized from n-hexane, m.p. 70-71°; mixed m.p. with $(Et_3P)_2Pd(CH_3)Br$, 71-73°.

5. Potassium thiocyanate

$$(Et_3P)_2Pd(CH_3)Br + KSCN \longrightarrow (Et_3P)_2Pd(CH_3)SCN + KBr$$

An immediate white precipitate occurred on adding solid potassium thiocyanate (0.089 g.) to the monomethyl compound (0.400 g.) in alcohol (5 mls.). More alcohol (5 mls.) was added and the suspension was warmed. The ethanol was pumped off and the light yellow solid was dried, washed with water, separated, dried in air and recrystallized from methanol-water as beautifully long colourless needles, m.p. 86-87°.

Analysis Found: C, 40.4%; H, 8.1%.

$C_{14}H_{33}P_2PdSN$ requires C, 40.4%; H, 7.99%.

6. Silver nitrite

$$(Et_3P)_2Pd(CH_3)Br + AgNO_2 \longrightarrow (Et_3P)_2Pd(CH_3)NO_2 + AgBr$$

Silver nitrite, $AgNO_2$, was prepared from $AgNO_3$ and $NaNO_2$ and the precipitated material was washed with water and ethanol and dried. In an agate mortar a small amount of monomethyl compound and the nitrite were ground together. Immediate decomposition took place.

2. The preparation of bis(triethylphosphine)dimethylpalladium

$$(Et_3P)_2PdBr_2 + 2CH_3Li \longrightarrow (Et_3P)_2Pd(CH_3)_2 + 2LiBr$$

The dibromide (10.0 g., 0.02 moles) was placed in a 500 ml. flask and ether (200 mls.) was added with a trace of triethylphosphine and the flask was cooled (-60°). Methyl-lithium (0.045 moles) in ether (38 mls.) was added during 15 minutes after which the flask was allowed to attain room temperature and then stirring was continued for 15 minutes. Colour test for methyl-lithium was negative. After cooling (0°), water (100 mls.) was added.

At -35° the ether phase became colourless and during addition of water the contents of the flask became densely white but this colour disappeared on addition of more water, leaving two clear phases.

Isolation of the product

Separation of the two phases and evaporation of the

ether phase gave a white solid which was soluble in acetone, alcohol (decomposition), and n-hexane. Recrystallization from n-hexane gave a white solid m.p. 47-49°.

Analysis Found: C, 44.6%; H, 9.6%; Pd, 28.0%; 27.9%.

$C_{14}H_{36}P_2Pd$ requires C, 45.1%; H, 9.7%; Pd, 28.6%.

Yield 7.4 g., 90%.

Decomposition and reactions of $(Et_3P)_2Pd(CH_3)_2$

1. Sublimation

The compound was found to sublime in a mercury vapour pump vacuum at 40-50°.

2. Decomposition by heat

A small amount of the compound was sealed off under vacuum and the bulb was placed in a water bath at 100° for 16 hours, after which time the contents of the bulb appeared to be totally decomposed. The bulb was now sealed into the vacuum apparatus and after evacuating the whole system, the bulb was broken. Any gas evolved was allowed to pass through two traps at liquid air temperature before being forced into a gas burette by means of a Töpler pump. A volume of gas (I) was obtained.

The liquid air traps were now replaced by methylene chloride/liquid air traps (-96°) and a further quantity of gas (II) was obtained.

An infrared spectrum of gas (II) was taken and there was very strong absorption at 950 cm^{-1}, characteristic of ethylene.

Analysis by combustion with a known excess of oxygen over a platinum wire showed the gas (II) to have a composition 92% ethane, 8% ethylene.

Results

Wt. of dimethyl compound	=	0.1566 g.
No. mmoles	=	0.4196
Volume of CH_4 equivalent to one methyl group	=	9.4 N-c.c.
Volume of CH_4 equivalent to two methyl groups	=	18.8 N-c.c.
Volume of C_2 gas equivalent to both methyl groups	=	9.4 N-c.c.
Volume of gas (I)	=	0.028 N-c.c.
Volume of gas (II)	=	12.12 N-c.c.

Note: 1 N-c.c. is one c.c. of gas at standard temperature and pressure.

Conclusions.

1. There is little or no methane formed during thermal decomposition.

2. Free radicals are formed during decomposition giving

rise to C_2H_6 and C_2H_4.

3. There is a free radical attack on the triethylphosphine residue as the total amount of C_2 gas obtained is greater than could have been obtained from the two methyl groups.

3. With aqueous ethanolic hydrobromic acid

$$(Et_3P)_2Pd(CH_3)_2 + 2HBr \longrightarrow (Et_3P)_2PdBr_2 + 2CH_4$$

To the dimethyl compound in the reaction vessel (A) was added aqueous-ethanolic hydrobromic acid from the dropping funnel (E) after the acid had been degassed by evacuation through tap (F).

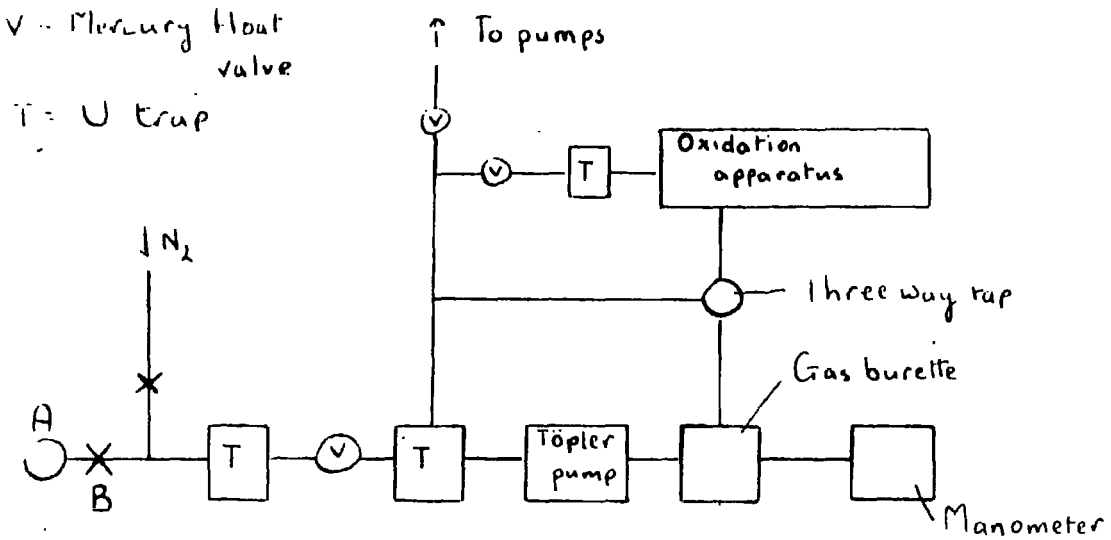
The gaseous product from the rapid reaction was pumped through two traps at liquid air temperature, to remove ethanol and water, and measured (I) in a gas burette.

Results

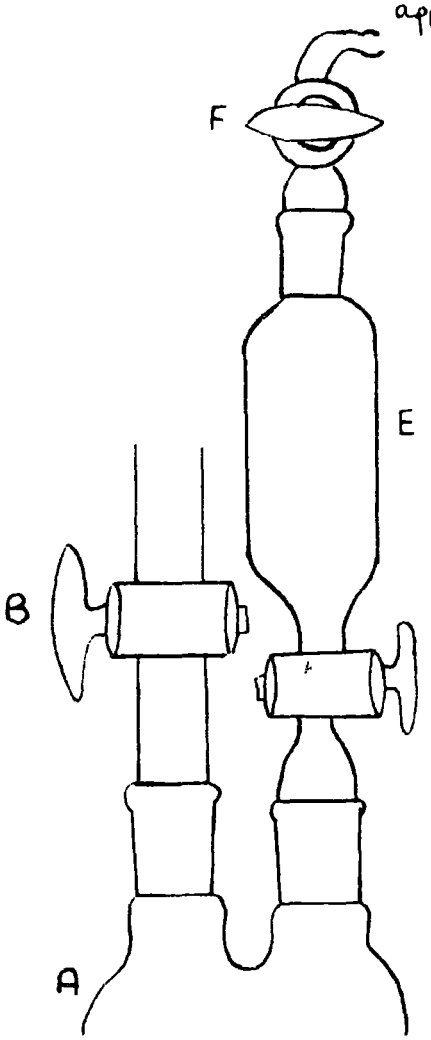
Wt. of dimethyl compound	=	0.0953 g.
No. mmoles	=	0.2553
Volume of CH_4 equivalent to both methyls	=	11.4 N-c.c.
Volume of gas (I)	=	11.1 N-c.c.

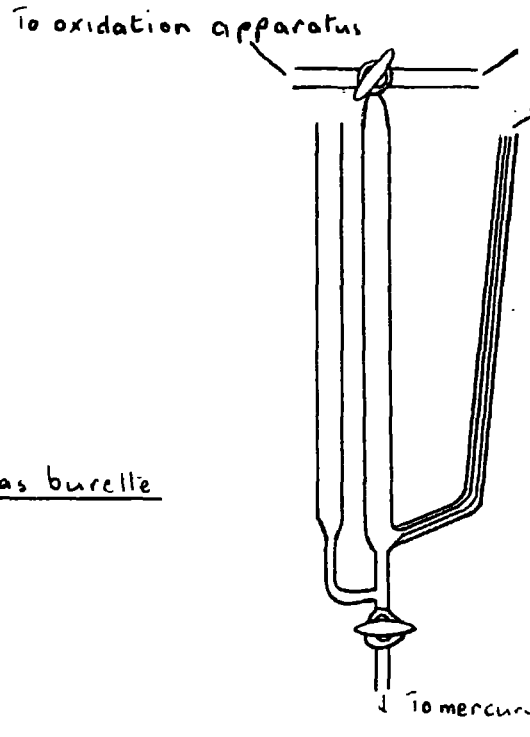
Conclusions

Hydrobromic acid displaces both methyl groups with evolution of methane.

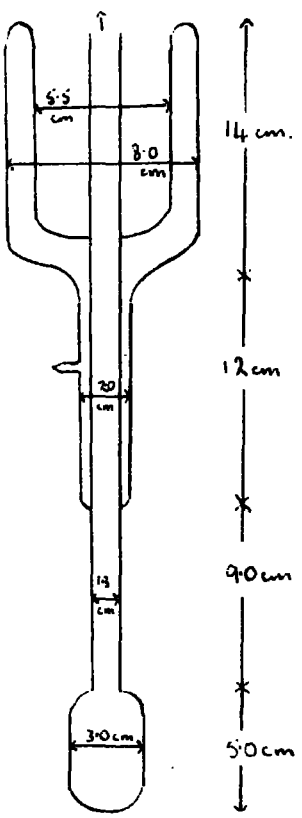


Schematic representation of the vacuum apparatus.





Gas burette



Fractionating Column, C

4. Decomposition by ethanol

a. An exploratory experiment

$$(Et_3P)_2Pd(CH_3)_2 + EtOH \longrightarrow (Et_3P)_2Pd(OEt)CH_3 + CH_4$$

$$\downarrow EtOH$$

$$Et_3P + Pd + CH_4 + C_2H_6 + C_2H_4 + CH_3CHO$$

A weighed amount of the dimethyl compound was placed in the reaction vessel (A) and the system was evacuated via tap (B). The flask was then cooled in liquid air, tap (B) was closed, and degassed ethanol added. The flask was allowed to warm up to room temperature. Near room temperature a vigorous reaction set in, a gas being evolved but there was no sign of metallic palladium being deposited. After this initial reaction the flask was cooled again and a gas (I) collected after passage through two liquid air traps. With tap (B) closed the flask was warmed (about 50°C) for two hours and then allowed to stand at room temperature for thirty six hours.

After this time a gas (II) was collected after passage through liquid air traps.

The bulk of the reaction mixture was then condensed into the fractionating set C, and the volatile material was fractionated through three traps at -78°, -96° and -78° respectively. A gas (III) was collected which was burnt to

CO_2 over copper oxide at about 500°.

Results

Wt. of dimethyl compound	=	0.1268 g.
No. of mmoles of dimethyl compound	=	0.3397
Volume of CH_4 equivalent to one methyl	=	7.61 N-c.c.
Volume of CH_4 equivalent to two methyls	=	15.22 N-c.c.
Volume of gas (I)	=	5.99 N-c.c.
Volume of gas (II)	=	7.31 N-c.c.
Total volume of methane	=	13.3 N-c.c.
Volume of gas (III)	=	2.68 N-c.c.
Volume of CO_2 after combustion	=	5.76 N-c.c
Volume of CO_2 expected had (III) been a pure C_2 gas	=	5.36 N-c.c.

Conclusions

1. The decomposition by ethanol takes place in two stages; an initial rapid reaction not accompanied by general decomposition and a second, slower reaction accompanied by a general decomposition.

2. A greater volume of gas was obtained than could have come from the two methyl groups and there is again evidence of free radical attack on the triethylphosphine residue or the solvent or both.

b. A more careful study of the decomposition by ethanol

The dimethyl compound was placed in reaction vessel (A) and the system was evacuated. Degassed ethanol (10 mls.) was added at room temperature with tap (B) closed. The very rapid reaction was allowed to proceed until the first sign of darkening appeared at which point the reaction vessel was cooled in liquid air and the volume of gas (I) formed was measured after passage through two liquid air traps. After volume measurement a fraction of gas (I) was burnt over copper oxide.

All volatile material was condensed back into vessel (A) and the whole system was evacuated.

The second stage of decomposition was now allowed to take place by warming (A) for three hours.

More gas (II) was obtained after passage through liquid air traps. All the volatile material remaining was transferred to the fractionating set (C) and fractionated through three traps at -78°. A volume of gas (III) was collected. An infrared spectrum of (III) was taken and a mass-spectrometer determination was carried out on (II), by Mr. P. Kelly at King's College, Newcastle.

Results

Wt. of dimethyl compound	=	0.1341 g.
No. mmoles	=	0.3593
Volume of CH_4 equivalent to one methyl	=	8.05 N-c.c.
Volume of CH_4 equivalent to two methyls	=	16.1 N-c.c.
Volume of gas (I)	=	8.53 N-c.c.
Volume of gas (I) used for combustion to CO_2	=	6.75 N-c.c.
Volume of CO_2 recovered	=	6.65 N-c.c.
% conversion of CH_4	=	98.5%
Volume of gas (II)	=	4.57 N-c.c.
Volume of gas (III)	=	2.60 N-c.c.

Spectrum of gas (III)

The spectrum showed strong absorptions at 1767 $cm.^{-1}$ and 1757 $cm.^{-1}$ (aldehydic C = O) and at 950 $cm.^{-1}$ (ethylene).

