

Complexes of Unsaturated Phosphines

by

Ian Charles Taylor

A Thesis presented for the degree of
Doctor of Philosophy
in the Faculty of Science
of the
University of Leicester
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Statement

The experimental work described in this Thesis has been carried out by the author at the Petrochemical and Polymer Laboratory of Imperial Chemical Industries Limited between October 1967 and April 1970.

No part of this work has been presented or is concurrently being presented for any other degree.

Signed

A handwritten signature in dark ink, appearing to read 'I. C. Taylor', with a long horizontal flourish extending to the right.

I. C. TAYLOR

July 1970

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His many colleagues at the Laboratory for providing a stimulating environment.

Summary

Some reactions of Group VIII metal complexes of unsaturated phosphines are described. The project falls into three parts. The first section deals with various aspects of the preparation of unsaturated phosphines and includes a review of the factors effecting the course of the reaction between metal phosphides and alkyl halides. An improved method of generating lithium dialkylphosphide is described, using naphthalene as a catalyst for the cleavage of tetra-alkyldiphosphine in tetrahydrofuran. Using this technique several new dialkylphosphino derivatives have been prepared. As an alternative route to 1,4-bis(dimethylphosphino)but-2-ene, the addition of tetramethyldiphosphine to butadiene was investigated; the course and the mechanism of this reaction are discussed. This section also includes the first reported preparation of β -acetylenic phosphines, and their rearrangement is described. The preparation of platinum(II) and palladium(II) complexes of unsaturated phosphines, together with a discussion of their structures, is described in the second section. It is apparent that whether there is co-ordination from the olefin or acetylene group to the metal in addition to that from the phosphorus depends on the length of the carbon chain between the two donors. Novel dimeric structures are suggested for the complexes of 1,4-bis(phosphino)but-2-enes. In the third section are described the reactions of the methoxide ion with olefins activated by co-ordination to platinum(II), and with olefins and acetylenes unco-ordinated to, but in the environment of, platinum(II). The physical and chemical evidence for the unusual structures involving platinum-carbon σ -bonds which are suggested for the resulting complexes is discussed.

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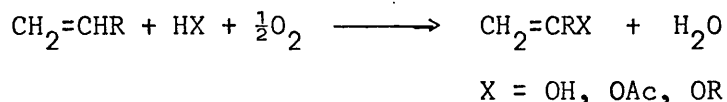
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PART A - INTRODUCTION

The activation of an unsaturated group by a transition metal is of considerable importance in synthetic organic chemistry. Co-ordination to a transition metal involves donation of electron density by the unsaturated group to the metal, and back-donation from filled metal d-orbitals into anti-bonding orbitals of the group.¹ For simple olefins which have no electronegative substituents, this mechanism of activation is important.

A number of reactions of olefins catalysed by transition metals have long been known, and in recent years the mechanistic as well as preparative aspects of these reactions have received much attention. The Hoechst-Wacker process for the preparation of acetaldehyde is an example of the oxidation of an olefin in the presence of an acid, HX, using a palladium(II) salt coupled with a redox system, e.g. $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$, as a catalyst.² Other aldehydes and ketones may be similarly prepared using substituted olefins. Vinyl acetate is prepared by the addition of acetic acid to ethylene co-ordinated to palladium(II).³ Alkyl vinyl ethers have been synthesised by the catalytic oxidation of ethylene in the presence of alcohols.



The addition of alkoxides to co-ordinated olefins has been studied in some detail in the past fifteen years. A further important reaction is the hydroformylation of olefins in the

presence of cobalt salts.⁴ This reaction too is of industrial importance and is used to prepare aldehydes and alcohols.

Acetylenes also undergo a hydroformylation reaction in the presence of rhodium, but only in low yield.⁵ Other reactions in which olefin co-ordination to a metal is believed to be important are hydrogenation,⁶ hydrosilation,⁷ dimerisation, oligomerisation, polymerisation,⁸ and isomerisation.⁹

The main objective of the work described in this thesis was to study reactions of olefins and acetylenes in complexes having a phosphine group bound to the unsaturated group. It was argued that stable intermediate species might be isolated by investigating the behaviour of such complexes in some of the reactions outlined above. The phosphine would be expected to co-ordinate to the metal and prevent the reacted olefin or acetylene leaving the environment of the metal. Further, the co-ordinated phosphine should hold an unsaturated group in close proximity to the metal, allowing the metal to have some influence on the group even if a bond was not initially formed. Much of the emphasis was placed on a study of reactions of nucleophiles, mainly methoxide, on co-ordinated and unco-ordinated olefins and acetylenes. Since attack by a methoxide ion usually occurs when the olefin is co-ordinated to palladium (II) or platinum(II) it is with these metals that the thesis is concerned.

The project falls into three parts. Firstly various aspects of the preparation of a number of unsaturated phosphines is dealt with in Section I. A few of the phosphines were already known, but the majority involved new preparations, and a

considerable part of this work involved a detailed investigation of preparative aspects of organo-phosphorus compounds. The preparation of platinum(II) and palladium(II) complexes of the unsaturated phosphines together with the spectroscopic investigation of their structures is described in Section II. In Section III the reactions of various complexes with methoxide ion is discussed, and in this section the novel structures of the products from these reactions are reported.

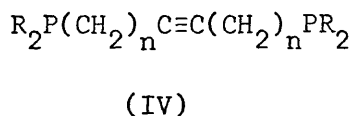
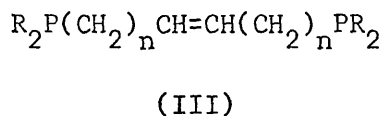
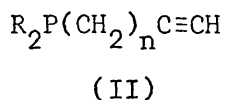
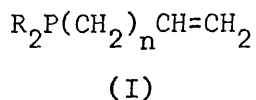
In addition to the study of the reactions of olefin and acetylene complexes with methoxide ion, the complexes described in Section II could well be employed in seeking a deeper understanding of the mechanisms of a number of the reactions outlined above.

PART B - RESULTS and DISCUSSION

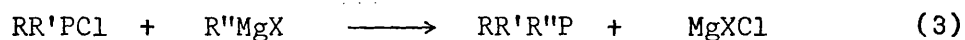
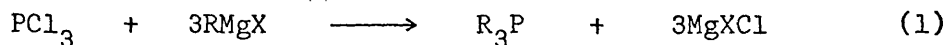
I. Preparation of Phosphines.

1. Introduction.

The work described in this thesis required the preparation of tertiary phosphines with one of the substituent groups unsaturated. It was planned to examine the complexes of four series of phosphines:



A well established route to tertiary phosphines is the reaction of phosphorus trichloride, phosphonous dichloride, or phosphinous chloride with a Grignard reagent, depending on whether identical or different substituents are required, and on the availability of the phosphorus compounds.

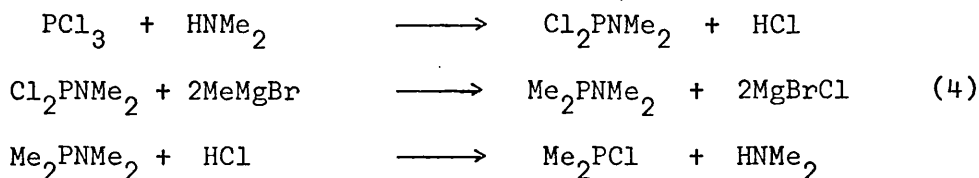


Successive alkylation of phosphorus trichloride to substitute with different groups is not practical. Phosphorus trichloride with one mole of Grignard reagents gives a mixture of mono-, di-, and tri-substituted products, and these may react with

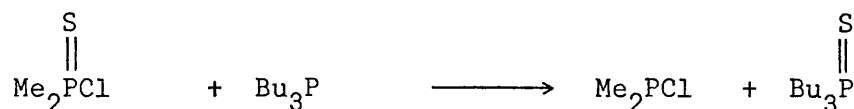
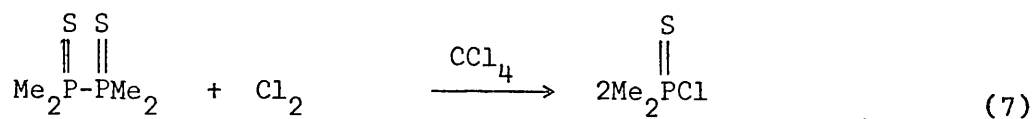
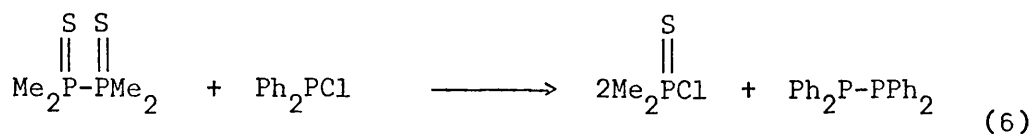
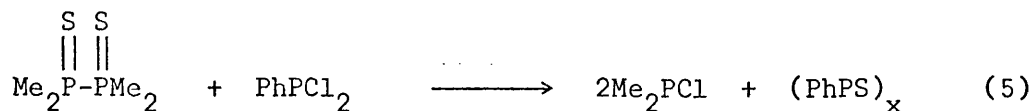
each other to give mixtures containing polyphosphines and phosphonium salts.¹⁰

To prepare the above series of phosphines, reaction (3), with $R = R'$, or the equivalent reaction using a di-Grignard reagent, would have to be used. Diphenylchlorophosphine is available commercially and this route has been used by other workers to prepare several unsaturated diphenylphosphines. Venanzi and co-workers¹¹ treated diphenylchlorophosphine with allyl-Grignard to obtain allyldiphenylphosphine in 18% yield. But-3-enyldiphenylphosphine and pent-4-enyldiphenylphosphine were similarly prepared by Issleib¹² and Bennett,¹³ who also prepared allylphenyl-¹⁴ and styryl-diphenylphosphine.¹⁵ This method has been favoured by many authors for the preparations of acetylenic phosphines.¹⁶⁻¹⁹

Dialkylchlorophosphines, however, are difficult to obtain. Diethylchlorophosphine may be prepared by Beeby and Mann's method²⁰ using tetraethyllead, but this is a long synthesis and involves using the dangerous reagent. Burg and Slota²¹ have developed a method for preparing dimethylchlorophosphine from phosphorus trichloride, by protecting one chloro-group with dimethylamine.

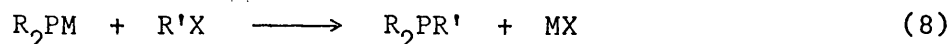


This method was improved by Issleib²² who used diethylamine and prepared diethyl-, dibutyl-, and dicyclohexyl-chlorophosphines. Again, the preparation is tedious and uses noxious reagents. Other routes, starting from tetra-alkyldiphosphine disulphide, have been used by Parshall (equ. 5)²³ and Maier (equ. 6 and 7).^{24,25}

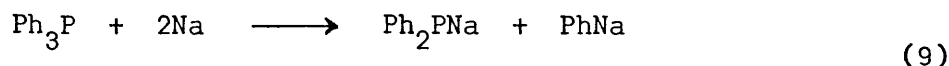


In spite of this difficulty in obtaining the starting material, several tertiary phosphines have been prepared in this way.²⁶⁻³¹

The other extensively used route, and the one employed in this study, is the reaction of an alkali metal phosphide with an alkyl or aryl halide.



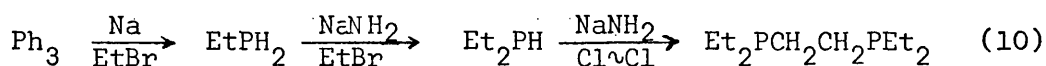
Sodium diphenylphosphide is readily formed when triphenylphosphine is cleaved with sodium in liquid ammonia.³² Ammonium chloride is used to destroy the sodium phenyl which is formed.



This cleavage, originally reported by Wittenberg and Gilman,³³ using lithium in tetrahydrofuran, has been carried out with a variety of alkali metals using different solvents. Aguiar³⁴

used lithium flakes in tetrahydrofuran, destroying the by-product with t-butyl chloride, while Issleib³⁵ preferred sodium or potassium in dioxan.

In a study of this cleavage reaction, Issleib³⁶ found that the trialkyl-phosphines would not cleave as readily as the triaryl- and arylalkyl- derivatives. To prepare the dialkylphosphides, therefore, some other route must be found. The choice is limited by the availability of convenient starting materials. Tetra-alkyldiphosphines may be prepared from thiophosphoryl chloride via the disulphide,³⁷ and may be cleaved to give the metal phosphide.³² This is dealt with in detail in Section I-3. It has been reported³⁸ that the disulphide may be treated directly with excess sodium to give the phosphide. Burg³⁹ found that sodium dimethylphosphide could be prepared from dimethylphosphine with sodamide in liquid ammonia, and Wymore and Bailar⁴⁰ made use of this reaction to prepare 1,2-bis(diethylphosphino)ethane.



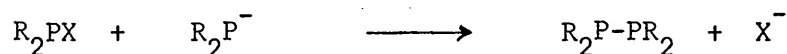
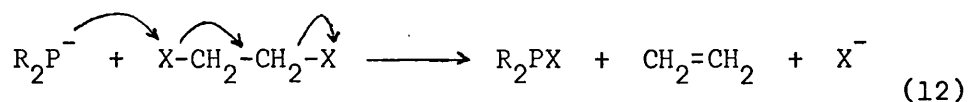
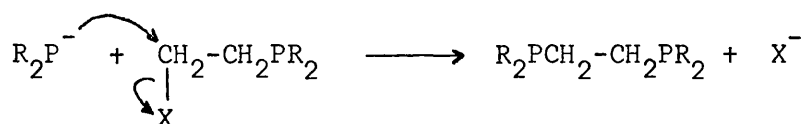
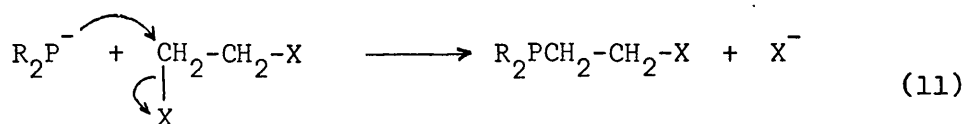
By analogous reactions, Chatt and Hayter⁴¹ prepared 1,2-bis(dimethylphosphino)ethane, and Hitchcock and Mann,⁴² who pointed out the necessity of adding the 1,2-dichloroethane last, prepared 1,2-bis(ethylphenylphosphino)ethane. Issleib⁴³ prepared lithium dialkylphosphides by the reaction of phenyl-lithium with the appropriate secondary phosphine, which he obtains⁴⁴ by reducing the tetra-alkyldiphosphine disulphide with lithium aluminium hydride.

These, and other methods of preparing tertiary phosphines are the subject of a review article by Maier.⁴⁵

The other divisions of this Section deal with the interesting points which have arisen from the preparation of members of the four series of phosphines.

2. Elimination and Substitution Reactions

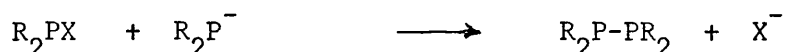
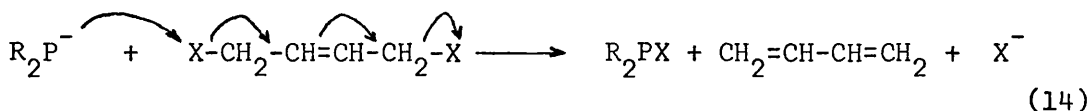
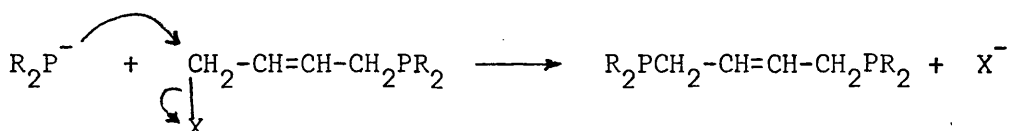
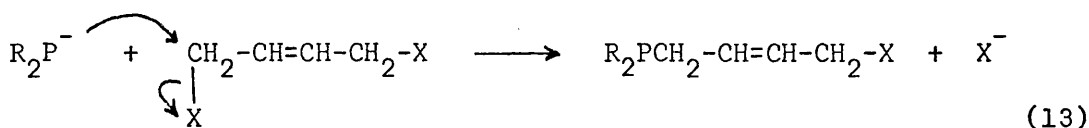
In 1959 Issleib and Muller⁴⁶ described the preparation of ditertiary phosphines of the type $R_2P(CH_2)_nPR_2$ by the metal phosphide route. They found that when $n > 2$ the expected phosphine was obtained in good yield, but when $n = 1$ or 2, in some cases, it was the diphosphine $R_2P.PR_2$ which was isolated. The explanation for this is presumably that in addition to the nucleophilic substitution reaction (equ. 11), an elimination reaction involving the loss of two halogen atoms (equ. 12) can occur.



When there are more than two carbon atoms between the halogen atoms the concerted elimination reaction shown above cannot take place. When $n = 1$, the diphosphine R_2P-PR_2 was obtained,

but no product from the methylene group has been isolated.

It was envisaged that an analogous reaction could occur when 1,4-dihalogenobut-2-ene was used to prepare the corresponding phosphines (equ. 13 and 14), and consequently a review of the factors effecting the balance between the two mechanisms was carried out. It is apparent that the tendency for substitution reaction over elimination reaction can be arranged as phenyl > ethyl > cyclohexyl; tetrahydrofuran > liquid ammonia, dioxan, ether; chloride > bromide.