Mass-spectrometer analysis of (II)

Constituent	Approx. mole %
H_2	0.7
CH_4	96.0
C_2H_5OH	0.4
O_2	0.5
N_2	1.9
Other products	0.4

Conclusions

1. Combustion to CO_2 and mass-spectrometer analysis shows that the first gas evolved is methane and that the equivalent of one methyl group is evolved.

2. Besides more methane, ethane and ethylene, acetaldehyde is formed during the decomposition in the second stage.

c. Decomposition by ethanol in presence of styrene

Freshly distilled styrene was condensed onto the dimethyl compound in reaction vessel (A) and, with tap (B) closed, alcohol was added at room temperature. The first rapid reaction gave a volume of gas (I) and this was followed by the usual general decomposition giving, after three hours warming and standing at room temperature overnight, a volume of gas (II). Both (I) and (II) were obtained after passage through liquid airtraps.

The remainder of the volatile material was fractionated at -78^{o} and a very small volume of gas (III) was obtained.

The reaction vessel (A) showed obvious signs of the presence of polystyrene. This was isolated by disconnecting the flask under nitrogen, dissolving the contents in warm benzene and filtering through hyflo super-cel into a large volume of methanol. A white precipitate of polystyrene was

thereby obtained.

Results

Wt. of dimethyl compound	=	0.1256 g.
No. mmoles	=	0.3365.
Volume of CH_4 equivalent to one methyl	=	7.54 N-c.c.
Volume of CH_4 equivalent to both methyls	=	15.07 N-c.c.
Volume of gas (I)	=	7.2 N-c.c.
Volume of gas (II)	=	4.9 N-c.c.
Total volume of methane	=	12.1 N-c.c.
Volume of gas (III)	=	0.13 N-c.c.
Wt. of polystyrene	=	0.38 g.

Conclusion

1. The fact that polystyrene has been produced with almost complete exclusion of a C_2 gas confirms that the decomposition involves the formation of methyl radicals in the second stage of the decomposition.

d. Decomposition by ethanol in presence of triphenylphosphine

An excess of triphenylphosphine was dissolved in ethanol and the dimethyl compound was added. Very soon a yellow precipitate appeared which was collected and stored under nitrogen, as it tended to turn orange in the air,

m.p. 95-105° (decomposition).

An infrared spectrum of this compound was identical with a spectrum of $(Ph_3P)_4Pd$ prepared as described by Malatesta and Angoletta.[49] No deposition of palladium from the ethanolic solution occurred.

5. Reaction with thiophenol

$$(Et_3P)_2Pd(CH_3)_2 + 2PhSH \longrightarrow (Et_3P)_2Pd(SPh)_2 + 2CH_4$$

N.B. If one postulates the formation of the intermediate $(Et_3P)_2PdCH_3(OEt)$ during decomposition of the dimethyl compound in presence of ethanol then one might expect that the thiol grouping would also displace one or more methyls and that the intermediate would in this case be stable, sulphur being a stronger donor than oxygen towards palladium.

To the dimethyl compound (0.58 g., 1.56 mmoles) in n-hexane (10 mls.) was added thiophenol (2.12 mmoles). The solution turned yellow immediately and there was evolution of a gas. Beautiful orange-yellow crystals formed when the solution had stood overnight; these were collected on a filter and recrystallized from n-hexane, m.p. 141°.

Analysis Found: C, 51.3%; H, 7.2%.

$C_{24}H_{40}P_2S_2Pd$ requires C, 51.0%; H, 7.2%.

6. Reaction with p-nitrophenylacetylene

$$(Et_3P)_2Pd(CH_3)_2 + 2p\text{-}NO_2C_6H_4C{\equiv}CH \longrightarrow (Et_3P)_2Pd(C{\equiv}CC_6H_4NO_2)_2 + 2CH_4$$

To the dimethyl compound (0.5 g., 0.99 mmoles) in benzene (10 mls.) was added p-nitrophenylacetylene (1.98 mmoles) in benzene (10 mls.). The resulting solution rapidly darkened, and after it had stood two days at room temperature it was chromatographed through an alumina column, being eluted with n-hexane and then benzene. A clear yellow band separated and this band was collected and on evaporation a yellow solid was obtained; m.p. 123-125° (decomposition).

Analysis Found: C, 52.6%; H, 6.0%.

$C_{28}H_{38}P_2N_2O_4Pd$ requires C, 52.9%; H, 6.03%.

This was the first coloured orangopalladium compound to have been identified in this work.

7. With 1,2-Bis(diphenylphosphino)ethane

To $(Et_3P)_2Pd(CH_3)_2$ (0.37 g.) in benzene (5 mls.) was added 1,2-bis(diphenylphosphino)ethane (0.78 g., 2 mol.) in benzene (5 mls.). A yellow colour developed in the solution

and after the reaction mixture had stood at room temperature for four hours the benzene was pumped off and a light yellow solid (A) (0.7 g.) was obtained.

The material so obtained was recrystallized from acetone by cooling m.p. 140°, mixed m.p. with authentic $C_2H_4(Ph_2P)_2$ (B), 139-140°.

A spectrum of (A) was similar to one of (B) with three added peaks.

The filtrate from the recrystallization of (A) deposited a white solid on standing, m.p. 253° (decomposition) but this solid did not contain palladium. No palladium (0)-phosphine compound was isolated though the rapid development of a yellow colour at the beginning of the reaction suggests that such a compound was, at least transiently, formed.

Structure

There is evidence that this compound $(Et_3P)_2Pd(CH_3)_2$ isomerizes spontaneously.

A sample of the material was prepared and found to have a m.p. 47-49°, and it was stored under nitrogen at room temperature for about six months until its dipole moment could be measured. After this time the sample, after

recrystallization from n-hexane, had a m.p. 66-67° and the dipole moment was rather low (1.4 Debye units) indicating that most of the material had a trans structure.

When more material was prepared for a more exact measurement of its dipole moment a m.p. of 43° was recorded and the dipole moment was found to be 4.6D indicating a cis structure.

A third specimen was prepared, m.p. 46-47°, and was found to have a dipole moment of 4.68 D. A sample of this material was sublimed and had a m.p. 50-51°. The benzene solutions from the dipole moment measurements were evaporated and the solid which remained was recrystallized from n-hexane, m.p. 71-72° and a specimen of this material was sublimed, m.p. 77°.

1-2 g. of the dimethyl compound (m.p. 46-47°) were dissolved in benzene and a small amount of triethylphosphine (0.25 ml.) was added. After the solution had stood at room temperature for three days it was evaporated and the solid remaining was recrystallized from n-hexane, m.p. 44°.

Spectra of all the different specimens, isolated were taken but no significant differences were noted.

3. Reaction between $(Et_3P)_2PdBr_2$ and ethylmagnesium bromide

To the dibromide (10.0 g., 0.02 moles) suspended in ether (200 mls.) at -45° was added ethylmagnesium bromide (0.047 moles) in ether (50 mls.). No change took place at the low temperature but on warming up to -10° the contents of the flask turned milky white and there was no sign of the yellow starting material.

At 0° the reaction mixture was hydrolysed and the ether phase developed a brown colour. The reaction mixture was filtered, the phases separated and the ether phase evaporated to produce a very dark solid (I) (8.3 g.)

Solid I

In view of the instability of the product only hydrocarbon solvents of the n-hexane and benzene types were tried as solvents for recrystallization and benzene appeared to give most hope of obtaining a pure specimen.

About half of the material isolated was eluted with benzene from an alumina column and various fractions were taken. These benzene solutions decomposed on standing, but filtering through super-cel gave a clear light yellow solution which, on evaporation gave a smallamount of a light yellow solid (II) m.p. 105° (decomposition).

To a few mgs. of (II) in a test tube was added ethanolic hydrobromic acid but no gas evolution was noticed.

Solid (II) was recrystallized from n-hexane as yellow needles, m.p. 129°, mixed with authentic $(Et_3P)_2PdBr_2$ 133°.

No other crystalline organic material was isolated.

4. The preparation of bis(triethylphosphine)bromo(phenyl)-palladium

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

The dibromide (10.0 g; 0.02 moles) was placed in a 500 ml. flask and ether (200 mls.) was added and the flask was cooled (-60°). Phenylmagnesium bromide (0.022 moles) in ether (75 mls.) was added during 20 minutes and the flask was allowed to attain room temperature at which stirring was continued for 30 minutes. The flask was then cooled (0°) and water (100 mls.) was added.

No reaction took place at the low temperature (-60°) but at -40° a brown colour developed at the gas-liquid interface and by -20° the whole content of the flask was dark red. A colour test for Grignard reagent was negative. The addition of water resulted in disappearance of the red colour and the ether phase became dark brown.

Isolation of the product

After separation of phases the ether phase was evaporated

and a light yellow solid (I) (7 g.) was obtained. Most of this solid was dissolved in alcohol, the solution filtered and cooled. A light yellow solid (II) was obtained. The mother liquor carried suspended material and was filtered through hyflo super-cel. A clear brown solution was obtained but this decomposed slightly overnight.

Solid (II) was recrystallized again from alcohol and then eluted from an alumina column with alcohol. On evaporating the solvent until the material came out of solution, a light yellow solid was obtained m.p. 127-128°.

Analysis Found: C, 29.3%; H, 6.2%.

$C_{12}H_{30}PdP_2Br_2$ requires C, 28.6%; H, 6.0%; m.p. 135°.

Thus solid II is starting material.

n-Hexane was then tried as a solvent for recrystallization for the remainder of (I). It was found to be much more readily soluble in n-hexane and a sample (III) obtained by cooling had a m.p. 87° (decomposition).

(III) was eluted from an alumina column with n-hexane and a yellow band moved down the column. Material from this band was rejected and the remaining n-hexane collected. This solution was concentrated, cooled and filtered. A white solid m.p. 88° was obtained.

Analysis Found: C, 42.0%; H, 7.0%.

$C_{18}H_{35}PdP_2Br$ requires C, 43.2%; H, 7.1%.

A further crystal fraction was obtained from the mother liquor, m.p. 89°.(decomposition)

Found: C, 42.2%; H, 7.0%.

Structure The dipole moment was found to be 3.6 D indicating a trans structure.

5. The preparation of bis(triethylphosphine)diphenylpalladium

$$(Et_3P)_2PdCl_2 + 2PhLi \longrightarrow (Et_3P)_2PdPh_2 + 2LiCl$$

The dichloride (7.04 g., 0.017 moles) was placed in a 500 ml. flask with ether (200 mls.) and the flask was cooled (-75°). Phenyl-lithium (0.034 moles) in ether was added during 35 minutes and the mixture was stirred (40 minutes) at the low temperature after which time the flask was allowed to attain room temperature. Colour test was negative. Water (100 mls.) was added after cooling (0°).

Isolation of the product

The reaction mixture was filtered, the liquid phases separated, and the ether phase concentrated. This produced a yellow-green solid (7.8 g.) and after it was washed with methanol it was recrystallized by cooling from acetone, m.p. 95° (decomposition).

Analysis Found: C, 58.4%; H, 8.3%; Pd 21.9%, 21.5%.
$C_{24}H_{40}P_2Pd$ requires C, 58.0%; H, 8.1%; Pd 21.5%.
Yield 4.7 g., 55%. (recrystallized).

The methanol washings on evaporation gave a crystalline white solid which, when treated with concentrated nitric acid and boiled for four hours, gave a white solid which crystallized from alcohol in white needles, m.p. 235-238°. (m.p. 4,4'-dinitrodiphenyl 233°).

Structure A small value for $\Delta\epsilon/f$ clearly indicates a trans configuration and the dipole moment is zero.

Reactions and properties

Readily soluble in ether, petroleum ether (60-80°), benzene, n-hexane, and xylene, soluble in acetone and cyclohexane but soluble in alcohol and methanol only on warming. In all cases warming resulted in decomposition.

6. The preparation of bis(triethylphosphine)di(phenylethynyl)-palladium

$$(Et_3P)_2PdBr_2 + 2PhC{\equiv}CMgBr \longrightarrow (Et_3P)_2Pd(C{\equiv}CPh)_2 + 2MgBr_2$$

The dibromide (12.6 g., 0.025 moles) in ether (150 mls.) was cooled (-60°) in a 500 ml. flask and phenylethynyl-magnesium bromide (0.055 moles) in ether (100 mls.) was added during 30 minutes. The reaction mixture was stirred

(15 minutes) at the low temperature and was then allowed to attain room temperature.

The flask was cooled (0^{o}) and water (100 mls.) added.

Isolation of the product

The reaction mixture was filtered and a solid (I) was isolated on the filter and the two liquid phases were separated. Evaporation of the ether phase afforded an orange solid which decomposed overnight.

The solid (I) (9 g.) was dried and found to be insoluble in ether, only slightly soluble in acetone, but soluble in ethanol, n-hexane and cyclohexane, and methanol on warming. It was soluble in cold toluene and recrystallization from toluene by cooling gave a white solid, m.p. 162-164° decomposition.

Analysis Found: C, 61.6%; H, 7.7%; Pd, 20.0%.

$C_{28}H_{40}P_2Pd$ requires C, 61.7%; H, 7.4%; Pd 19.6%.

Yield 66%.

Structure The compound is trans having zero dipole moment.

7. The preparation of bis(triethylphosphine)bromo(mesityl)-palladium

$$(Et_3P)_2PdBr_2 + Me_3C_6H_2MgBr \longrightarrow (Et_3P)_2Pd(Me_3C_6H_2)Br + MgBr_2$$

The dibromide (10 g., 0.02 moles) in ether (175 mls.) was placed in a 500 ml. three-necked flask which was cooled

to -52°. A solution in ether (65 mls.) of mesitylmagnesium bromide (0.044 moles) was added during 10 minutes. The solution was stirred (20 minutes) and then allowed to warm up.

After reaching 10° the colour deepened from red to darker red and, as a colour test was negative reaction was assumed to be over. Water (100 mls.) was added after cooling (0°).

Observations

Immediately on adding the Grignard solution the reaction mixture became less dense and the ether solution was yellow. By 0° the colour was red.

The addition of water produced an immediate yellow colouration. The ether phase was yellow with a white suspension in the aqueous phase.

Working up of reaction products

The reaction mixture was filtered and the phases were separated. A white solid, soluble in dilute acetic acid, remained on the filter.

Ether phase

Ether was pumped off at 12 mm. and then at about 0.01 mm. and a light yellow solid (I) was obtained but which, on becoming dry, began to decompose until the

contents of the flask were quite black.

Solubility

Soluble in the cold in methyl ethyl ketone, n-hexane, benzene, acetone, petroleum ether, chloroform and carbon tetrachloride, insoluble or slightly soluble in the three alcohols methanol, ethanol and propanol but very soluble on warming. The alcoholic solutions darkened on long standing.