One of the major factors is the substituent on the phosphorus atom. Until this study, there were no cases reported where an elimination reaction occurs with diphenylphosphide, yet elimination reactions have been reported with diethyl- and dicyclohexylphosphides. With dichloromethane in dioxan, only the diphenylphosphide ion gave the substitution product,⁴⁶ and the same result was found in the reactions with 1,2-dibromoethane.⁴⁶ Sodium dimethylphosphide also gave low yields of the substitution product in comparison to sodium diphenylphosphide; with 1,2-

dichloroethane in liquid ammonia the dimethylphosphide gave about 35% of the substitution product,⁴¹ while the diphenylphosphide gave about 80%.^{29,32} Dicyclohexylphosphide tends to cause elimination reactions even more than diethylphosphide. With 1,2-dichloroethane in tetrahydrofuran both lithium diphenylphosphide²⁹ and lithium diethylphosphide³² gave the substitution product in good yield, while with lithium dicyclohexylphosphide only a 50% yield of the substitution product was obtained, and in addition, 20% of the elimination products.⁴⁷ In ether, no substitution occurred with dicyclohexylphosphide, yet the reaction of diethylphosphide proceeded by substitution (30%) and elimination (40%).⁴⁷

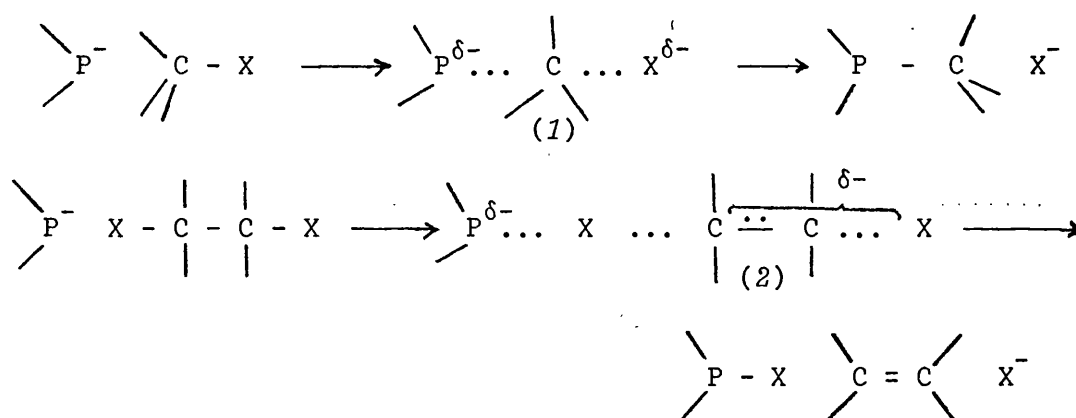
The solvent also plays an important role in the course of the reactions. The substitution product was obtained in good yield from the reaction of diethylphosphide with 1,2-dichloroethane in tetrahydrofuran,³² but in ether the yield dropped to 30%, and the elimination product (45%) was also isolated.⁴⁷ In dioxan only the elimination product was found.⁴⁶ A similar result was obtained from the reaction of dicyclohexylphosphide with 1,2-dichloroethane; in tetrahydrofuran the ratio of substitution:elimination was 2.7:1,⁴⁷ while in dioxan and ether only the elimination product was found.⁴⁶ Sodium dimethylphosphide reacted with 1,2-dichloroethane in liquid ammonia to give the substitution product in 35% yield,⁴¹ while it is reported in this thesis that in tetrahydrofuran a 60% yield can be obtained (Section I-3).

Whether dichloro- or dibromoethane is used also has some effect. Lithium diethylphosphide with 1,2-dichloroethane in

ether gave about 40% elimination and 30% substitution,⁴⁷ whereas with 1,2-dibromoethane in dioxan (which has similar solvent properties to ether in this sort of system - see above), 96% elimination was found.⁴⁷ The same result was observed with potassium cyclohexylphosphide and sodium phenylphosphide; with 1,2-dichloroethane,^{47,48} the corresponding substitution products were obtained, but with 1,2-dibromoethane,^{49,50} elimination products were isolated.

Hewertson and Watson³² observed a trend depending on the Group V element. With 1,2-dichloroethane in liquid ammonia they obtained the substitution product in good yield with sodium diphenylphosphide and diphenylarsenide, but the elimination product with sodium diphenylstibide.

To rationalise these observations one needs to consider the transition states (1) and (2) of the two reactions.



Hughes and Ingold⁵¹ postulated that if charge is reduced, destroyed or dispersed in the transition state, the rate of reaction will be decreased by polar solvents. In both cases charge is dispersed in the transition state, but as state (2) has a greater dispersion than (1), it is to be expected that a change to polar solvents would decrease the rate of the

elimination reaction with respect to the substitution reaction, and the latter would predominate. The effect of the substituent on the phosphorus is to alter the nucleophilicity of the phosphide ion. Whereas phenyl substituents have the effect of delocalising the negative charge of the phosphorus on to the rings thus reducing the nucleophilicity of the phosphide ion, the inductive effect of alkyl groups is to increase the charge on the phosphorus, making the phosphide a stronger nucleophile. It would be expected, therefore, that a phosphide ion with alkyl substituents would be less discriminating in its position of attack, and would be more dependent on other influences, such as solvent and halogen. The difference between the ethyl and cyclohexyl substituted phosphides is probably due to a steric effect. The cyclohexyl group is large and bulky, and a phosphide with two such groups would prefer to attack a terminal position of a chain (the halogen) rather than an internal position (the carbon). This preference will not be so marked for a phosphide with smaller ethyl substituents. The difference between the susceptibility of bromide and chloride atoms to nucleophilic attack is discussed in terms of bond strengths and polarisability in a review article by Miller.⁵²

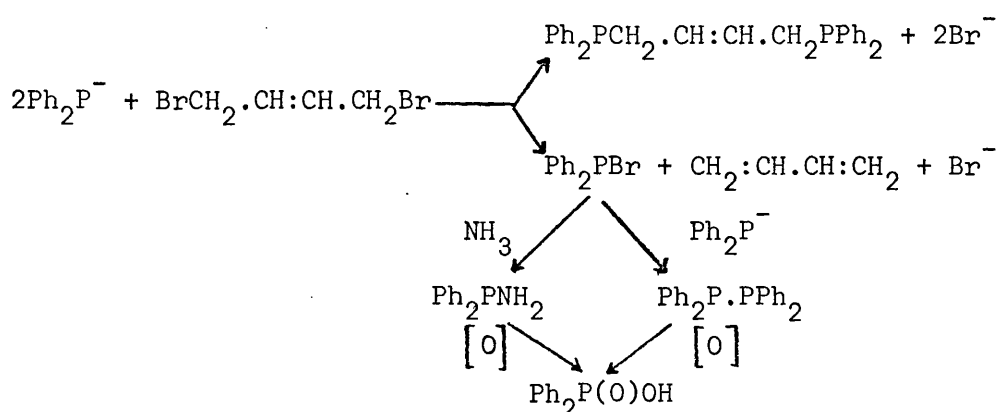
It is difficult to predict by which route a given reaction will proceed. It would seem to depend on a balance of the various effects discussed above. The system which was studied to prepare phosphines of Series III was the reaction of metal diaryl- or dialkylphosphide with 1,4-dihalogenobut-2-ene. The two possible reactions, substitution and elimination, are shown in equations (13) and (14) respectively. In the light of the above information it was decided to use 1,4-dichlorobut-2-ene, and to carry out

the reactions in tetrahydrofuran. In this way trans-1,4-bis(diphenylphosphino)but-2-ene, trans-1,4-bis(diethylphosphino)but-2-ene, and cis- and trans-1,4-bis(dimethylphosphino)but-2-ene were prepared in 80%, 30%, 40% and 55% yields respectively. The low yield of the ethyl substituted phosphine is probably due to other factors which are discussed in Section I-3, and the low yield of the cis-methyl-substituted phosphine due to the experimental technique tried for this reaction [see Part C Section VII-1(f)].

The reaction with sodium diphenylphosphide was examined in greater detail. The reaction with trans-1,4-dichlorobut-2-ene was carried out in tetrahydrofuran, liquid ammonia, and ether, to investigate a possible solvent effect. It was found, however, that the substitution product, trans-1,4-bis(diphenylphosphino)but-2-ene, was obtained in good yield (79-95%) in each case. Presumably the delocalising property of the phenyl groups on the phosphorus means that the solvent polarity is a less important factor.

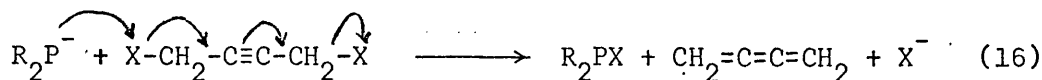
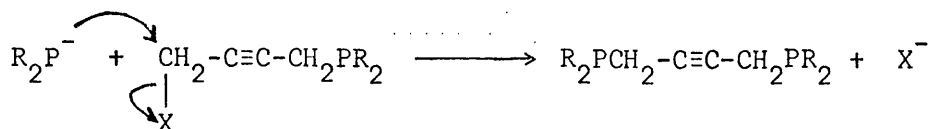
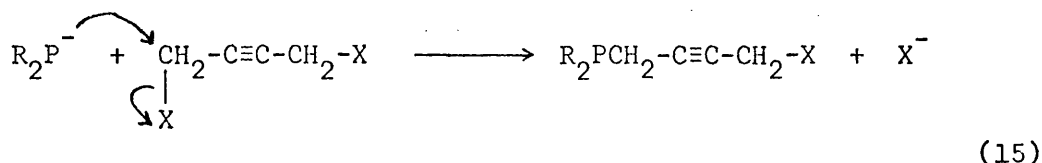
An effect was observed on changing the halogen group. Whereas sodium diphenylphosphide reacted with trans-1,4-dichlorobut-2-ene in liquid ammonia to give the substitution product in 95% yield, with trans-1,4-dibromobut-2-ene in the same solvent only a 30% yield was obtained. The two reactions were repeated using a vacuum line (shown in App. 4 - Figure 1) and any volatile products were trapped out for examination by mass spectroscopy. The sample from the chloride experiment showed only ammonia (solvent) and benzene (from the preparation of the phosphide): the sample from the bromide experiment showed ammonia, ether (used as solvent

for the bromide) and butadiene [from an elimination reaction - equ. (14)]. Some diphenylphosphinic acid (33%) was isolated after oxidation of the residue from the second experiment. This is presumably from the product of the secondary reaction of diphenylbromophosphine.