A small amount (1-2 g.) of the dark, impure solid (I) was placed in a double Schlenk tube under nitrogen and methyl ethyl ketone (20 mls.) was added together with a little hyflo super-cel. The solution was filtered and a clear brown solution was obtained which on cooling precipitated a grey powder. This was collected on the filter, washed and dried, m.p. 162° (decomposition) darkening above 158°. (For Schlenk tube see Diagram V).

All impure material (I) was then recrystallized similarly and the once recrystallized solid was recrystallized again from methyl ethyl ketone, m.p. 161-162° (decomposition). Analysis Found: C, 46.4%; H, 7.7%; Pd 19.5%; 19.3%. $C_{21}H_{41}PdP_2Br$ requires C, 46.5%; H, 7.6%; Pd 19.7%.

Great care was taken during the last recrystallization to remove suspended palladium and the methyl ethyl ketone

solution was passed through an alumina column and filtered twice through hyflo super-cel under gravity. In this way a clear almost colourless solution was obtained which was evaporated in a Schlenk tube before cooling. A pure white solid was obtained.

Yield 2.05 g., 19%.

Ethanolic HBr

Addition of aqueous ethanolic HBr to an ethanolic solution of the monomesityl compound produced no observed change and the compound appears to be stable in air over great lengths of time.

Structure The monomesityl compound has a trans structure having a dipole moment of 3.52 D.

Repeat of the previous reaction using 1 molecule of Grignard reagent

To $(Et_3P)_2PdBr_2$ (10 g., 0.02 moles) in ether (150 mls.) in a 500 ml. three-necked flask cooled to -60° was added mesitylmagnesium bromide (0.022 moles) in ether (52 mls.). The mixture was allowed to reach room temperature at which it was stirred for 30 minutes. After cooling (0°), water (100 mls.) was added.

It was noted that a temperature rise occurred immediately on adding the Grignard solution and coagulation also took

place. The ether phase became red-coloured by 0^{o} and addition of water produced a clear red colour.

Working up of reaction products

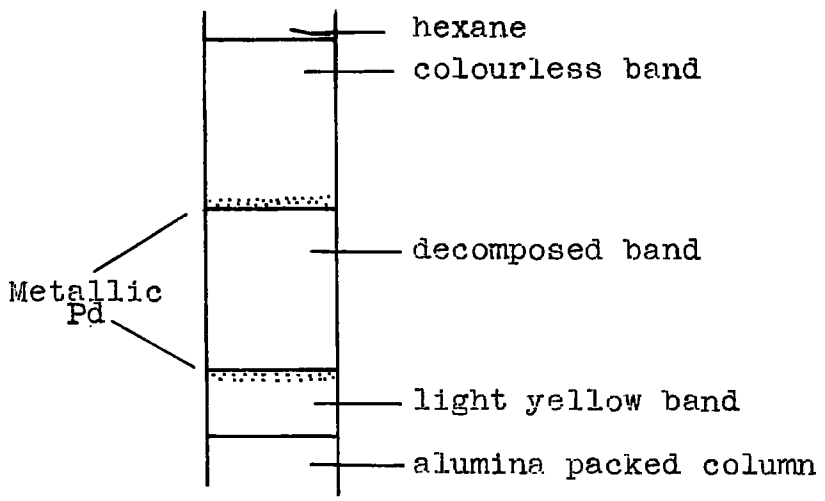
The phases were separated and the ether phase was dried ($MgSO_4$). Evaporation under reduced pressure gave a light brown solid which was transferred to a Schlenk tube and methyl ethyl ketone was added. The solution was filtered, cooled in acetone/CO_2 which produced a light yellow solid (II) which was collected and washed with pure solvent. The solid (II) was dried and recrystallized from ethanol as yellow needles, m.p. 134-5°; mixed m.p. with the initial dibromide, 134-5°. 4.0 g., of (II) were obtained.

The mother liquor of the methyl ethyl ketone filtration was concentrated to half its initial volume and cooled to -78°.

A much lighter coloured component was precipitated which was thought to be a mixture of the white monomesityl derivative with the initial dibromide (2.8 g.) It was thought that it might be possible to separate the two components chromatographically.

Methyl ethyl ketone was tried but this was unsuccessful as the "yellow band" (dibromide) came through too quickly.

n-Hexane was next tried and here movement of the yellow band was slow. The whereabouts of the other component, the mesityl compound, was not known. However on standing over night the column assumed the appearance shown.



It was considered not profitable to pursue the purification further.

Conclusions of reactions between mesitylmagnesium bromide and $(Et_3P)_2PdBr_2$

The only product isolated has been trans-$(Et_3P)_2PdBrC_6H_2(CH_3)_3$ which was obtained from the action of 2 mols. of Grignard on the dibromide. It is a fairly stable compound but decomposes on melting. The action of 1 mol. of Grignard produced 40% dibromide unchanged and 30% of a mixture of the dibromide and the monomesityl compound.

Thus the better method of preparation is the former method as this produces no contamination by starting material and it is assumed that the decomposition which occurred during drying of the ether soluble components was due to the dimesityl derivative.

8. The reaction between $(Et_3P)_2PdBr_2$ and styrylmagnesium bromide

The dibromide (12.6 g., 0.025 moles) was placed in a 500 ml. flask with ether (200 mls.) and the flask was cooled (-60°) and styrylmagnesium bromide (0.05 moles) in ether (115 mls.) was added during 60 minutes. The flask was allowed to attain room temperature and stirring was continued for 15 minutes after which the flask was cooled (0°) and water (100 mls.) was added.

Isolation of reaction product

The reaction mixture was filtered and a white solid (I) remained on the filter. The two liquid phases were separated.

The white solid (I) was pumped dry and found to be slightly soluble in benzene, soluble in toluene and insoluble in acetone, alcohol, cyclohexane, n-hexane, methanol, ethylacetate, chloroform and methylene chloride. About 1 g. of the solid was placed, under nitrogen, in a

double Schlenk tube and toluene (10 mls.) was added. Immediate decomposition occurred. A further sample was washed with acetone and after cooling (0°), toluene was added and after filtering, the filtrate was cooled to (-78°). Only a trace of solid was obtained and this was slightly dark in colour.

The ether phase was evaporated and a sticky solid was obtained which was washed with n-hexane to remove any purely organic material. This produced a white solid which decomposed during drying.

Thus it was concluded that the reaction product, by analogy with previous reactions, $(Et_3P)_2Pd(CH{=}CHPh)_2$, or possibly $(Et_3P)_2PdBr(CH{=}CHPh)$ was thermally unstable.

9. The preparation of bis(triethylphosphine)-bis-(4-dimethylaminophenyl)palladium

$$(Et_3P)_2PdCl_2 + 2\ 4\text{-}Me_2NC_6H_4Li \longrightarrow (Et_3P)_2Pd(C_6H_4NMe_2\text{-}4)_2 + 2\ LiCl$$

The dichloride (12.4 g., 0.03 moles) in ether (200 mls.) in a 500 ml. flask was cooled (-65°) and 4-dimethylaminophenyllithium (0.063 moles) in ether (100 mls.) was added during 40 minutes. Stirring was continued for 15 minutes and a colour test was positive. The flask was allowed to attain

room temperature when a colour test was positive but faint and after more stirring (10 minutes) the flask was cooled (0°) and water (100 mls.) was added.

A gradual colour change occurred during addition of 1 mole equivalent of lithium compound, the change being from yellow to white. This white colour intensified during addition of the second equivalent and addition of water produced a brown-black colour in the ether phase.

Isolation of the product

After filtering, and separating the phases, the ether phase was evaporated by pumping and a white solid (14 g.) was obtained which was readily soluble in ether, n-hexane and benzene, slightly soluble in alcohol and insoluble in acetone. A sample of the compound (1-2 g.) was recrystallized twice from n-hexane by cooling m.p. 99-100° (decomposition). Recrystallization had to be carried out rapidly as the compound tended to decompose in solution.

Analysis Found: Pd, 18.0%.

$C_{28}H_{50}P_2N_2Pd$ requires Pd 18.8%.

Yield 80%.

The Methiodide

The remainder of the base (about 12 g.) was dissolved in ether and an excess of methyl iodide was added. After

standing for four hours, formation of the dimethiodide was judged to be complete and the white precipitate was collected and dried. m.p. 140° (decomposition). A sample was recrystallized from methanol.

Analysis Found: Pd, 12.9%; I, 30.0%.

$C_{30}H_{56}I_2N_2P_2Pd$ requires Pd, 12.3%; I, 29.3%.

The methiodide appeared to be very stable and did not decompose in solution and remained unchanged on exposure to air over a long period.

10. The preparation of bis(triethylphosphine)bromo(p-trifluoromethylphenyl)palladium

$$(Et_3P)_2PdBr_2 + p\text{-}CF_3C_6H_4MgBr \longrightarrow (Et_3P)_2Pd(p\text{-}CF_3C_6H_4)Br + MgBr_2$$

The dibromide (10.0 g., 0.02 moles) was suspended at -55° in ether (150 mls.) and p-$CF_3C_6H_4MgBr$ (0.022 moles) in ether (43 mls.) was added during 20 minutes. The mixture was stirred at the low temperature for 20 minutes and then allowed to warm up to room temperature. After stirring for 20 minutes between 10° and 20° the ether solution was cooled (0°) and water (100 mls.) was added.

Observations

The colour at -55° after addition of Grignard was a "clean" light brown colour. This colour intensified during warming up. The most noticeable change occurred

at -20 to -10°. At 0° on stopping the stirrer a fine white powder was seen to be present in the flask and the ether phase was an opaque brown colour. Addition of water produced a cherry-red ether phase.

Working up of reaction products

The phases were filtered and separated. A small amount of a dark solid remained on the filter.

Ether phase

On evaporation a light brown solid was obtained, 9.5 g. It was soluble in the cold in methylcyclohexane, acetone and benzene, but soluble on warming in n-hexane and ethanol. The last two solvents produced a white granular precipitate on cooling to room temperature.

Purification

About 1-2 g. of impure solid were recrystallized under normal atmospheric conditions from n-hexane. The hot liquid after filtering was a clear golden-yellow colour. On cooling white granular crystals came out of solution which had scattered amongst them yellow needles of a second compound. The solid material (I) was collected on a filter and dried. The mother liquor was cooled (-70°) and a large amount of yellow solid (II) was precipitated. (II) recrystallized as yellow needles from ethanol, m.p. 126°;

mixed with $(Et_3P)_2PdBr_2$, 132°.

Solid (I) was placed in a beaker and n-hexane was added (3-4 mls.) which dissolved out the yellow component. The purified solid (III) was separated, washed with more n-hexane and dried, m.p. 145-146.5°, without decomposition.

The remainder of the crude material was purified as above, i.e. a first crop of crystals from n-hexane was further purified by dissolving out, at room temperature, the more soluble (dibromide) material.

The second crystal crop (solid II) was dissolved in n-hexane and passed through an alumina column and when all the yellow band had passed through, the column was eluted with n-hexane and the clear solution obtained was evaporated and cooled. A small amount of pure material (III) was obtained.

Yield (purified) 2.2 g., 19.4%.

A small amount was recrystallized from n-hexane for analysis.

Analysis Found: C, 39.5%; H, 6.2%; Br, 13.7%; F, 9.9%. $C_{19}H_{34}P_2PdBrF_3$ requires C, 40.17%; H, 6.03%; Br, 14.06%; F, 10.03%.

11. The preparation of bis(triethylphosphine)phenyl(para-trifluoromethylphenyl)palladium

The preparation of the mono-p-trifluoromethylphenyl compound was repeated.

Yield 80%; m.p. 145-147°.

$$(Et_3P)_2Pd(p\text{-}CF_3C_6H_4)Br + PhLi \longrightarrow (Et_3P)_2PdPh(p\text{-}CF_3C_6H_4) + LiBr$$

The monobromide (6.8 g., 0.012 moles) was dissolved in ether (150 mls.) and the solution was cooled (-40°) and phenyl-lithium (0.014 moles) in ether (25 mls.) was added. The suspension was allowed to warm up to room temperature when a colour test was positive but very faint. More phenyl-lithium was added (total amount added was 0.021 moles) and a colour test (Michler's ketone) was positive. The solution was stirred at room temperature for 30 minutes and then hydrolysed with water (100 mls.) at 0°. The reaction mixture was filtered and the two phases separated.

Observations

The initial suspension at -40° was white but after addition of the phenyl-lithium the ether phase was clear and colourless. Addition of water produced a dark brown colour.

Ether phase

On evaporation of the ether phase a white solid (5.8 g.) was obtained, readily soluble in n-hexane, acetone and benzene but less readily soluble in ethanol and methanol. Recrystallized from acetone by cooling as a pure white powder, m.p. 74-75°(decomposition).

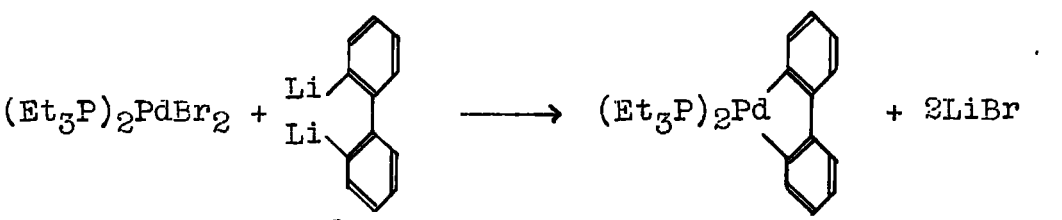
Analysis Found: C, 53.2%; H, 7.5%; Pd, 18.42%; 18.79%. $C_{25}H_{39}P_2PdF_3$ requires C, 53.13%; H, 6.7%; Pd, 18.88%.

Thus the reaction has led to the formation of bis(triethylphosphine)phenyl(p-trifluoromethylphenyl)-palladium.

Yield 85%.

This is the first organopalladium compound to be isolated with two different organic groups bonded to the metal atom.

12. The reaction between $(Et_3P)_2PdBr_2$ and 2,2'-dilithio-biphenyl



To a cooled (-50°) solution of the dilithium compound (0.05 moles) was added during 40 minutes a solution of the dibromide (12.4 g., 0.025 moles) in ether (250 mls.). A colour test was positive and on allowing the flask to

warm up to room temperature the colour test was still positive but on refluxing for 45 minutes a colour test was negative. The flask was cooled (0^{o}) and water (100 mls.) was added.

After refluxing the solution was more green in colour compared with the initial yellow colour. Addition of the first 10 mls. of water produced a dense white colour and this changed to yellow, dark yellow and clear brown on addition of more water. The final colour was very dark.