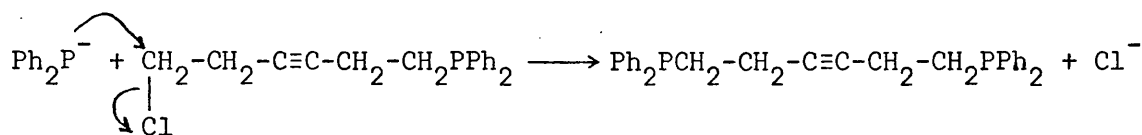
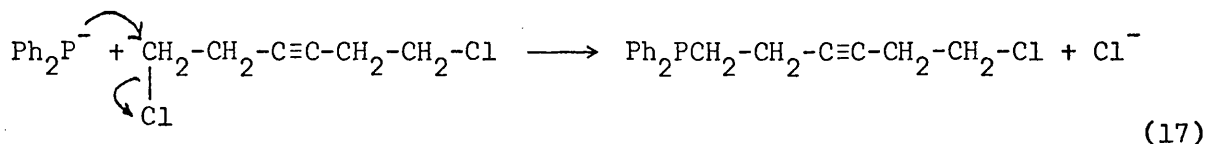


The geometry of the but-2-ene does not appear to have any effect on the course of the reaction. Lithium dimethylphosphide with cis-1,4-dichlorobut-2-ene in tetrahydrofuran did give some trans-isomer in the product: this is discussed in Section I-3. A crystalline product could not be isolated from the reaction of sodium diphenylphosphide and cis-1,4-dichlorobut-2-ene in either tetrahydrofuran or liquid ammonia. It was shown, however, that the substitution product was in fact formed by oxidising the oil to the dioxide which was crystalline. A 28% yield of the cis-dioxide, $\text{Ph}_2\text{P(O)CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{P(O)Ph}_2$, was obtained.

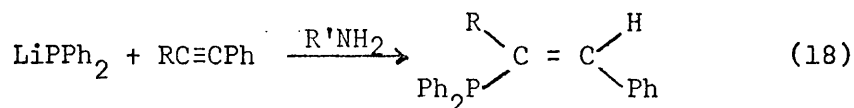
The possibility of a similar elimination reaction occurring between sodium diphenylphosphide and 1,4-dihalogenobut-2-yne was considered (equ. 15 and 16).



The reaction with 1,4-dichlorobut-2-yne was carried out in liquid ammonia and in tetrahydrofuran. In both cases a brown solid was obtained. This could not be purified, but it was shown that this was the substitution product by oxidation to the dioxide which was crystalline. An attempt to reduce the oxide using Horner and Balzer's method⁵³ failed to give any of the phosphine. Only a 26% yield of the dioxide was obtained, but this is even higher than the yield of 1,6-bis(diphenylphosphino)hex-3-yne prepared by an analogous reaction (equ. 17), and the concerted elimination reaction cannot occur in this case.

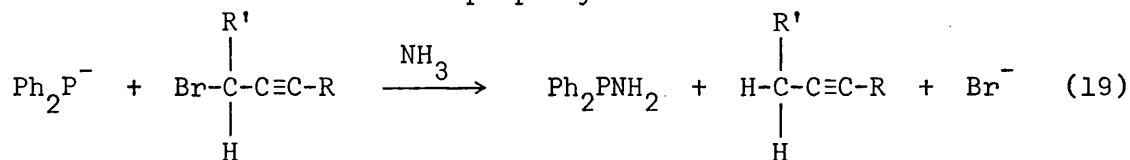


It is possible that the by-products from these reactions arise from nucleophilic attack by the phosphide ion on the acetylene group. Such reactions have been reported to occur between lithium diphenylphosphide and phenyl acetylenic compounds in the presence of primary amines (equ. 18).^{54,55}



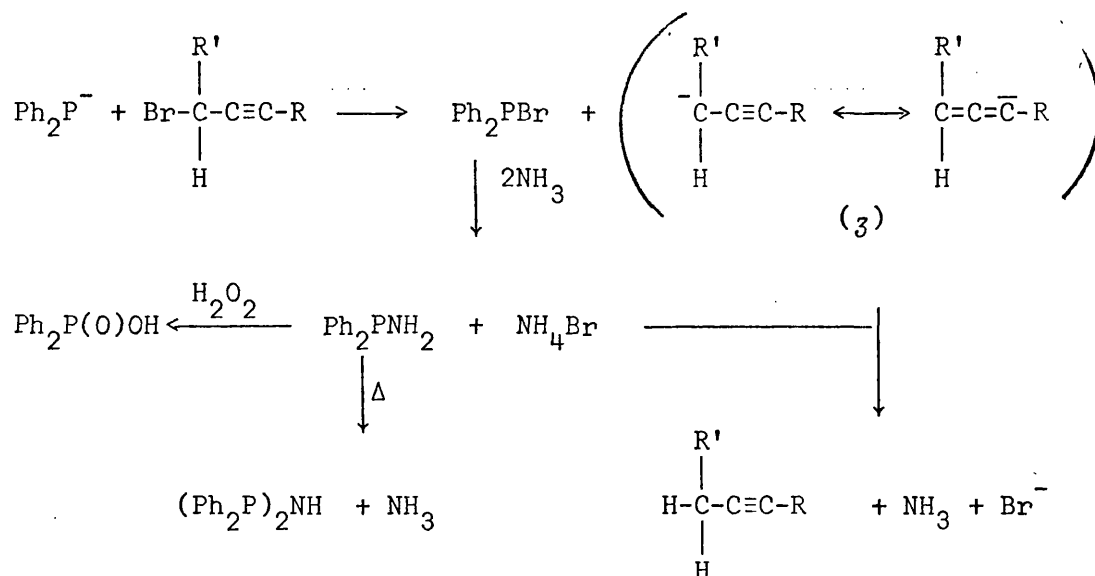
There are also cases in the literature of attack on alkyne groups by butyl lithium,⁵⁶ triphenylsilyl lithium,⁵⁷ and lithium mercaptides.⁵⁸

Attack on the halogen atom was observed in some cases when sodium diphenylphosphide was treated with prop-2-ynyl halides in liquid ammonia. The phosphide reacts with 3-chloroprop-1-yne, 3-chlorobut-1-yne and 1-chlorobut-2-yne to give the corresponding substitution product or a derivative of it (see Section I-5). With the bromides, however, products derived from attack on the halogen atom were observed in two cases.⁵⁹ 1-Bromobut-2-yne gave but-2-ynyldiphenylphosphine with sodium diphenylphosphide, but the major product from both 3-bromoprop-1-yne and 3-bromobut-1-yne was diphenylphosphinoamine, Ph_2PNH_2 . Propyne was isolated from the reaction of 3-bromoprop-1-yne.



Diphenylphosphinoamine undergoes disproportionation on heating to bis(diphenylphosphino)amine and ammonia, and it was isolated either as this secondary amine, or was oxidised to diphenylphosphinic acid. It is suggested that the reaction proceeds by initial attack on the bromine atom rather than carbon in the same way as attack occurs on the halogen in the dihalogenoethane and -but-2-ene reactions. In this case the reaction is not a true elimination, but the intermediate carbanion abstracts a proton from the ammonium bromide which is obtained during the formation

of diphenylphosphinoamine. The mechanism shown in the Scheme outlined below is proposed.

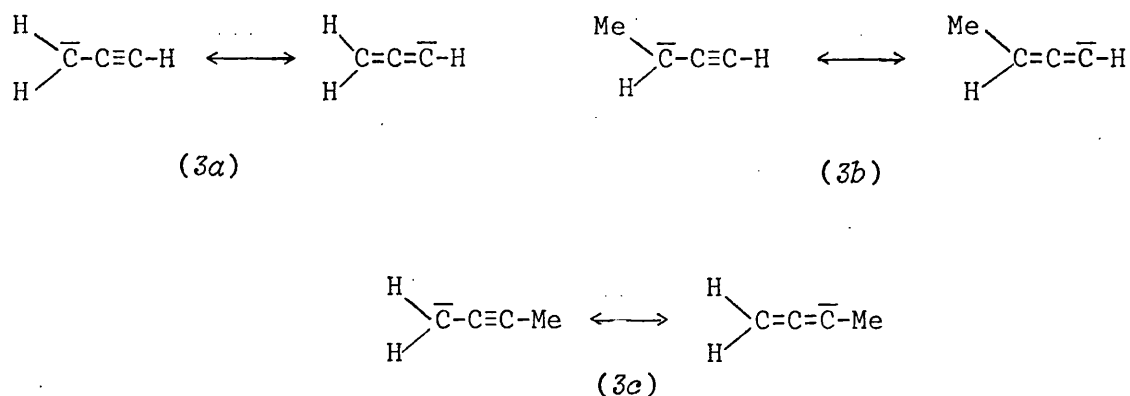


Consistent with this Scheme is the fact that propyne was isolated from the reaction of 3-bromoprop-1-yne before hydrolysis of the reaction mixture. In addition, the mass spectrum of the crude product obtained from the reaction of 3-bromobut-1-yne showed the presence of fragments derived from small quantities of tetraphenyldiphosphine. This could arise from competition between diphenylphosphide ion and ammonia in the reaction with the intermediate diphenylbromophosphine, and is found in the systems described earlier where the reaction was carried out in inert solvents.⁴⁶

Ammonolysis of diphenylchlorophosphine to diphenylphosphinoamine has been described,⁶⁰ together with its subsequent disproportionation and oxidation.