Isolation of the product

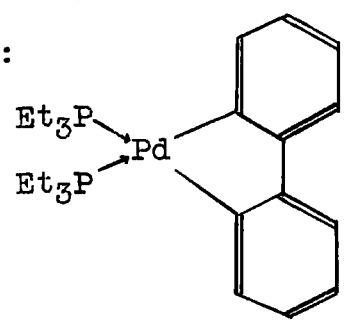
After separating the phases the ether phase was evaporated and a black solid was isolated which appeared to be slightly soluble in n-hexane and methylcyclohexane. Cooling the solutions produced a light coloured compound.

Recrystallization from hexane gave an almost white amorphous looking powder m.p. 83^{o}. A larger scale recrystallization gave a compound m.p. 95^{o} and recrystallization from methanol gave a sample which was analysed.

Halogen was detected in the compound.

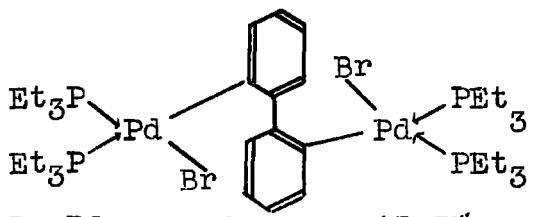
Analysis Found: C, 47.8%; H, 6.8%; Pd, 19.1%.

The cis compound:



$C_{24}H_{38}P_2Pd$ requires C, 58.2%; H, 7.7%; Pd 21.5% and contains no halogen.

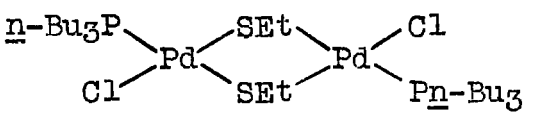
The trans compound:



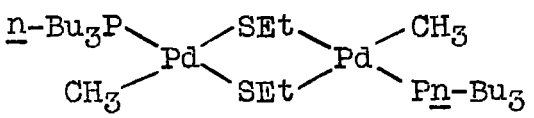
$C_{36}H_{68}P_4Br_2Pd_2$ requires C, 43.3%; H, 6.9%; Pd, 21.4%.

It would appear therefore that the cis compound has not formed but that an impure sample of the trans compound has been isolated.

13. Preparation of dimethylbis(tri-n-butylphosphine)-μ,μ'-bis(ethanethio)dipalladium



+ $2CH_3Li \longrightarrow 2LiCl$ +



To the dichloride (16.2 g., 0.02 moles) in ether (150 mls.) at -40° was added methyl-lithium (0.0405 moles) in ether (26 mls. of a 1.57N solution). After warming up to room temperature a colour test was negative and more methyl-lithium (5.2 mls.) was added. After hydrolysis the phases were separated after filtering and a small

amount of starting material was isolated on the filter.

Ether phase

On evaporation a dark solid was isolated (13 g.) soluble in toluene, n-hexane and acetone. The acetone solution deposited a buff coloured compound (m.p. 48°) on cooling to -70°. The bulk of impure material was dissolved in acetone under nitrogen filtered and the filtrate cooled. A white powder was deposited which darkened in places on standing. The solid was collected, dried, stored overnight cold, and next day washed with a little acetone and the washings were decanted off. Subsequent solution in acetone and cooling gave a pure white solid m.p. 51-53° (no decomposition).

Analysis Found: C, 47.1%; H, 9.1%.

$C_{30}H_{70}P_2Pd_2S_2$ requires C, 46.8%; H, 9.1%.

Yield 84%.

The above preparation using 1 mol. of methyl-lithium produced only an oily material, probably a mixture of isomers.

14. Reaction between dichlorobis(tri-n-butylphosphine)-$\mu_2\mu'$-bis(ethanethio)dipalladium and phenyl-lithium

To the dichloride (16.2 g., 0.02 moles) in ether (200 mls.) cooled to -58° was added phenyl-lithium (0.05 moles) in ether (56 mls.). The flask was allowed to warm up to room temperature when the contents of the flask appeared quite black. After hydrolysis with water (100 mls.) at 0°, the reaction products were filtered through hyflo but only a few crystals of starting material remained on the hyflo.

Ether phase

On evaporating a black solid mass (9.0 g.) was obtained. It was difficult to see exactly what happened in the various solvents tried because of the black colour or suspension present in the liquid. The solid appeared to be soluble in benzene, petroleum ether, n-hexane, alcohol, methanol and acetone.

A portion of the impure semi-solid mass was placed, under nitrogen in a Schlenk tube, alcohol was added, and the solution filtered, concentrated and cooled. On filtering the cooled solution only a small amount of solid was obtained.

An alumina column in n-hexane was prepared and a concentrated ethanolic solution was added and the column was

eluted with n-hexane. An intense black band remained at the top of the column and a dark solution came through, which was much lighter than the initial solution. On evaporation a black oil was obtained.

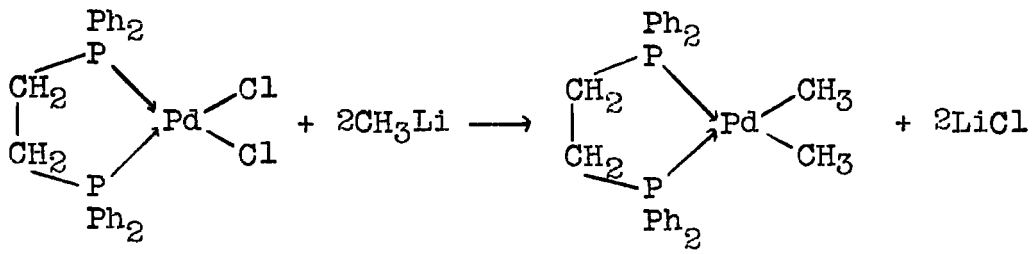
There appeared to be no great hope of obtaining a pure specimen of the diphenyl derivative.

15. The reaction between $(n\text{-}Bu_3P)ClPdCl_2PdCl(Pn\text{-}Bu_3)$ and methyl-lithium

To the suspended bridged chloro compound (22 g., 0.029 moles) in ether (150 mls.) was added methyl-lithium (0.062 moles) in ether (26.4 mls. of a 2.35N solution) at -45°. During addition of the methyl-lithium a vigorous reaction occurred with extensive decomposition and deposition of metallic palladium.

The reaction mixture was set aside for some time and on working up only metallic palladium was isolated.

16. The preparation of 1,2-Bis(diphenylphosphino)ethane-dimethylpalladium



The dichloride (8.1 g., 0.014 moles) was suspended in ether (150 mls.) at -55° and methyl-lithium (0.03 moles) was added in ether (16.5 mls.). The reaction mixture was allowed to warm to room temperature but a colour test was negative. The flask was cooled again and more methyl-lithium was added until a positive colour test was obtained at room temperature, at which point the reaction mixture was stirred for one hour.

After this time the reaction mixture was hydrolysed with water (100 mls.) and a light coloured solid (I) present was collected on a filter. The phases were separated and the dark brown ether phase was evaporated to produce a dark solid (II) 1.7 g.

Solid I

This was dried at about 0.01 mm. (6.7 g.) and found to be insoluble in n-hexane, slightly soluble in benzene but soluble in acetone.

1-2 g. of solid were dissolved in acetone in a Schlenk tube, the solution filtered and cooled. The near white crystals were collected, washed, dried and immediately recrystallized from the same solvent as white needles, m.p. 162° (decomposition).

Analysis Found: C, 61.5%; H, 5.6%.

$C_{28}H_{30}P_2Pd$ requires C, 62.83%; H, 5.65%.

The compound was twice recrystallized from acetone and a pure white specimen m.p. 166-168°(decomposition)was obtained.

Found: C, 61.4%; H, 5.5%.

Conversion to dichloride

The compound undergoes a very rapid reaction with ethanolic hydrochloric acid to give the initial dichloride (spectrum identical to authentic material).

0.361 mmoles of solid (I) produced 0.354 mmoles of the dichloride.

Solid II

This was treated as above and a white solid m.p. 168°(decomposition)was obtained, mixed m.p. 162° with solid I.

Yield (impure) quantitative.

17. Reaction between 1,2-Bis(diphenylphosphino)ethane-dichloropalladium and phenyl-lithium

To the dichloride (0.014 moles, 8.07 g.) suspended in ether (200 mls.) at -50° was added phenyl-lithium (0.03 moles) in ether (34 mls.). On warming up to room temperature the reaction mixture became very dark and colour tests were obscured. A total of 3 mols. of phenyl-lithium was added.

The reaction mixture was hydrolysed at 0° with water (100 mls.), filtered and the phases were separated. A small amount (about 1 g.) of material remained on the filter.

Ether phase

This was evaporated and a dark solid (I) (10 g.) was obtained, soluble in acetone to give a very dark solution, slightly soluble in benzene, toluene and ethanol but insoluble in methylcyclohexane and n-hexane.

It was difficult to follow what happened in solution because of the very black colours produced.

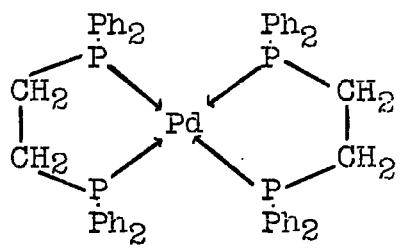
A small amount of (I) was dissolved in toluene, filtered and cooled but no precipitate appeared. An alumina column was then prepared in benzene and a benzene solution of (I) added and the column was eluted with benzene. A light yellow band immediately left the black band at the top of the column. The yellow band was collected.

Half of the solid (I) was purified similarly and a black tarry solid remained insoluble in the benzene. The light yellow band was collected and on evaporation an orange solid, m.p. 165° (decomposition) was obtained.

Analysis Found: Pd, 10.1%; 9.96%.

$C_{38}H_{34}P_2Pd$ requires Pd, 16.18%.

It is clear therefore that the material isolated is not the diphenyl derivative. It was thought that it might possibly be an impure sample of



(requires Pd, 11.8%)

II

which would be similar to the compounds of Pd(0) prepared by Malatesta and Angoletta.[49]

However attempts to prepare an authentic specimen of (II) failed.

Two methods were tried:-

a. Direct action of the phosphine on $(Et_3P)_2Pd(CH_3)_2$ in benzene.

b. Decomposing a specimen of $(Et_3P)_2Pd(CH_3)_2$ with alcohol in presence of the phosphine. Only metallic palladium was precipitated.

18. The preparation of bis(triphenylphosphine)dimethyl-palladium

$$(Ph_3P)_2PdCl_2 + 2CH_3Li \longrightarrow (Ph_3P)_2Pd(CH_3)_2 + 2LiCl$$

To the dichloride (14.0 g., 0.02 moles) suspended in ether (200 mls.) at -50° was added methyl-lithium (0.044 moles) in ether (75 mls.). The reaction mixture was then allowed to warm up to room temperature when a colour test was negative. Methyl-lithium was added to the cooled solution until a colour test was positive at room temperature. A total of 3 mols. of methyl-lithium was added after which the reaction mixture was hydrolysed with water (100 mls.) at 0°.

The reaction mixture was filtered and the liquid phases were separated. A light coloured solid (I, 12.5 g.) remained on the filter.

It was observed before hydrolysis that a white solid was present in a now light brown ether phase which turned black on hydrolysis but the solid present remained nearly white.

The ether phase on evaporation deposited only a small

amount of a dark coloured material.

Solid I

This proved to be a very difficult compound to purify and was neither very soluble nor very stable and this excluded heating the various solvents; even slight warming (35-40°) caused decomposition. Thus solution at room temperature and either evaporating or cooling to -78° had to be used and in all cases yields were small and the processes were very time-consuming.

The product was soluble (bearing in mind the above) in chloroform, benzene, toluene, methyl ethyl ketone, nitromethane and tetrahydrofurane.

The cooling technique was tried with methyl ethyl ketone and THF, and evaporation with chloroform and benzene. Melting points tended to vary: from methyl ethyl ketone, 177°; chloroform, 180°; and THF, 197-198°. In all cases decomposition occurred on melting.

Analysis Found: C, 71.3%; H, 6.0% (from benzene).

$C_{38}H_{36}P_2Pd$ requires C, 69.01%; H, 5.49%.

Yield 95%.

Conversion to the dichloride

$$(Ph_3P)_2Pd(CH_3)_2 + 2HCl \longrightarrow (Ph_3P)_2PdCl_2 + 2CH_4$$

The product (0.4871 mmoles) underwent reaction in

benzene solution with hydrochloric acid to give the dichloride which was precipitated as a yellow powder (0.4316 mmoles).

Spectral data (see Section "Infrared spectra") were in accordance with the dimethyl compound having been formed. Structure The dipole moment was found to be 4.6 D and therefore the compound has a cis configuration.

ii. With arsines as donors

19. Reaction between $o\text{-}C_6H_4(AsMe_2)_2PdBr_2$ and methylmagnesium bromide

To a suspension of the dibromide (1.0 g., 0.02 moles) in ether (150 mls.) was added during 25 minutes methylmagnesium bromide (0.03 moles) in ether (55 mls.) at -50°. The resulting mixture was stirred for 15 minutes at the low temperature and the flask and contents were allowed to warm to 4° when an ice bath was placed around the flask and after 10 minutes water (100 mls.) was added.

There was no apparent change at the low temperature after addition of the Grignard solution but on warming to -15° a black ring appeared at the gas-liquid interface. The colour of the reaction mixture turned brown until at 0° to 4° a black colour developed. Addition of water produced a white solid which darkened slightly.

Working up of reaction products

The contents of the reaction flask were filtered and a solid (I, 13 g.) was obtained. The two liquid phases were separated.

Ether phase

The ether was pumped off and a small amount of a white solid, soluble with darkening, in alcohol was obtained.

Solid I

This was washed on a sintered disc with water and ether and dried by pumping at about 0.01 mm.

Solubility

Soluble in hot acetone, alcohol, benzene and propanol, and slightly soluble in ethyl acetate and n-hexane. Later tests showed it to be soluble in hot chloroform and, to a greater extent, in nitromethane. Solubility in no case was very great.

A small amount was recrystallized from acetone as yellow needles. A test for presence of halogen was positive. On recrystallizing from chloroform successive fractions crystallizing out became lighter in colour, the last fractions being almost white. This was clear evidence of a change taking place in solution or of two components being present. A positive test for chlorine was obtained on a

sample recrystallized from chloroform.

Analysis Found: from acetone C, 23.8%; H, 3.5%.

from ethyl acetate 24.6%; 3.1%.

from chloroform 20.2%; 2.7%; Pd, 14.8%

$C_{11}H_{19}PdAs_2Br$ requires C, 27.1%; H, 3.93%; Pd, 21.88%.

$C_{11}H_{19}PdAs_2Br2CHCl_3$ requires C, 21.5%; H, 2.91%; Pd, 14.7%.