The course of these reactions may be discussed in terms of the relative susceptibilities of each alkynyl bromide to

nucleophilic attack on bromine and on carbon. Factors effecting attack on carbon have been well described in a review by Bunton.⁶¹ The ease with which attack on bromine occurs will depend on the stability of the carbanion intermediates (3).

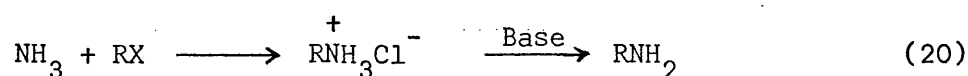


In the case of 3-bromoprop-1-yne, the carbanion (3a) is relatively stable,⁶² and although β -acetylenic halides are susceptible to nucleophilic attack,⁶¹ the balance is in favour of attack on bromine. The carbanion (3b) is less stable than (3a) (the order of stability of carbanions is primary > secondary > tertiary⁶²), however the susceptibility to attack on carbon will also be reduced by the α -methyl substituent. Again the balance favours attack on bromine. Similarly the carbanion (3c) will be unstable relative to (3a) and since the favoured canonical form (the primary form of the carbanion) has the charge in an orbital of less s-character, it will be less stable than (3b).⁶² As there is no corresponding reduction in the ease of attack on carbon in this case, it is by this route that the reaction proceeds.

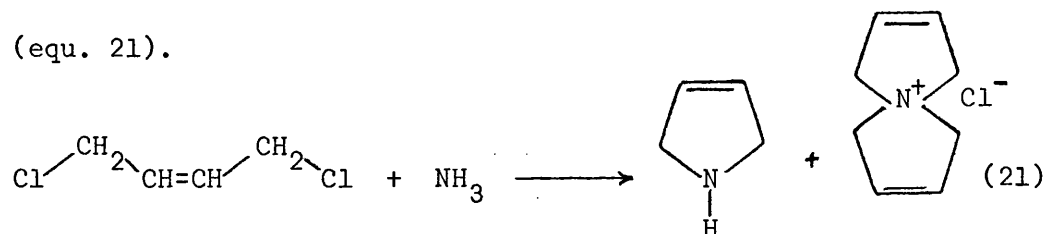
Both allyl chloride and allyl bromide react with sodium diphenylphosphide in liquid ammonia to give allyldiphenylphosphine

in good yield (70%). There was no evidence for attack on the halogen. The preparation of allyldiphenylphosphine by this route gives a much better yield than the reported preparation by Venanzi and co-workers¹¹ using allyl-Grignard and diphenylchlorophosphine (18%).

A possible side reaction in all the above systems involving liquid ammonia is a nucleophilic attack by the solvent on the alkyl halide (equ. 20).



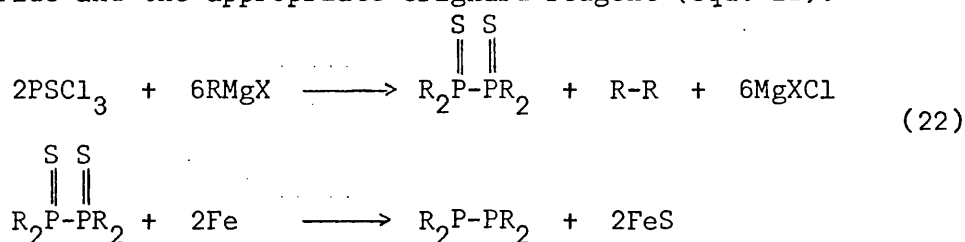
Ammonolysis of cis-⁶³ and trans-1,4-dichlorobut-2-enes⁶⁴ been described by Amundsen and co-workers. They found that trans-1,4-dichlorobut-2-ene and liquid ammonia yielded tars and rubbery polymers, but the cis-isomer with aqueous ammonia formed 3-pyrroline and 5-azaspiro-4,4-non-2,7-dienium chloride (equ. 21).



The reaction between ammonia and 1,4-dichlorobut-2-yne has been described by Johnson,⁶⁵ and it is possible that this reaction may account for some of the by-products in the reaction with sodium diphenylphosphide. In a paper on some acetylene - allene rearrangements, Gaudemar⁶⁶ describes in detail the preparation of propargylamines from 3-bromoprop-1-yne and liquid ammonia. Ammonolysis of allyl halides is well known.⁶⁷ No evidence of any products from such a reaction was found in this work. Apparently the diphenylphosphide ion behaves as a much stronger nucleophile than ammonia in this system, and reacts preferentially with the halide even though there is a large excess of ammonia.

3. Cleavage of Diphosphines

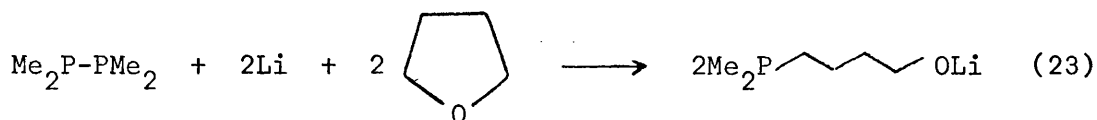
The methods of preparing tertiary phosphines are summarised in Section I-1. It is emphasised there that the choice of routes depends very much on the availability of the phosphorus containing compounds. A convenient starting material for dimethyl- and diethylphosphino derivatives is tetra-alkyldiphosphine, which can be prepared via the sulphide from thiophosphoryl chloride and the appropriate Grignard reagent (equ. 22).³⁷



A method of obtaining the alkali metal phosphide, MPR_2 , in good yield from the diphosphine is required. It has been reported that lithium cleaves tetraethyldiphosphine in tetrahydrofuran to give lithium diethylphosphide,³² and the cleavage of tetramethyldiphosphine with sodium in liquid ammonia has been used to generate sodium dimethylphosphide.^{68,69}

The cleavage with lithium in tetrahydrofuran has many disadvantages. It is a heterogeneous reaction and does not occur very easily. To present as large a surface as possible to the diphosphine, an excess (100%) of finely beaten lithium flakes is used. This means, however, that there is no indication of when the reaction is complete, and necessitates a filtration step in the reaction sequence before the alkyl halide can be added. At room temperature the cleavage occurs very slowly and it is usual to boil the solvent under reflux overnight.³²

It has been reported, however, that a reaction takes place between lithium dimethylphosphide and boiling tetrahydrofuran (equ. 23).⁷⁰

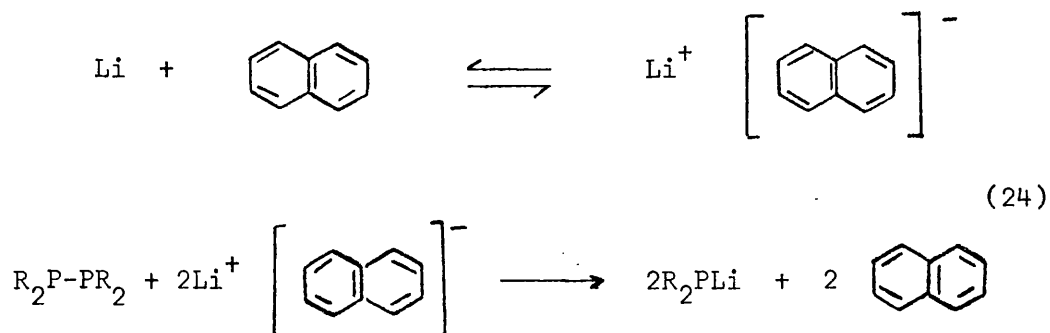


A similar product has been observed during the cleavage of tetraethyldiphosphine.⁶⁹ trans-Bis(dimethylphosphino)but-2-ene was prepared using the method outlined above, but only a low yield (30%) was obtained. Attempts to prepare the cis-isomer failed to give any diphosphinobutene. Although a high yield (94%) of product was reported from the reaction of lithium diethylphosphide with 1,2-dichloroethane,³² it is now known that the product contained some diethyl-4-hydroxybutylphosphine from the reaction with the solvent.⁶⁹

The alternative system using sodium in liquid ammonia overcomes these disadvantages, yet imposes restrictions of its own. Being a homogeneous reaction it occurs fairly rapidly. Excess metal does not need to be used, and there is a built-in indicator for the end-point of the reaction as the intense blue colour of sodium in liquid ammonia will give way to the orange of sodium dimethylphosphide. The product will not react with the solvent. However, liquid ammonia, as has already been shown (Section I-2), is not a good solvent for the preparation of ditertiary phosphines which have alkyl substituents. With 1,2-dichloroethane a low yield (35%) of 1,2-bis(dimethylphosphino)-ethane has been reported.⁴¹ Even a mixture of ammonia and

tetrahydrofuran does not greatly increase this amount.⁶⁹ As the preparation of some of the phosphines required involved using dihalides which could undergo concerted elimination reactions (equ. 13), the use of liquid ammonia seemed inappropriate.

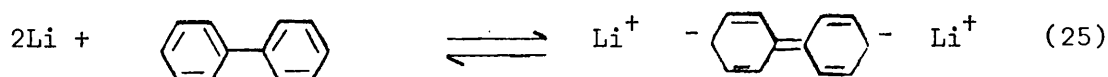
One solution to this problem would be to carry out the cleavage reaction in liquid ammonia, then to change the solvent to tetrahydrofuran for the addition of the alkyl halide. It was decided, however, to try a different approach. Naphthalene reacts readily with alkali metals in ethereal solvents to give metal naphthalenides,⁷¹ which are soluble. If naphthalene, therefore, is added to the reaction mixture of tetra-alkyldi-phosphine and lithium flakes in tetrahydrofuran, it will take the metal into solution where a homogeneous cleavage of the diphosphine can occur (equ. 24).



Only a catalytic amount of naphthalene should be required as it will be regenerated on reaction of the naphthalenide with the diphosphine. It was found that the addition of 5% of naphthalene was sufficient for the cleavage reaction to be complete after the reaction mixture was stirred at room temperature overnight.⁷² There is no reaction with the solvent

at this temperature, and a stoichiometric amount of lithium is used, eliminating the need to filter the reaction mixture. It is known when the reaction is complete as all the lithium is used. The alkyl halide or dihalide may be added directly to the tetrahydrofuran solution, and the corresponding phosphine is obtained in good yield.

Fearon and Gilman⁷³ used this method to cleave hexaphenyl- and dimethyltetraphenyldisilane. They found that biphenyl could also be used as a catalyst, and we found that it had a catalytic effect for organosubstituted diphosphines as well. The cleavage of carbon-carbon, carbon-oxygen, carbon-nitrogen, and carbon-sulphur bonds with biphenyl-lithium has been the subject of a study by Eisch and co-workers.⁷⁴⁻⁷⁶ Biphenyl differs from naphthalene in that it can react with two atoms of lithium as shown in equ. (25).⁷⁵



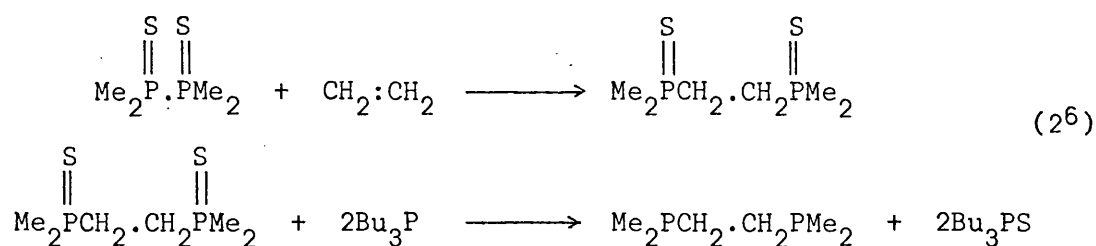
Using the system of lithium and naphthalene or biphenyl in tetrahydrofuran various alkyl substituted phosphines were obtained in good yield (see Table).

Reaction of R_2PLi with Unsaturated Alkyl Halides

<u>Halide</u>	<u>Phosphine</u>	<u>Yield</u>
$\text{CH}_2\text{:CH.CH}_2\text{Cl}$	$\text{CH}_2\text{:CH.CH}_2\text{PEt}_2$	74%
$\text{CH}_2\text{:CH.CH}_2\text{.CH}_2\text{Cl}$	$\text{CH}_2\text{:CH.CH}_2\text{.CH}_2\text{PEt}_2$	67%
$\text{t-C1CH}_2\text{.CH:CH.CH}_2\text{Cl}$	$\text{Me}_2\text{PCH}_2\text{.CH:CH.CH}_2\text{PMe}_2$	55%
$\text{c-C1CH}_2\text{.CH:CH.CH}_2\text{Cl}$	$\text{Me}_2\text{PCH}_2\text{.CH:CH.CH.CH}_2\text{PMe}_2$	38% & 48%

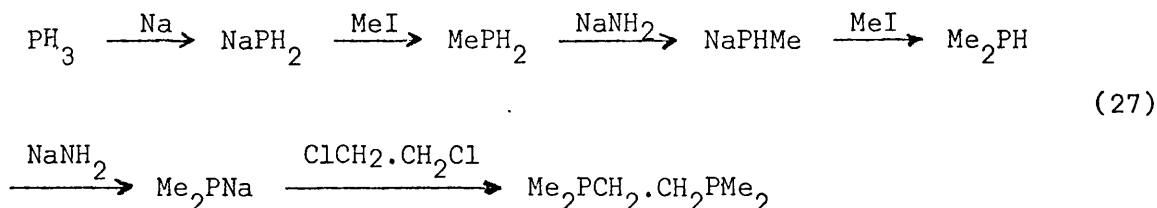
The low yield from the first preparation using cis-1,4-dichlorobut-2-ene is probably due to the less efficient technique used to work-up this reaction [see Part C, Section VII-1(f)]. Allyldialkylphosphines have not been previously prepared. The ^1H n.m.r. spectrum of trans-1,4-bis(dimethylphosphino)but-2-ene (App. 1 - Table 5) was used to identify the isomers from the reaction of butadiene and tetramethyldiphosphine (see Section I-4).

An important consequence of this work is in the improved preparation of 1,2-bis(dimethylphosphino)ethane. This phosphine is a good chelating ligand for use with transition metals, and has a stabilising effect on many complexes.^{41,77} Until now the methods of preparing this phosphine have either given a low yield, or involved using high temperatures for many hours. Burg⁷⁸ obtained the phosphine in yields from 63% to 79% by heating tetramethyldiphosphine and ethylene in a sealed tube at around 280° for up to 760 hr. In a similar reaction using the diphosphine disulphide and an iodine catalyst, Parshall⁷⁹ obtained 1,2-bis(dimethylphosphino)ethane disulphide, which could be de-sulphurised with tributylphosphine (equ. 26), in 60% yield.



Again this preparation involves severe conditions; 48 hr. at 275° in a sealed tube. Chatt and Hayter⁴¹ obtained the phosphine in low yield (35%) by a reaction using less drastic conditions,

but used phosphine as the starting material in the same way that Wymore and Bailar⁴⁰ prepared 1,2-bis(diethylphosphino)ethane (equ. 27). The reaction was carried out in liquid ammonia.



The phosphine is reported to have been prepared by the same reaction by King,⁶⁸ except that sodium dimethylphosphide was prepared by cleaving tetramethyldiphosphine with sodium in liquid ammonia. Unfortunately there are no details of the experiment, nor is the yield of product recorded. The phosphine has been prepared in up to 50% yield using a solvent system of liquid ammonia and tetrahydrofuran in a 1:1 mixture.⁶⁹

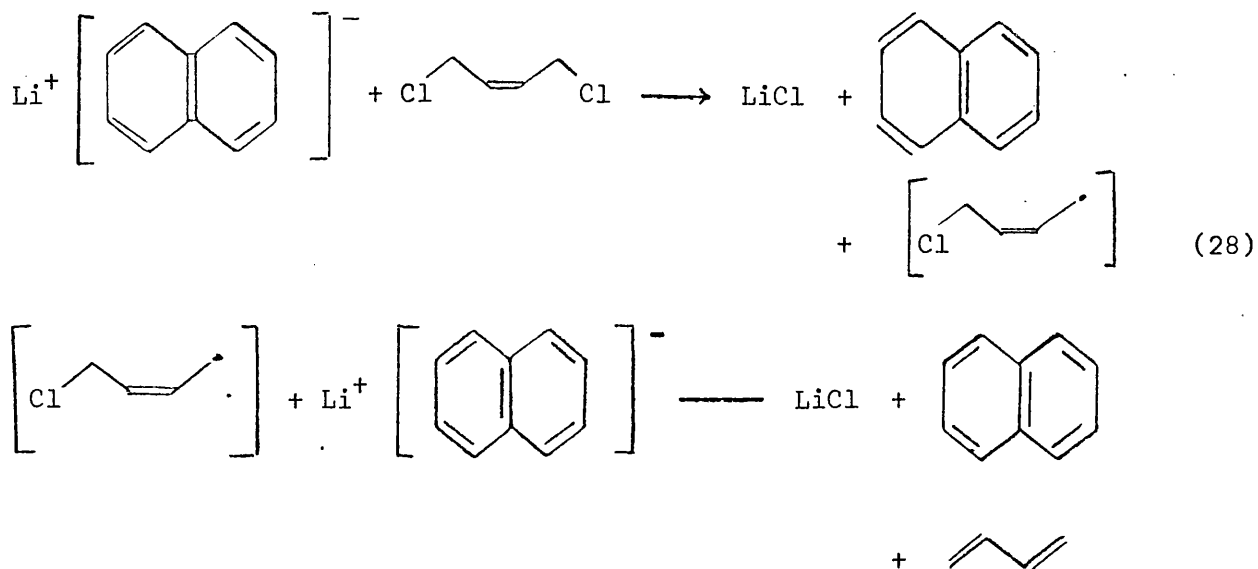
The technique described in this thesis does not involve the use of drastic conditions, uses a readily available starting compound, and gives 1,2-bis(dimethylphosphino)ethane in a good yield - 60%. An attempt was made to prepare bis(dimethylphosphino)-methane $(\text{Me}_2\text{P})_2\text{CH}_2$, using this same technique. Issleib, in an attempt to prepare the ethyl analogue using lithium diethylphosphide and dichloromethane in dioxan, obtained tetraethyl-diphosphine, presumably by an elimination mechanism (Section I-2).⁴⁶ It was hoped that by using tetrahydrofuran as solvent, the substitution reaction would predominate. The reaction between lithium dimethylphosphide and dichloromethane was carried out in tetrahydrofuran at -40° . Tetramethyldiphosphine (46% yield and a small amount of a higher boiling phosphine were obtained. The i.r. and ^1H n.m.r. spectra of this higher boiling fraction

were not inconsistent with those of the required ditertiary phosphine. The yield of this phosphine is 11%. It would appear that with this dichloride attack on the halogen by the dimethylphosphide ion predominates even in tetrahydrofuran.