The indication was therefore that chloroform was present as solvent of crystallization. A sample was sent for infrared analysis and a characteristic peak of chloroform was obtained.

Recrystallization from nitromethane failed to give a pure specimen.

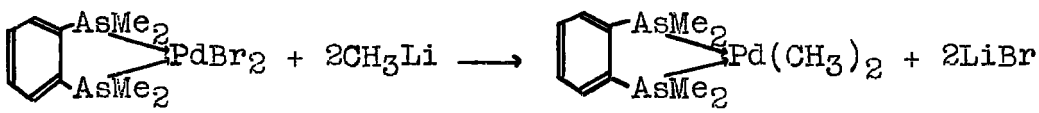
Conclusion

There is little doubt that the monomethyl derivative was formed in the reaction and the compound is not very soluble; nitromethane and chloroform being far from ideal solvents. It was thought that greater solubility would be obtained by having less symmetry in the molecule, e.g. by replacing an $-AsMe_2$ group by $-PBu_2$ or $-PEt_2$.

As detailed in the section on preparation of starting materials the method given in the literature for the preparation of n-Bu_2PCl could not be duplicated even after very careful experimentation. The idea of having the

n-Bu_2P- group in the starting material was dropped in favour of the more readily obtainable Et_2P- group from Et_2PCl. This work is described below (22,23).

20. The preparation of o-phenylenebisdimethylarsinedimethyl-palladium



1. An initial reaction was carried out on the dibromide (11.05 g., 0.02 moles) in ether using methyl-lithium (0.0405 moles) under standard conditions and from the ether phase a white solid (6.0 g.) was obtained m.p. 104-105° decomposition, soluble in acetone but insoluble in n-hexane and toluene.

Analysis Found: C, 29.9%; H, 4.8%.

$C_{12}H_{22}PdAs_2$ requires C, 34.1%; H, 5.2%.

$C_{11}H_{19}PdAs_2$ Br requires C, 27.1%; H, 3.9%.

It was concluded therefore that a mixture of di- and mono-methyl compounds had been isolated and that it would be easier to repeat the reaction than try to isolate the individual components from the mixture.

2. To the dibromide (10.0 g., 0.018 moles) suspended in ether (200 mls.) at (-50°) was added methyl-lithium (0.042 moles) in ether (22 mls.). The flask was allowed to

warm up to room temperature when a colour test was negative. The flask was cooled and more methyl-lithium was added (5 mls.) and on warming a colour test was positive. The reaction mixture was stirred for 90 minutes and no solid material was visible after this time. A colour test was still positive.

The reaction mixture was hydrolysed at 0^{o} with water (100 mls.). The ether phase remained clear, and the reaction mixture was filtered and liquid phases were separated.

Ether phase

This was evaporated and a light yellow compound was obtained, soluble in acetone, slightly soluble in benzene but insoluble in n-hexane. The compound remained unchanged for three weeks in its initial impure state.

1-2 g. were recrystallized by cooling from acetone as white needles which were collected under nitrogen, washed with cold solvent and dried. On transferring to a nitrogen purged, three-necked flask the compound turned brown immediately.

The recrystallization was repeated but this time the storage flask was kept at -78^{o}. However the solid turned brown on standing overnight in a refrigerator and the solid isolated is clearly unstable in a pure state. m.p. 105^{o} (decomposition).

An analysis was carried out by converting a weighed sample of the product, dissolved in ethanol, to the initial dibromide by the action of aqueous ethanolic hydrobromic acid.

0.2894 g. of the dimethyl compound (0.684 mmoles) gave 0.3574 g. of the dibromide (0.65 mmoles).

Analysis Found: Pd, 24.84%.

$C_{12}H_{22}As_2Pd$ requires Pd, 25.36%.

21. The reaction between $C_6H_4(AsMe_2)_2PdBr_2$ and phenyl-lithium

The dibromide (11.0 g., 0.02 moles) in ether (200 mls.) in a three-necked flask was cooled (-50°) and phenyl-lithium (0.042 moles) in ether (35 mls.) was added during 20 minutes. The solution was stirred for 20 minutes at -40° when colour test was negative and a 30% excess of phenyl-lithium was then added but colour test remained negative. The flask was cooled (0°) and water (100 mls.) was added.

Observations

No colour change was apparent at the low temperature after addition of phenyl-lithium. At room temperature before addition of water there was no sign of decomposition; the ether phase was clear, light brown in colour and a light brown solid was present. Addition of water produced rapid and pronounced blackening of the contents of the flask.

Working up of reaction products

Filtering through a Buchner funnel gave a black solid (5) on the filter, a black ether phase and a yellow aqueous phase. The two liquid phases were separated.

The ether phase

Before pumping dry a little of the solution was passed through an alumina column. This removed most of the black material and the liquid which passed through the column contained a white solid (3); recrystallized from ethanol, m.p. 66-67°.

The rest of the ether phase was evaporated by pumping at about 0.1 mm. and an orange-red solid (1) (2.3 g.) was obtained which was washed with n-hexane and a light brown solid (2) was left behind (210 mg.) m.p. 60-70° impure. The hexane washings on evaporation and recrystallization of the solid deposited, from alcohol, gave a white solid (4) m.p. 65°, 395 mg.

The two solids (3 and 4) were combined and recrystallized from alcohol; m.p. 65°, mixed m.p. with diphenyl 65-67°. Total amount of diphenyl was 670 mg.

The solid (2) was, insoluble in n-hexane, methylcyclohexane, or petroleum ether, soluble in acetone and benzene.

The solid phase (5)

15.3 g. of impure solid were obtained which remained damp after pumping at 0.1 mm. for two hours.

It was insoluble in n-hexane, ethanol and benzene, soluble in acetone. Evaporation of the acetone solution produced a grey solid which did not melt below 325°.

The whole of (5) was extracted with n-hexane (no solid obtained on evaporation) and the solid was dried and washed with acetone. This produced a black acetone solution and an insoluble orange compound (6) was left behind (3 g.). This solid (6) looked like starting material. Confirmation of this was difficult owing to the high melting point of the initial dibromide and the fact that the infrared spectrometer had not been installed and spectra could not be compared.

Acetone washings of (5)

Small scale experiments on the acetone solution showed a light coloured component to be present and attempts were made to remove the black component. Elution through alumina columns and filtration through hyflo still gave black solutions. Slow evaporation of the acetone solution gave a light coloured compound (0.58 g.) which was recrystallized from alcohol/acetone, m.p. 340-350° decomposition. The

compound gave a positive test for palladium. More recrystallizations were carried out and a test for halogen was positive.

Analysis Found: C, 21.0%; H, 2.9%.

$C_{22}H_{26}As_2Pd$ requires C, 48.3%; H, 4.79%.

$C_{16}H_{21}As_2BrPd$ requires C, 34.95%; H, 3.85%.

22. The reaction between dibromo-o-diethylphosphinephenyldimethylarsinepalladium, o-$PEt_2C_6H_4AsMe_2PdBr_2$, and methylmagnesium bromide

The dibromide (10.7 g., 0.02 moles) was placed in a 500 ml. three-necked flask and ether (200 mls.) was added. The flask and contents were cooled (-55°) and methylmagnesium bromide (0.045 moles) in ether (44.5 mls.) was added during 20 minutes. The reaction mixture was stirred for 15 minutes at the low temperature and after warming to room temperature was stirred for a further 15 minutes. After cooling (0°), water (100 mls.) was added.

Observations

The initial dibromide was present as a green-yellow suspension in the ether and no change took place during addition of the Grignard solution. On reaching -3° the solid matter disappeared leaving behind a clear colourless ether phase. This did not change until water was added after

which a white precipitate appeared.

Working up of reaction products

The reaction mixture was filtered (Whatman No. 4) and the clear almost colourless phases were separated. A white solid (I) was collected on the filter and the two liquid phases were separated.

Ether Phase

This was pumped dry and a white solid (II) (3 g.) was obtained which darkened slightly on standing.

Solubility of (II)

Insoluble in n-hexane, and methylcyclohexane; soluble in acetone, methyl ethyl ketone and ethanol and in hot benzene. Effervescence occurred in ethanol with decomposition.

Recrystallization was attempted from toluene in a double Schlenk tube under nitrogen. The toluene was warmed, filtered and allowed to cool. No crystals appeared and the solution darkened and on concentrating decomposition became more pronounced.

Solid I

This was dried and found to be soluble in hot methyl ethyl ketone, ethanol and toluene but insoluble in hot or cold n-hexane or cyclohexane.

The compound recrystallized beautifully as light yellow needles (III) (m.p. 184°) from hot ethanol (no decomposition but see below).

Analysis Found: C, 26.0%; H, 3.8%.

$C_{12}H_{20}PAsBr_2Pd$ requires C, 26.85%; H, 3.8%.

A test for halogen on (III) was positive.

The ethanolic mother liquor was almost colourless and this solution was cooled in acetone/CO_2 and a further quantity of light coloured crystals was obtained (IV) m.p. 265° decomposition.

Analysis Found: C, 29.2%; H, 4.4%.

$C_{13}H_{23}PAsBrPd$ requires C, 33.1%; H, 4.91%.

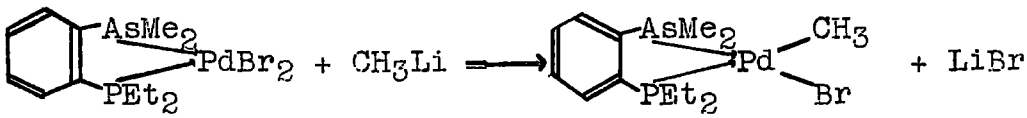
A small amount of (I) was recrystallized from hot toluene but the solution darkened.

A few mgs. of IV were recrystallized from hot ethanol but the solution rapidly turned black and on cooling yellow needles and a white powder came out of solution.

Conclusion

There has obviously been formation of a methyl derivative but attempts to separate it from starting material were not successful.

25. The preparation of o-diethylphosphinephenyldimethylarsine(methyl)bromopalladium



The dibromide (10.7 g., 0.02 moles) was suspended in ether (150 mls.) at -50° and methyl-lithium (0.041 moles) in ether (26 mls.) was added. The solution was allowed to warm up to room temperature at which it was stirred for 30 minutes. Hydrolysis at 0° followed and the reaction mixture was filtered.

A grey powder (I, 2 g.) remained on the filter and the liquid phases were separated.

Ether phase

On evaporation a white solid (II, 6 g.) was isolated.

Solubility

Insoluble in n-hexane, methylcyclohexane, and petroleum ether 80-100°; soluble in acetone, methanol, toluene, ethyl acetate. Recrystallized from acetone as a white powder, m.p. 98-100° (decomposition).

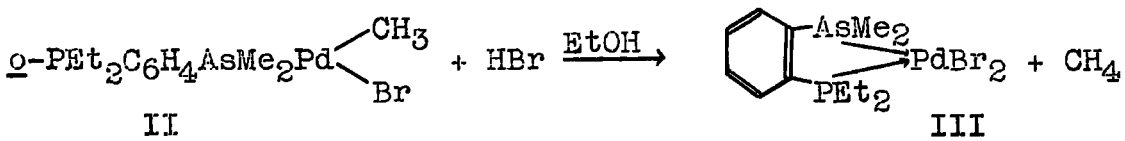
Analysis Found: C, 33.5%; H, 4.8%.

$C_{13}H_{23}PPdAsBr$ requires C, 33.1%; H, 4.91%.

Yield 6 g., 0.0127 moles, 64%.

Reaction with alcoholic hydrobromic acid

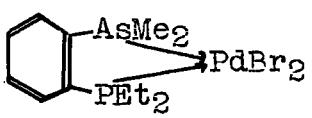
When an aqueous alcoholic solution of hydrobromic acid was added to an alcoholic solution of the product an immediate yellow precipitate appeared. This indicates the reaction



II III

0.6997 mmoles of the reaction product (II) gave, after reaction with excess aqueous alcoholic HBr, 0.7004 mmoles of the dibromide (III). An infrared spectrum of (III) and authentic dibromide were identical.

24. The reaction between mesitylmagnesium bromide and



To a suspension of the dibromide(13.4 g., 0.025 moles) in ether (150 mls.) in a 500 ml. three-necked flask was added mesitylmagnesium bromide (0.055 mole) in ether (66 mls.) at -56°. The mixture was stirred at the low temperature for 30 minutes and then allowed to warm up. After stirring at 10 to 15° for 30 minutes the mixture was cooled (0°) and water (100 mls.) was added.

Observations

A temperature rise of 2 to 3° occurred immediately on adding the Grignard solution but no apparent change was visible at the low temperature. By 14° the contents of the flask looked much darker in colour and a chocolate brown precipitate was present in the flask. The colour deepened further after 30 minutes stirring, and addition of water produced rapid darkening.

Working up of products

The reaction mixture was filtered and a dark solid (I) obtained. The phases were separated.

Solid I

This was washed with water and ether, 7.5 g., were obtained after drying. 1-2 g. of solid were placed on the sintered disc of an extraction apparatus and the solid was extracted with ethanol. A small amount of a very soluble material appeared to come through first and the alcohol in the pot was changed. After extracting for five hours and allowing the alcohol to cool a light yellow crystalline compound came out of solution; m.p. 335° (decomposition); darkening 315-320°; not depressed when mixed with the initial dibromide.

About 20-30 mg. of a grey solid were obtained on

covering the remainder of the impure solid (I) with acetone, decanting, and evaporating the solvent.

Ether phase

This was dried ($MgSO_4$) and ether was pumped off at 12 mm. initially and finally at about 0.01 mm. but the compound (II) would not dry. The colour was coal black and in the bottom of the flask there was present about 4 mls. of a heavy oily liquid. This was probably the most decomposed ether soluble material so far encountered. An alumina column in benzene was prepared and about 1 g. of the oil solid (II) was placed on top of the alumina in about 3 mls. of benzene and the material was eluted with benzene. A clear slightly yellow band immediately left the dark top layer and continued elution gave various fractions until the decomposed material worked its way down the column. Only a few mgs. of material were obtained.

A small amount of the oil/solid was washed with ethanol and a light, white-grey solid was left behind. The ethanol was black in colour. The whole of the material (II) from the ether phase was treated similarly and 1.5 g. of grey solid (III) were obtained, soluble in hot nitromethane, hot methylcyclohexane but insoluble in benzene in the cold.

About half of (III) was recrystallized from methylcyclohexane by heating, filtering the solution, cooling, collecting the solid on a filter and washing with pure solvent. A light yellow crystalline solid was obtained in solution but on isolating turned to an amorphous powder, m.p. 174-177° (decomposition). Clear single crystals in solution became opaque in air. The mother liquor was evaporated.

The same procedure was employed using nitromethane and a white powder, m.p. 177-178° (decomposition) was obtained.