A disadvantage of this technique of using lithium and naphthalene or biphenyl is the volatility of the catalyst. The boiling points of naphthalene and biphenyl are 210° and 256° respectively, and both tend to distil with the phosphine which is being prepared. A way to separate the catalyst would be to acidify the reaction mixture during the work-up procedure. The usual work-up is to remove the tetrahydrofuran and to extract the residue with ether and water. Acidification before the initial ether extract is removed would cause the phosphine to go into the water layer as the phosphonium salt. The catalyst could then be removed in the ether, fresh ether added, the solution neutralised, and the phosphine extracted. For most purposes, however, the presence of small amounts of the hydrocarbons is not troublesome, and the amount can be determined by n.m.r. spectroscopy.

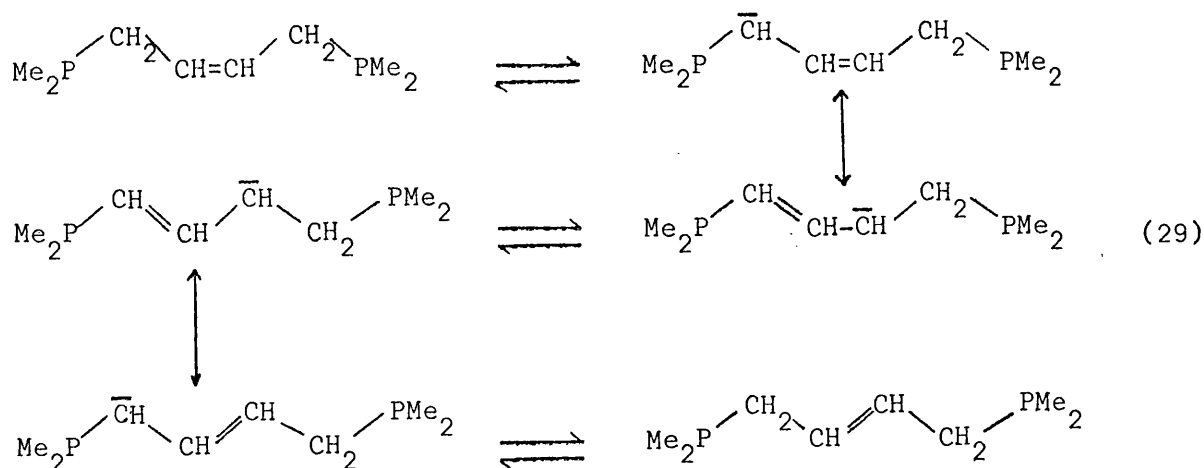
The product from the reaction of lithium dimethylphosphide and cis-1,4-dichlorobut-2-ene, which was shown by g.l.c. to contain none of the trans-isomer, was found by ^1H n.m.r. spectroscopy to be a mixture of cis- and trans-1,4-bis(dimethylphosphino)but-2-ene in the ratio 66:33. (A comparison of this spectrum with that of the pure trans- isomer is given later - Section I-4). Isomerisation of the dichloride is not likely as it reacts as soon as it is added to the reaction mixture (as shown by the colour changes), therefore it would appear that it is the cis-phosphine that is undergoing isomerisation. A small amount of lithium naphthalenide is present

in the reaction mixture before any dichloride is added, however the dichloride reacts with the naphthalenide in preference to the phosphide (the reaction mixture rapidly changes from green of the naphthalenide to orange of the phosphide as the dichloride is added), so destroying it before any phosphine is formed (equ. 28).



That the naphthalenide was not responsible for the isomerisation was confirmed by destroying it with i-propyl bromide before the dichlorobutene was added. Some isomerisation still occurred, a cis:trans isomer ratio of 85:15 being obtained.

It would appear therefore that the isomerisation of the cis-phosphine is induced by the excess basic phosphide present until all the chloride has been added. Presumably an allylic proton is removed by the base and rearrangement to the more stable trans-isomer occurs by a system of equilibria (equ. 29).



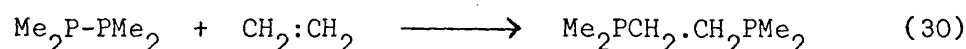
An 85:15 mixture of the cis- and trans- isomers was stirred with sodamide in liquid ammonia for 1½ hr. On work-up with ether and water, after treatment with ammonia chloride, the isomer ratio had changed slightly to 80:20. It is expected that the soluble Me_2P^- ion would cause more rapid isomerisation. If this theory of base catalysed isomerisation is correct, it should be possible to prepare the pure cis-isomer by reverse addition of the phosphide to the dichloride as this would eliminate any excess base being in contact with the phosphine.

The difference in the ratio of isomers from the experiments with and without the addition of i-propyl bromide is probably due to the addition of i-propyl bromide, and the different work-up procedures employed. By adding i-propyl bromide and then the dichlorobutene there was more than sufficient halide to destroy all the lithium base. In the first case, however, it is possible that there was a slight deficiency in the amount of dihalide so leaving a small excess of base. Also, in the first reaction, the mixture was not extracted with water and ether, therefore any excess base would not be hydrolysed.

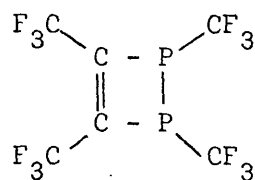
4. Reaction of Tetramethyldiphosphine with Butadiene

Until the discovery of the use of naphthalene as a catalyst for the cleavage of diphosphine (Section I-3), dimethylphosphino derivatives were difficult to prepare. As a possible route to 1,4-bis(dimethylphosphino)but-2-ene, therefore, the addition of tetramethyldiphosphine to butadiene was investigated.

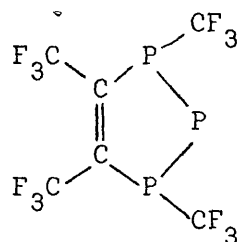
Burg⁷⁸ has described the 1,2-addition of diphosphines to olefins; tetramethyldiphosphine reacts slowly with ethylene under forcing conditions to give 1,2-bis(dimethylphosphino)ethane (equ. 30). The reaction, which is catalysed by iodine, requires temperatures of about 280° for up to 700 hr.



This reaction was extended by Burg and Grant⁸⁰ to tetrakis(trifluoromethyldiphosphine which they found to be more reactive; 1,2-addition products were obtained with ethylene, tetrafluoroethylene and acetylene. A similar addition reaction to an acetylene has been reported;⁸¹ cyclic polyphosphines $(\text{CF}_3\text{P})_n$ ($n = 4,5$) react with perfluorobut-2-yne to yield P-P bonded cyclic systems (4) and (5).

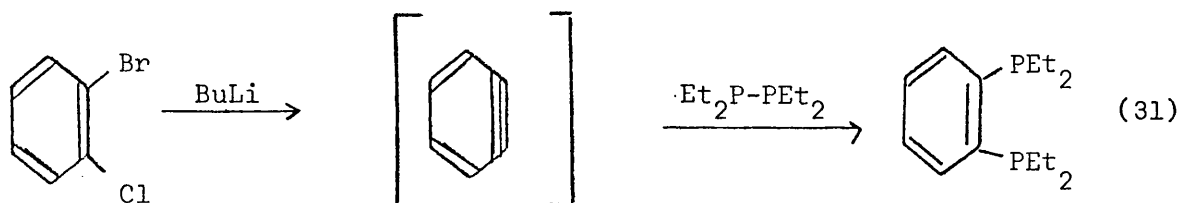


(4)

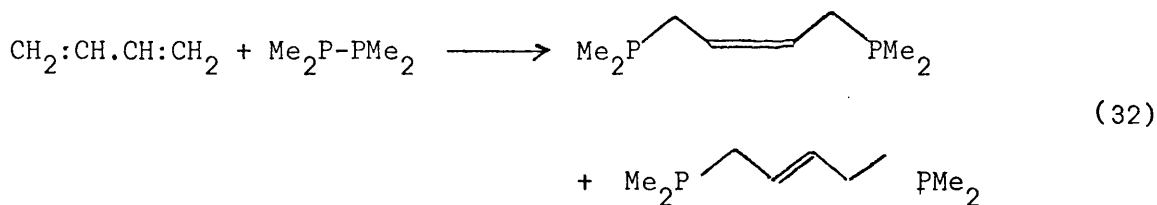


(5)