The material which had been once recrystallized from methylcyclohexane was recrystallized again from the same solvent, and a white amorphous powder was obtained, m.p. 177° (decomposition).

Analysis Found: C, 53.1%; H, 6.0%.

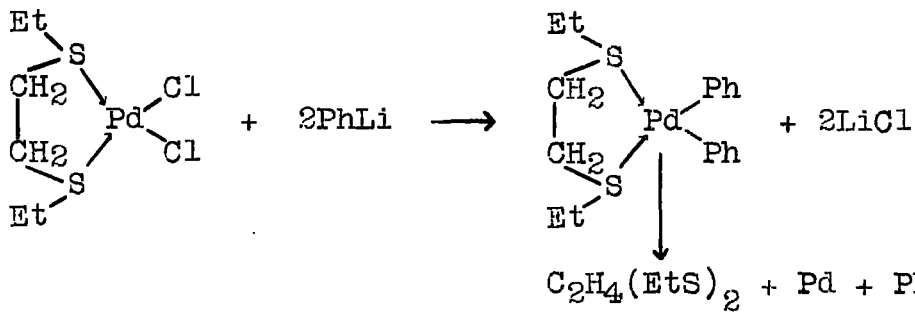
$C_{30}H_{42}PdAsP$ requires C, 58.6%; H, 6.9%.

$C_{21}H_{31}PdAsPBr$ requires C, 43.7%; H, 5.4%.

Thus it would appear that an impure specimen of the dimesityl derivative has been isolated which is reasonably soluble in some solvents.

iii. With sulphides as donor

25. The reaction between 1,2-di(ethylthio)ethanedichloropalladium and phenyl-lithium



The dichloride (11.5 g., 0.035 moles) was suspended in ether (250 mls.) in a 500 ml. flask, cooled to -60°. Phenyl-lithium (0.07 moles) was added in ether (77 mls.) during 35 minutes. The first few mls. of phenyl-lithium solution produced vigorous reaction, the temperature rising to -55° after four minutes and the colour changing from bright-yellow to olive-green. After addition of the phenyl-lithium the flask was allowed to attain room temperature when a colour test on a now black reaction mixture was negative. Water (100 mls.) was added and the mixture stirred for a further five minutes.

Working up reaction products

The two phases were filtered and the black residue which remained was dried at 120° for 20 hours. 5.2 g. Pd(+ moisture) were obtained (100% Pd recovery).

The liquid phases were then separated, the ether phase having a faint yellow colour and the aqueous phase being orange. The ether phase was evaporated to dryness and the

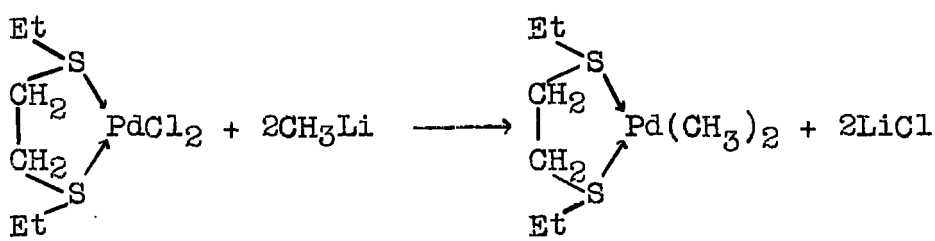
white solid remaining was recrystallized from alcohol as white plates, m.p. 68-69°; mixed m.p. with diphenyl 67-69°. 2.1 g. (39%) diphenyl obtained.

On warming the aqueous phase, a brown solid was deposited which was soluble in ammonium sulphide to give a dark red solution. 0.2 g. of this solid, probably palladium sulphide were obtained.

Conclusions

Complete decomposition has taken place during reaction. Presence of diphenyl in fairly large yield may indicate formation of an unstable phenyl-palladium compound.

26. The reaction between 1,2-di(ethylthio)ethanedichloro-palladium and methyl-lithium



To the dichloride (6.5 g., 0.02 moles) suspended in ether (150 mls.) at -50° was added methyl-lithium (0.0405 moles) in ether (26 mls. of a 1.57 N solution). After warming up to room temperature and stirring for twenty minutes the reaction mixture was hydrolysed with water (100 mls.) at 0°.

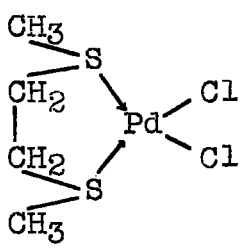
The products were filtered and the liquid phases separated.

Ether phase

On evaporation an oil was left behind which was very unstable. Metallic palladium was deposited and there was a very strong smell of the disulphide.

It was, however, possible to take an infrared spectrum of the oil and this clearly showed the presence of the $Pd-CH_3$ group. Frequencies characteristic of the $Pd-CH_3$ bond occurred at 518 and 502(s) $cm.^{-1}$

27. The preparation of 1,2-di(methylthio)ethanedimethyl-palladium



$$+ 2CH_3Li \longrightarrow C_2H_4(CH_3S)_2Pd(CH_3)_2 + 2LiCl$$

To the dichloride (12.0 g., 0.04 moles) suspended in ether (175 mls.) at -50° was added methyl-lithium (0.084 moles) in ether (36 mls. of a 2.35 N solution). After addition of the methyl-lithium the reaction mixture was stirred at -10° for 90 minutes before being allowed to warm up to room temperature when a colour test was negative.

An excess of 30% methyl-lithium was added before a positive colour test was obtained.

Hydrolysis followed at 0° with water (100 mls.) and the phases were filtered and separated.

It was observed that no colour change took place below -10° but above this temperature the yellow colour of the dichloride disappeared.

The ether phase

Evaporation and drying gave a buff coloured solid (4-5 g.).

Solubility

Insoluble in n-hexane and methylcyclohexane, slight solubility in ethanol but decomposed on warming, soluble in benzene, acetone and methyl ethyl ketone.

About 0.25 g. was dissolved in acetone, the solution filtered, cooled and a light coloured compound was isolated on a filter, m.p. 75° (decomposition).

A small quantity was dissolved in ethanol at room temperature and aqueous ethanolic hydrochloric acid was added. An orange solid, m.p. 238°, was precipitated. This indicates the reaction

$$C_2H_4(CH_3S)_2Pd(CH_3)_2 + 2HCl \xrightarrow{EtOH} C_2H_4(CH_3S)_2PdCl_2 + 2CH_4$$

is taking place.

Reaction between $C_2H_4(CH_3S)_2Pd(CH_3)_2$ and hydrochloric acid

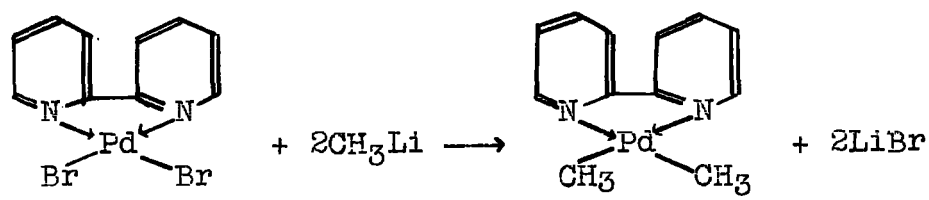
The dimethyl compound (0.0520 g., 0.201mmoles) underwent reaction with aqueous ethanolic hydrochloric acid to give methane (8.72 N-ccs.) and the dichloride (0.0604 g., 0.201 mmoles), m.p. 238-240°, mixed with authentic dichloride 239°. $C_2H_4(CH_3S)_2Pd(CH_3)_2$ required 8.99 N-ccs. methane.

Dipole moment

The dipole moment of $C_2H_4(CH_3S)_2Pd(CH_3)_2$ is 6.4 D.

iv. With nitrogen as donor

28. Preparation of dipyridyldimethylpalladium



To the dibromide (0.024 moles; 10.0 g.) suspended in ether (200 mls.) at -60° was added methyl-lithium (0.065 moles) and the reaction flask was allowed to warm up. A colour test at room temperature was negative and the flask was cooled again and more methyl-lithium was added to a total amount of 3 mols. On warming up a colour test was positive and the suspension was stirred at room temperature for one hour. A dark coloured solid was present at this stage.

The mixture was hydrolysed with water (100 mls.) and filtered. A dark solid (I) collected on the filter and the liquid phases were separated. The ether phase was found to contain only a small amount of material.

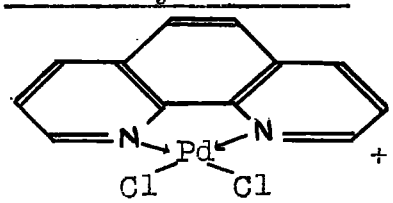
Solid I

Soluble in acetone in the cold, more so on warming (no decomposition), slightly soluble in benzene but insoluble in n-hexane. The impure material was recrystallized from acetone by cooling as beautiful orange needles, m.p. 153° (decomposition). This solid (II) did not change when left standing on a filter paper in the air for a week and gave every indication of being a very stable compound. It underwent a smooth conversion to the dichloride when an alcoholic solution of hydrochloric acid was added to an acetone solution of the product. A gas was evolved.

0.72 mmoles of II gave 0.71 mmole of dipyPdCl_2.

Yield Recrystallized once from acetone 4 g., 57%.

29. The reaction between phenanthrolinedichloropalladium and methyl-lithium



+ $2CH_3Li$ ⟶ (phen)Pd$(CH_3)_2$ + 2LiCl

To the dichloride (7.1 g., 0.02 moles) suspended in ether (200 mls.) was added methyl-lithium (0.045 moles) in ether (33 mls.) at -55°. On warming up to room temperature the colour deepened to dark brown and a colour test was positive. The solution was stirred for one hour and then hydrolysed with water (100 mls.).

The mixture was filtered and a dark solid (I, 3 g.) was collected. The phases were separated.

Ether phase

On evaporation a black tarry solid (3.7 g.) was obtained.

Solid I

This was very dark in colour and would not dry. Soluble in toluene, acetone and THF to give black solutions, slightly soluble in benzene and insoluble in n-hexane and propanol.

0.5 g. of solid (I) was dissolved in THF to give a black solution which was filtered. A dark solid remained on the filter. On cooling the filtrate a brown, apparently crystalline solid was precipitated which was collected on a filter and dried on the glass sinter by pumping at 12 mm. However on touching the solid with a spatula it turned into a dark oil. The filtrate on standing overnight deposited a light brown solid (II).

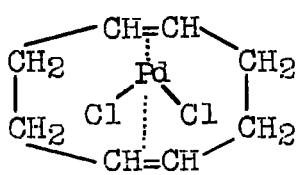
The bulk of impure (I) was recrystallized as above and the solid obtained after filtering the cooled solution was dried on a water pump. Again the solid turned into an oil and the semi-solid was transferred to an alumina column and eluted with THF. The column broke up but it was possible to collect a yellow band which proceded the decomposed material down the column. Only a few mgs. of material were obtained and the solid decomposed.

Spectrum of solid (II)

This showed characteristic CH_3 frequencies in the 3μ region at 2951, 2924, 2881 cm.$^{-1}$ and a characteristic CH_3 frequency at 1151 cm^{-1} (8.69μ) but no Pd-CH_3 frequency at 20μ.

v. With dienes as donor

30. The preparation of cyclo-octa-1,5-dienedimethylpalladium



+ $2CH_3Li \longrightarrow$ cyclo-octa-1,5-dienedimethylpalladium + 2LiCl

To the dichloride (8.5 g., 0.03 moles) suspended in ether (150 mls.) at -40^{o} was added methyl-lithium (0.066 moles) in ether. The reaction mixture was allowed to warm up to room temperature when the contents of the flask

looked very black. The mixture was hydrolysed, filtered and the liquid phases were separated. Metallic palladium remained on the filter.

The ether phase

This was light yellow in colour and on evaporating a small amount of white solid was left behind. This tended to darken at room temperature and it was stored at -78°.

Recrystallization was carried out by dissolving in ether in a Schlenk tube at room temperature under nitrogen and filtering into a pre-cooled (-78°) limb. These operations were carried out with all possible speed. The filtrate was cooled to -78° and the small amount of liquid in the first limb soon turned dark and a palladium mirror formed. A white crystalline solid was precipitated and this was filtered off, washed with cold ether, dried and stored under nitrogen at -78°.

Analysis Found: 43.2% , palladium

$C_{10}H_{18}Pd$ requires Pd,43.56%

Conversion to the dichloride

A weighed sample (0.4790 g., 1.955 mmoles) was dissolved in ether and ethanolic hydrochloric acid was added. A gas was evolved and on standing yellow needles crystallized out. All the material was transferred to a weighed crucible and

solvent was evaporated off on a water bath. A yellow crystalline residue remained (0.5400 g., 1.89 mmoles). The infrared spectrum of this material was identical with cyclo-octa-1,5-dienedichloropalladium. Thus the following reaction has occurred:-

cyclo-octa-1,5-dienedimethylpalladium + 2HCl ⟶ cyclo-octa-1,5-dienedichloropalladium + $2CH_4$

Copper

The preparation of triethylphosphinephenylethynylcopper

a. The preparation of phenylethynylcopper[50]

To an ammoniacal solution of cuprous chloride (0.5 moles, 46.4 g.) was added slowly and with good stirring a solution in alcohol (400 mls.) of phenylacetylene (41 g., 0.4 moles). The bright yellow acetylide was collected and washed with water, benzene, alcohol and acetone. It was dried at 40°. Yield 53.4 g., 80%.

b. The reaction between phenylethynylcopper and triethylphosphine

$$PhC{\equiv}CCu + PEt_3 \longrightarrow PhC{\equiv}CCu \leftarrow PEt_3$$

Phenylethynylcopper (0.02 moles, 3.3 g.) was placed in the left hand limb of a double Schlenk tube, under nitrogen and cyclohexane (45 mls.) was added followed by

triethylphosphine (0.02 moles, 4 mls., excess). Warming (44-55°) caused all the acetylide to go into solution, which was brown in colour having in it a greenish impurity. Filtration into the right hand limb gave a golden brown solution and concentration produced a yellow solid which was collected on the filter, washed and dried. Recrystallization was carried out from n-hexane.

Analysis Found: C, 59.1%; H, 7.2%; Cu, 22.21%.

$C_{14}H_{20}PCu$ requires C, 59.6%; H, 7.1%; Cu, 22.47%.

Gold

1. Preparation of triethylphosphinemonomethylgold

$$Et_3P \longrightarrow Au\text{-}Cl + CH_3Li \longrightarrow Et_3P \longrightarrow Au\text{-}CH_3 + LiCl$$

To the monochloride (3.6 g., 10.3 mmoles) suspended in ether (100 mls.) at -50° was added methyl-lithium (5 mls. of a 2.35 N solution in ether). On warming up to room temperature a colour test was positive and more methyl-lithium (10%) was added to the cooled solution.

After warming to room temperature the reaction mixture was hydrolysed and filtered. Two clear phases were obtained and these were separated.

Ether phase

The ether was pumped off and a white solid (2.7 g.)

obtained, soluble in n-hexane, benzene, acetone, ethanol, methanol and petroleum ether.

A small amount was recrystallized from n-hexane; m.p. 60-62°.

Analysis Found: C, 25.4%; H, 5.4%.

$C_7H_{18}PAu$ requires C, 25.4%; H, 5.5%.

Yield 80%, 8.2 mmoles.

Reaction with ethanolic hydrochloric acid

$$Et_3P \longrightarrow Au\text{-}CH_3 + HCl \longrightarrow Et_3P \longrightarrow Au\text{-}Cl + CH_4$$

When ethanolic hydrochloride acid was added to a solution of the monomethyl compound in ethanol, rapid effervescence occurred and a white crystalline solid was precipitated, m.p. 84-85°; m.p. authentic $Et_3P \longrightarrow Au\text{-}Cl$ 86°.

Structure The dipole moment was found to be 5.5 D, indicating a linear structure.

2. Preparation of triethylphosphinemonophenylgold

$$Et_3P \longrightarrow AuCl + PhLi \longrightarrow Et_3P \longrightarrow AuPh + LiCl$$

The monochloride (5.0 g., 0.0147 moles) was suspended in ether (150 mls.) at -60° and phenyl-lithium (0.015 moles) was added in ether (23 mls.). The flask was then allowed to warm up. Difficulty was experienced with the Michler's ketone colour test; metallic gold was deposited and only a transient green colour was obtained. 2 mols. of phenyl-lithium were therefore added and the mixture was hydrolysed

with water (100 mls.).

No change occurred during addition of the lithium compound but on hydrolysis, two clear and colourless phases were obtained.

On filtering through a No.3 sintered disc no solid matter was seen to be present and the phases were separated and the ether phase was evaporated to dryness. At this stage it was noted that the aqueous phase had developed a brown colour due to metallic gold and the brown solid material was collected (0.8 g.). Clearly this has come from a water soluble gold compound, possibly $\left[Ph_2Au \leftarrow PEt_3\right]^- Li^+$

On evaporation of the ether phase a white solid (4.0 g.) was obtained. This was soluble in methanol and n-hexane, m.p. 68°; it was recrystallized as large white plates from methanol.

Analysis Found: Au, 50.43%.

$C_{12}H_{20}PAu$ requires 50.24%.

Yield 10.02 mmoles 70%.

Reaction with aqueous ethanolic hydrochloric acid

When aqueous ethanolic hydrochloric acid was added to an alcoholic solution of the monophenyl compound

there was no deposition of the monochloride.

4. Infrared Spectra

Introduction

The infrared spectra were obtained on the compounds isolated using the KBr or KI disc technique and a Grubb Parsons, GS 2A Grating Spectrometer.

At the beginning of the present investigation no data had been published on the spectra of organopalladium compounds.

1. Methyl derivatives

a. 5μ - 24μ region

A comparison of the spectra of $(Et_3P)_2PdBr_2$ and $(Et_3P)_2Pd(CH_3)Br$

$(Et_3P)_2PdBr_2$ Frequency (cm^{-1})	$(Et_3P)_2Pd(CH_3)Br$ Frequency (cm^{-1})
1449	1449
1408	1408
1371	1370
1248	1248
1236	1234
	1162+
1032	1033
1029	1025
1008	1010
1000	1000
984	sh
763	762
728	723
709	704
629	627
	510+

From this comparison of the spectra it is obvious that there are two main differences; one at 1162 cm^{-1} the other at 510 cm^{-1}.

Region 1160 cm^{-1}, 8.62μ

In the table below are given the data on this region obtained for several organopalladium compounds. cis-$(Et_3P)_2Pt(CH_3)_2$ has been added for comparison.

Table I

Compound	Frequency, cm^{-1}
$(Et_3P)_2Pd(CH_3)_2$	1164
$(Et_3P)_2Pd(CH_3)Br$	1162
$(Et_3P)_2Pd(CH_3)I$	1159
$(Et_3P)_2Pd(CH_3)SCN$	1180
$(Et_3P)_2Pd(CH_3)CN$	1161
n-$Bu_3P(CH_3)Pd(SEt)_2Pd(CH_3)P$n-$Bu_3$	1148
$(Ph_2PCH_2CH_2PPh_2)Pd(CH_3)_2$	1149
$(Ph_3P)_2Pd(CH_3)_2$	1129
o-$C_6H_4(AsMe_2)_2Pd(CH_3)_2$	1160
$C_2H_4(EtS)_2Pd(CH_3)_2$	1160
$C_2H_4(CH_3S)_2Pd(CH_3)_2$	1168
dipy $Pd(CH_3)_2$	1174
cis-$(Et_3P)_2Pt(CH_3)_2$	1177*

* Compound supplied by Dr. J. Chatt.

The region 500 cm^{-1}, 20μ

In the case of the simple phosphine, thiol and nitrogen donors, this was a very good region to investigate because of the absence of any other absorptions, but in the case of the more complex aryl phosphines the region is difficult to investigate owing to absorption by the phosphine.

Below is given a table of the frequencies obtained in the region under consideration for a series of cis- and trans- complexes. Spectral data for cis-$(Et_3P)_2Pt(CH_3)_2$ and $Et_3P \longrightarrow AuCH_3$ are included as they provide useful comparisons.

Compound	Structure	Frequency cm^{-1}.
$(Et_3P)_2Pd(CH_3)Br$	trans	510
$(Et_3P)_2Pd(CH_3)SCN$	trans (probably)	526
$(Et_3P)_2Pd(CH_3)CN$	trans	502
$(n\text{-}Bu_3P)_2(CH_3)_2Pd_2(SEt)_2$	trans	501
$Et_3P \longrightarrow AuCH_3$	linear	532
$(Ph_3P)_2Pd(CH_3)_2$	cis	529, 482
$C_2H_4(EtS)_2Pd(CH_3)_2$	cis	518, 502
$C_2H_4(MeS)_2Pd(CH_3)_2$	cis	525, 512
Dipy $Pd(CH_3)_2$	cis	534, 522

cont.

$(Et_3P)_2Pt(CH_3)_2$		cis	523, 506
o-$C_6H_4(AsMe_2)_2Pd(CH_3)_2$		cis	498), 435 489)
$(Et_3P)_2Pd(CH_3)_2$	m.p.	probable structure	
	44°	cis	491, 457
	63°	cis	501, 451
	71-72°	trans	501
	43-45°		500

b. 2.5μ - 3.7μ region

In order to see clearly the frequencies due to the methyl group bonded to the central metal atom, the spectra of those compounds having no other methyl groups in the molecule were studied carefully in the 3μ region.

Parent dihalide	Frequency cm^{-1}	dimethyl compound	Frequency cm^{-1}
$dipyPdCl_2$	3108 3072 3050	$dipyPd(CH_3)_2$	3103 3067 3041 2919 2842
$(Ph_3P)_2PdCl_2$	3066 3052 3006	$(Ph_3P)_2Pd(CH_3)_2$	3073 3052 3036 3001 2945 2876

In two other cases, listed below it has been possible to detect a very low aliphatic CH stretching frequency when

comparing the organometallic compound with the parent halide.

Halide	Frequency cm^{-1}	methyl derivative	Frequency cm^{-1}
o-$C_6H_4(AsMe_2)_2PdBr_2$		o-$C_6H_4(AsMe_2)_2Pd(CH_3)_2$	
	3046		3052
	3003		3032
	2992		2982
	2968		2935
	2911		2913
			2854+
$Et_3P \longrightarrow AuCl$		$Et_3P \longrightarrow AuCH_3$	
	2962		2963
	2950		2927
	2904		2910
	2873		2872
			2853+

2. Phenyl derivatives

These show typical absorption peaks, for example:

Compound	Frequency cm^{-1}	Group
$(Et_3P)_2PdPh_2$	3125	$C_{\overline{ar}}H$ stretching
	3113	
	3038	
	3016	
$(Et_3P)_2Pd(C{\equiv}CPh)_2$	3076	
	3071	
	3049	
	3029	
$Et_3P \longrightarrow AuPh$	3050	
	3024	
	3006	
$(Et_3P)_2PdPh_2$	1618,1564,1464	C=C skelatal in-plane vibration
$(Et_3P)_2Pd(C{\equiv}CPh)_2$	1590,1562	
$Et_3P \longrightarrow AuPh$	1570	
$(Et_3P)_2PdPh_2$	735, 706	$C_{\overline{ar}}H$ out-of-plane deformation
$(Et_3P)_2Pd(C{\equiv}CPh\ NO_2\text{-}\underline{p})_2$	858	

3. Substituted phenyl derivatives

$(Et_3P)_2Pd(C{\equiv}CC_6H_4NO_2p)_2$	$(Et_3P)_2Pd(C{\equiv}C\text{-}Ph)_2$	Group
Frequency cm^{-1}	Frequency cm^{-1}	
2092	2097	-C≡C- Usually 2260-2190 cm^{-1}
1585 1507	1590 1562	C=C skelatal in-plane vibration
1353		Aromatic NO_2 sym. frequency; usually 1350 cm^{-1}

4. Cyanide and thiocyanate groups bonded to palladium

$(Et_3P)_2Pd(CH_3)CN$	$(Et_3P)_2Pd(CH_3)SCN$	Group
Frequency cm^{-1}	Frequency cm^{-1}	
2127		C≡N[51]
2117		Dm $K_2Pd(CN)_4H_2O$, 2143 cm^{-1}
	2083	SCN[52] 2090-2020 cm^{-1}

Conclusions to be drawn from the infrared data

The data collected from several organo-palladium, -platinum and -gold compounds indicates that, while the phenyl and para-substituted phenyl derivatives absorb in regions characteristic for these groups the methyl derivatives have absorptions peculiar to the methyl group bonded to these metals.

In all cases it has been possible to make a direct

comparison between the parent mono- or di- halide and the methyl derivatives.

1. Phenyl and p-substituted phenyl compounds

In the case of the di(phenylethynyl) derivatives it is clear from the acetylenic absorption frequency of 2092 or 2097 cm^{-1} that the triple bond remains intact and therefore is not very strongly affected by bonding to palladium.

Both the phenyl and p-substituted phenyl derivatives show the normal absorptions for the $C_{ar}-H$ stretching frequency (about 3030 cm^{-1}), C=C skelatal in-plane vibrations (about 1600, 1550 and 1450 cm^{-1}) and $C_{ar}-H$ out-of-plane deformation frequencies (about 700 or 850 cm^{-1}).

2. Methyl derivatives

a. 2.5-3.7 μ region

Basically, in this region, one has the normal aliphatic C-H stretching frequency at 2900 and 2850 cm^{-1} but it is possible in some cases to detect a low frequency at 2854 cm^{-1} apparently characteristic of the methyl attached to the metal. This low frequency is seen clearly in the spectra of o-$C_6H_4(AsMe_2)_2Pd(CH_3)_2$, $Et_3P \rightarrow AuCH_3$, dipy$Pd(CH_3)_2$ and $(Ph_3P)_2Pd(CH_3)_2$.

b. 8.6μ region

Absorption in the region 1129-1180 cm^{-1} must be due to the presence of the methyl group on the central metal atom. The spectra of all the methyl derivatives obtained show a well defined absorption in this region, and this absorption is absent in the parent halide. As detailed in Table I the data were obtained from a wide variety of compounds. In no case was absorption in this region missing for a knownmethyl derivative.

It is not unreasonable therefore to assign this absorption to a methyl deformation frequency. The absorption occurs where one might expect it for a methyl group bonded to a heavy metal. Dr. N. Sheppard (Cambridge) is of the opinion that this frequency can be assigned as described above.

c. 20μ region

We ascribe the absorption observed in most methyl-palladium compounds in this region to a Pd-methyl stretching frequency. There seems no other reasonable interpretation of this absorption.

3. Cyanide and Thiocyanate

The values obtained for the C≡N stretching frequency,

2127 cm^{-1} and the SCN stretching frequency, 2083 cm^{-1}, agree with those reported in the literature.[51,52]

Discussion

Group VIII metals

Some general remarks

The investigation has shown that it is possible to prepare relatively stable organometallic compounds of nickel, platinum and palladium, by the action of Grignard reagents or organolithium compounds on the complex metal halides.

In the case of the first two metals the investigation has confirmed the findings of J. Chatt and B.L. Shaw,[48,53,54] in that with nickel, the di(phenylethynyl) derivative $(Et_3P)_2Ni(C{\equiv}CPh)_2$ is stable whereas the styryl derivative could not be isolated.

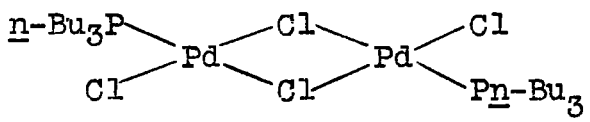
Two very stable platinum-phenyls, $(Et_3P)_2PtPh_2$ and $C_2H_4(EtS)_2PtPh_2$, have been prepared, in contrast to the organopalladium compounds which are rather unstable and of which only one or two remain undecomposed at room temperature for any length of time. As described in the experimental section the organopalladium compounds isolated are liable to sudden and rapid decomposition, especially in solution. The stability of the compounds has been found to vary according to the nature of the donor group and

the organic group.

The donor group

As might be expected, phosphines have been found to give the most stable complexes. With triethylphosphine as the donor molecule, mono- and di-methyl, mono- and di-phenyl, di(phenylethynyl), mesityl and various p-substituted phenyl derivatives have been prepared. The mono- and di-methyl compounds are sufficiently stable to allow exchange and replacement reactions to be carried out.

A single phosphine co-ordinated to the palladium atom is not sufficient to cause stability as was demonstrated by the decomposition which occurred in the reaction between methyl-lithium and



When the chlorine bridge was replaced by two -SEt groups a stable dimethyl derivative was obtained.

With triphenylphosphine as donor a less stable and less soluble (compared with the triethylphosphine analogue) dimethyl derivative was obtained.

The chelating diphosphine $C_2H_4(PPh_2)_2$ afforded a dimethyl compound, more stable (and more soluble) than the triphenylphosphine derivative.

The stronger stabilizing effect of phosphorus relative to arsenic is shown by a comparison of the ease of formation and isolation of o-$C_6H_4(AsMe_2)_2$ $Pd(CH_3)_2$ and o-$PEt_2C_6H_4AsMe_2Pd(CH_3)Br$. The diarsine derivative, when isolated in a pure state, turned brown almost immediately whereas the phosphine-arsine compound was reasonably stable.

All methyl palladium compounds containing sulphur as donor (as a chelating disulphide) were rather unstable and no aryl derivatives could be obtained. The stabilization effected by sulphur is evidently weak in comparison with that effected by phosphorus as might be expected from the ready displacement of sulphides from palladium complexes by phosphines and arsines. The only crystalline methyl palladium compound prepared was that derived from 1,2-di(methylthio)ethane; the 1,2-di(ethylthio)ethane analogue melted below room temperature.

The nitrogen donors tried were found to behave inconsistently. Thus a relatively stable orange compound, dipy$Pd(CH_3)_2$ was isolated, and remained unchanged in the air over long periods of time but the ortho-phenanthroline analogue, (phenanthroline)$Pd(CH_3)_2$ could not be isolated.

It was clear from the reaction between methyl-lithium and cyclo-octa-1,5-dienedichloropalladium that the limit

of instability had just about been reached. From the amount of metallic palladium formed during the reaction, the small amount of product isolated and its low stability it was clear that the bonding between the diene and palladium was only just strong enough to permit the formation of a methyl derivative.

It is significant, in attempting to draw up a relative order of donor strengths, that phenyl derivatives were only obtained with phosphines, though we have no evidence that bis(triethylarsine)dibromopalladium would not afford aryl derivatives.

Thus a relative order of the stabilizing effect of different types of donors on organopalladium compounds would appear to be:

$$P \rangle As \rangle S \rangle \text{dienes.}$$

It is scarcely possible to place nitrogen in this series, since dipyridyl afforded an unusually stable compound whereas no product could be isolated from a phenanthroline complex.

During the present investigation there have been several indications that the presence of free donor decreases the rate of decomposition of the organopalladium compounds.

For example, o-$C_6H_4(AsMe_2)_2Pd(CH_3)_2$ remained for three weeks in an impure condition, contaminated with some free diarsine, without deposition of metallic palladium whereas the compound decomposed very quickly after it was purified by recrystallization.

The organic group

Most success in the preparation of organopalladium compounds has been obtained with methyl derivatives. Phenyl compounds were formed in only two cases, $(Et_3P)_2Pd(Ph)Br$ and $(Et_3P)_2PdPh_2$ and in all other cases reaction between the parent dihalide and Grignard reagent or organolithium compound led to immediate decomposition or to a mixture of products from which it was difficult to isolate a single crystalline component.

Instances of this type of behaviour are very common, as described in the experimental section, but attention may be drawn to one special case.

Although a dimethyl derivative was formed starting from $C_2H_4(EtS)_2PdCl_2$ and methyl-lithium, the effect of phenyl-lithium led to complete decomposition even at low temperature.

This type of behaviour is very different from that of platinum where, in general, the Pt-aryl derivatives are more

easily prepared and purified, and more stable than the aliphatic. In contrast, the mono- and di-phenyl derivatives of palladium prepared in the course of this work have decomposed at an appreciable rate standing at room temperature.

The only aryl derivatives which have been kept undecomposed at room temperature are those in which the aryl group bears an electro-negative substituent, or in which the palladium is bonded to the electro-negative carbon of an acetylenic group, e.g. $(Et_3P)_2Pd(C{\equiv}C\text{-}Ph)_2$. The effect of electron attracting substituents is shown by the instability of the dimethylaminophenyl compound, $(Et_3P)_2Pd(\underline{p}\text{-}Me_2N\cdot C_6H_4)_2$, which was isolated with difficulty and tended to decompose in solution, and the much higher stability of the dimethiodide of this compound $\left[(Et_3P)_2Pd(\underline{p}\text{-}Me_3N\cdot C_6H_4)_2\right] I_2$. Similarly the p-trifluoromethylphenyl and the parachloro-(and bromo-)phenyl derivatives (the last two prepared by Mr. P.S. Dixon in these laboratories) remained undecomposed for considerable periods at room temperature.

The phenylethynylpalladium derivatives isolated, $(Et_3P)_2Pd(C{\equiv}CPh)_2$ and $(Et_3P)_2Pd(C{\equiv}CC_6H_4NO_2)_2$ show a stability greater than that of the phenyl derivatives and

because the C≡C stretching frequency found in these compounds occurs near the normal acetylenic frequency, their stability may be attributed to the electronegativity of the acetylenic carbon atoms rather than to conjugation.

The one pure o-substituted phenyl derivative isolated, $(Et_3P)_2Pd(mesityl)Br$, is of some interest when compared with its platinum analogue. The compound isolated by J. Chatt and B.L. Shaw[48] $(Et_3P)_2Pt(mesityl)Br$ has a cis structure whereas the palladium derivative is trans. Indeed no cis aryl palladium compounds have been prepared although, from the reaction between o-$PEt_2 \cdot C_6H_4 \cdot AsMe_2PdBr_2$ and mesitylmagnesium bromide, an ether soluble white compound m.p. 177° (decomposition) was isolated which when analysed had values for carbon and hydrogen approaching those for the dimesityl compound and certainly much higher than those required for the monomesityl derivative.

The stable trans-$(Et_3P)_2Pd(mesityl)Br$ was isolated from a reaction between the dihalide and two mols. of Grignard reagent and some decomposition occurred during working up processes. Thus, as in the case of platinum, although there is plenty of room for a second mesityl group there must be a kinetic difficulty preventing entry of the second group.

Now that a large amount of data have been published on

the alkyl and aryl derivatives of platinum,[48,53] and nickel and cobalt[54] it is possible to see where palladium stands in the triad Ni, Pd, Pt.

	Ni	Pd	Pt
1.	No methyls	Methyls stable, higher alkyls unstable.	Methyls stable and higher alkyls isolated.
2.	No phenyls	Phenyls less readily prepared than methyls	Phenyls more readily prepared than methyls
3.	No p-substituted phenyls	p-(negatively) substituted phenyls more stable than phenyls.	p-substituted phenyls of same apparent stability as phenyls.
4.	o-Substituted phenyls very stable. Dimesityl derivative and di-(o-tolyl)derivative formed.	o-Substituted phenyl stable.	o-Substituted phenyls stable. Only mono mesityl but di-(o-tolyl) derivatives formed.
5.	Ethynyl and substituted ethynyl derivatives very stable.	Substituted ethynyl derivative very stable.	Ethynyl and substituted ethynyl derivatives very stable.

It can be seen therefore that palladium stands at an intermediate position relative to the other two metals. Clearly steric factors play a very important part in the

formation of stable nickel (and cobalt) organometallic compounds, whereas for palladium and platinum electronic effects play at least as important a role and steric effects may be of secondary importance. There is no doubt that the stability of the organometallics falls in general in the order Pt> Pd> Ni.

Methyl palladium compounds

Thus, with palladium, the methyls occupy a rather special place in that it is possible to prepare derivatives with even the very weak donors e.g. sulphur and dienes. The methyl group is a small group compared with, for example, a mesityl or o-tolyl group and steric factors are probably not the prime cause of stability but rather some electronic effect.

J. Chatt and B.L. Shaw have suggested that the stability of the Pt-phenyls could be due to two causes, 1. increased M-C bond strength due to addition of a certain amount of π-bonding between the metal and carbon atoms and 2, increased splitting of the 5d-energy levels.

It is possible that the CH_3 group might also behave in a similar fashion. As described by C.A. Coulson[55] it is possible for a methyl group to form a group orbital which is evidently similar to a normal π-type orbital. It is possible

therefore that $\bar{\pi}$-delocalization may occur as in the case of the $\bar{\pi}$-molecular orbitals in benzene in the platinum compounds.

This $\bar{\pi}$-delocalization would not occur with ethyl derivatives to the same extent, and one would expect a marked falling off in stability (as found experimentally).

This type of behaviour may be similar to that which is suggested in comparing the stabilities of a series of (methyl)-amine-platinous complexes.[56] It was found that trimethylamine has a low affinity for platinum (II) as compared with ammonia. It is pointed out that in ammonia and amines the electronic effects of replacing a hydrogen atom by a methyl group increases the electron-donor tendency of the nitrogen atom. Thus, if complex stability depended only on that donor tendency, the stability of the complexes should depend on the amine present in the complex and increase in the order:-

$$NH_3 < NMeH_2 < NMe_2H < NMe_3$$

As stated the authors find a different order of stability and suggest that a possible cause of stability of the NH_3 complexes relative to those of NMe_3 might be due to interaction between the d-orbitals of the metal and NH bonds. They point out that heterocyclic tertiary aromatic amines

such as pyridine which form stable complexes with transition metals but which have no N-hydrogen atoms, may owe the stability of their complexes to interaction of the metal d-orbitals with the $\overline{\pi}$-electronic system of the amine.

They also point out that there are not enough data available to be certain that the d-orbital-NH interaction is sufficiently strong to account for the enhanced stabilities of the less methylated methylamines relative to the trimethylamine complex.

Other factors, e.g. steric repulsion between the NMe_3 group and the rest of the molecule might also play a part in causing a decrease in stabilities, but the authors conclude that the interaction of d-electrons in the transition metal with the N-hydrogen atoms of the amine is on the whole the most probable cause of stability.

It can be seen therefore that the case of the stability of the methyls of palladium relative to the ethyl derivative may be directly analogous and the controlling factor in the stability of the methyl-palladium bond might well be interaction between the $C{\equiv}H_3$ molecular orbital grouping and the palladium d-electrons.

Structure

Most of the organopalladium compounds isolated have had a trans structure (apart from the necessarily cis derivatives of the chelating donors).

It would appear that during alkylation of trans-$(R_3P)_2PdBr_2$ [R = Et or Ph] there is a change in structure to cis for triphenylphosphine and to a mixture of cis and trans with triethylphosphine. It would also appear that $(Et_3P)_2Pd(CH_3)_2$ isomerizes spontaneously. Arylation of $(Et_3P)_2PdBr_2$ produces no change in structure.

There was no change in configuration during the exchange reactions of trans-$(Et_3P)_2Pd(CH_3)Br$, the cyano derivative having a trans structure. It was not possible to replace the bromine by a nitro, NO_2, group which is rather strange in view of the stability of the bromide and cyanide, and the large number of known nitro palladium complexes.

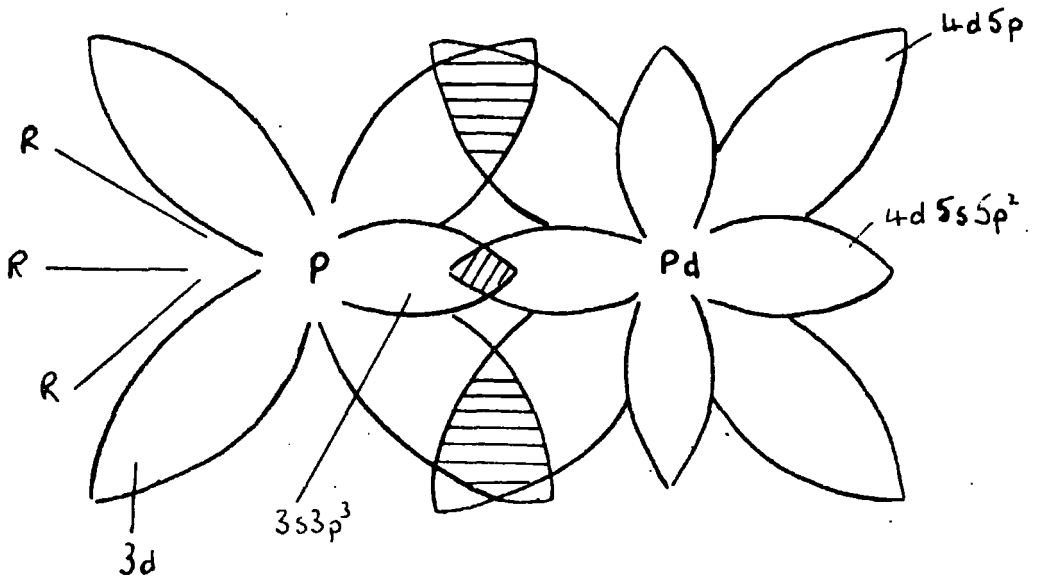
Electronic structure and stability

J. Chatt and B.L. Shaw have put forward a theory to account for the stability of the organometallic compounds of transition metals.[53] They point out that in transition metals the penultimate d-orbitals are on an energy level close to that of the valency s- and p-orbitals and suggest that electrons can easily be promoted from the relatively high

energy filled non-σ-bonding d-orbitals into antibonding σ-orbitals of the metal-to-carbon bond, or if the d-orbitals are empty from the carbon-to-metal bonding orbitals into a d-orbital, in either case providing a relatively low energy process for the breaking of the metal-to-carbon bond.

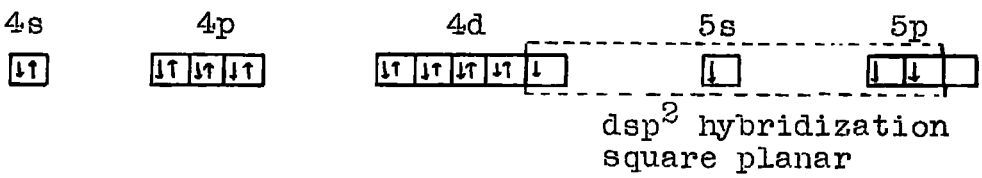
One can say therefore that for the formation of a stable organometallic compound one must have a maximum energy difference between the highest energy orbital which contains electrons and the lowest energy level which is vacant. For nickel, palladium and platinum the highest occupied energy levels are the non-σ-bonding d-orbitals in the penultimate shell of the metal atom. The lowest vacant level is an antibonding σ-orbital. The best way therefore to increase the energy difference between these levels would be to reduce further the energy of the non-σ-bonding d-orbitals (in the case of palladium 4d) by combining them with π-type orbitals of low energy in suitable ligands. In other words it is necessary to form a strong dative π-bond between the metal and a suitable ligand, for example and pre-eminently phosphorus.

Palladium has 46 electrons and has an electronic structure $1s^2 2s^2 p^6 3s^2 p^6 d^{10} 4s^2 p^6 d^{10}$ and its electronic configuration when forming a π-bond with phosphorus will be



Schematic representation of the formation of a σ bond (////) and a dative π bond (≡) between

R_3P and Pd.



Copper and Gold

The work on these two metals constitutes only a small part of the investigation and, with copper led to the formation of one new complex. This work has been carried further in these laboratories.[57]

The work on gold (I) compounds showed that organo derivatives of aurous gold can be prepared with a phosphine co-ordinated to the metal. The two compounds isolated $Et_3P \longrightarrow AuCH_3$ and $Et_3P \longrightarrow AuPh$ were easily obtained and reasonably stable. There is every reason to suppose that phenylethynyl derivatives would be stable.

The two compounds differed in their reaction towards aqueous ethanolic hydrochloric acid, the methyl compound being converted quantitatively to the chloride with evolution of a gas whereas the phenyl compound showed no apparent change.

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