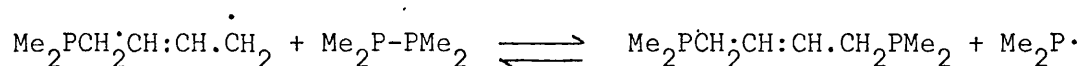
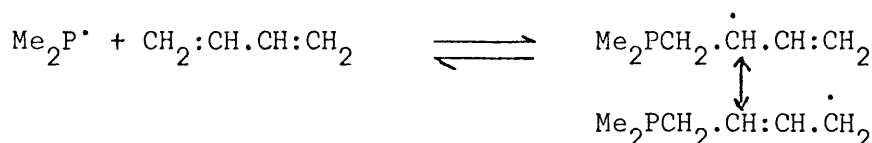
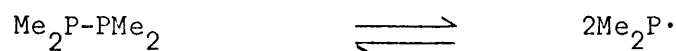
It has been suggested that the formation of o-phenylenebis(diethylphosphine) can occur by the addition of tetraethyldiphosphine to benzyne (equ. 31).⁸²



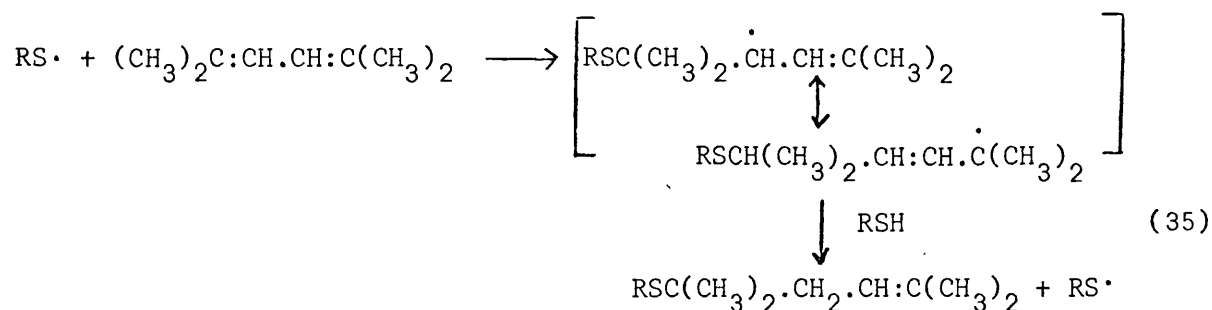
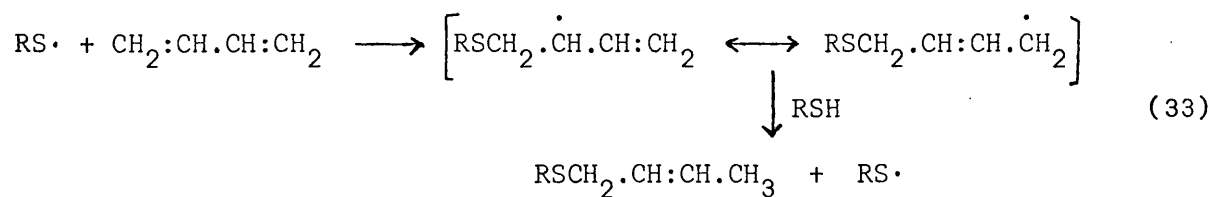
Tetramethyldiphosphine and butadiene (1:1) react slowly at 100° under autogenous pressure in the absence of catalyst or solvent. The reaction is apparently more rapidly than that of ethylene.⁷⁸ After 6 hr. a 20% conversion of reactants was observed; a further 7 hr. at 105-140° gave a total conversion of 48% of both reactants. The product was isolated using a vacuum line (App. 4 - Figure 1), and was shown by ¹H n.m.r. spectroscopy to be a mixture of cis- and trans-1,4-bis(dimethylphosphino)but-2-ene in the ratio 30:70. No 1,2-addition product, 3,4-bis(dimethylphosphino)but-1-ene, was detected, and the yield was almost quantitative (based on reactants used).

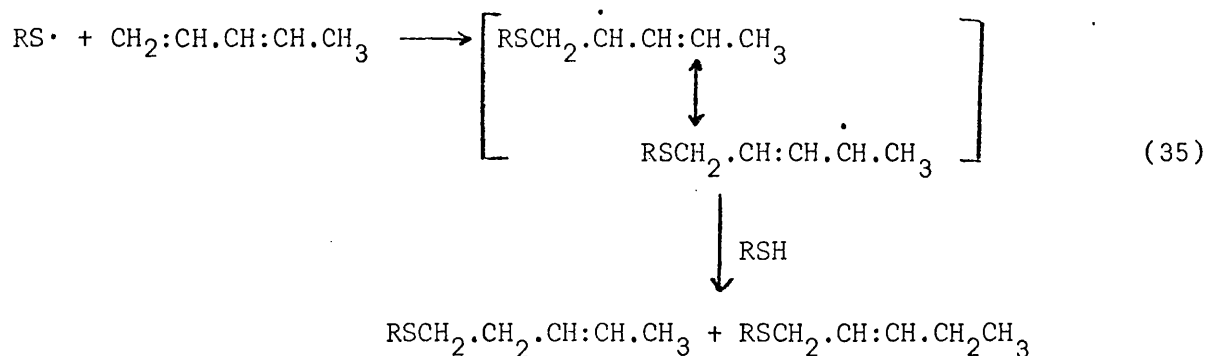


A free radical mechanism, involving the attack of an $\text{Me}_2\text{P}^\bullet$ radical to give an allylic radical intermediate which abstracts from $\text{Me}_2\text{P}^\bullet$ from tetramethyldiphosphine, is suggested for this reaction.



In a series of papers⁸³⁻⁸⁶ Oswald and co-workers examined the free radical addition of thiols to conjugated dienes. They found that the product obtained was the one derived from the less highly substituted allyl radical. Thus reactions of butadiene, 2,3-dimethylbutadiene, isoprene, and chloroprene proceed by 1,4-addition (e.g. equ. 33).⁸⁴ 1,1,4,4-Tetramethylbutadiene gives the product from 1,2-addition (equ. 34),⁸³ and with piperylene, where both canonical forms of the allyl radical intermediate are secondary, a mixture of 1,2- and 1,4-addition products are formed (equ. 35).^{84,86}

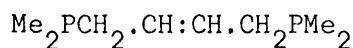




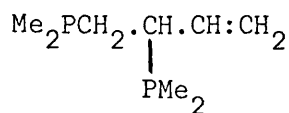
In the presence of oxygen the allylic radicals react to give an intermediate alkyl peroxy radical which yields "reversed" products, i.e. where 1,4-addition was found in the absence of oxygen, the co-oxidation reaction proceeded by a 1,2-addition, and vice versa.^{83,85,86} The results can be rationalised using Hammond's correlation.⁸⁷ As the abstraction from a thiol has a significant activation energy, the stability of the final product should make an important contribution to that of the transition state. Thus, the reaction proceeds via the transition state which leads to the thermodynamically more stable product, even though this is derived from the less stable (i.e. the less highly substituted) allylic radical. The reaction with oxygen has no significant activation energy and the stability of the transition state will depend on that of the allylic radical, and the product derived from the more stable radical is formed.

The abstraction of $\text{Me}_2\text{P}\cdot$ from tetramethyldiphosphine by the intermediate allylic radical probably has a high activation energy. Russian workers⁸⁸ have measured the dissociation energy, to which the activation energy of the abstraction will be coupled, of tetraethyldiphosphine by mass spectroscopic techniques, and found it to be $86 \text{ kcal.mole}^{-1}$. By the above arguments, then, one

would expect exclusive 1,4-addition to be observed, this giving rise to the more stable olefinic phosphine.



1,4-Addition Product



1,2-Addition Product

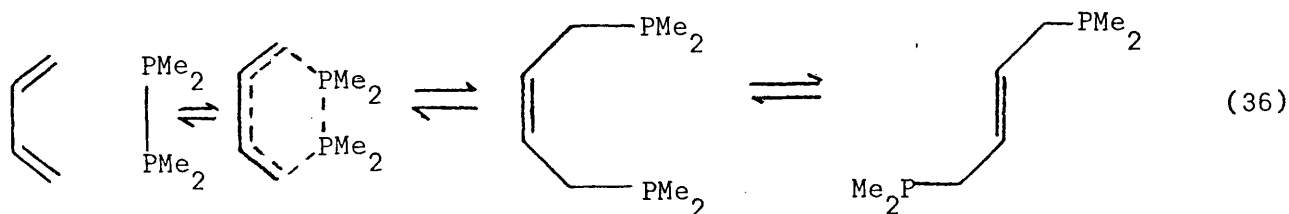
The radical addition of di-n-butylphosphine to butadiene at 79-84° gives mainly the 1,4-adduct (claimed to be the trans-isomer) together with a small amount (7%) of the diphosphine $\text{Bu}_2\text{P}(\text{CH}_2)_4\text{PBu}_2$ which is thought to be formed by two 1,2-additions.⁸⁹ The occurrence of a certain amount of 1,2-addition would indicate that the abstraction of hydrogen from Bu_2PH has a lower activation energy than the abstraction of $\text{Me}_2\text{P}\cdot$ from tetramethyldiphosphine.

Evidence has been presented that the short-lived allylic radicals maintain the geometry of their precursors.^{86,90} It was found that the free radical chlorination of cis- and trans-but-2-ene with t-butoxy chloride produced only the respective cis- and trans-1-chlorobut-2-enes. Based on this, it has been claimed that the ratio of cis-1,4- to trans-1,4-addition products from the radical reactions of butadiene reflects the relative amounts of the s-cis- and s-trans- forms of butadiene.⁹¹ Chemical and physical studies indicate that the s-cis to s-trans ratio is about 5:95 at room temperature,^{91,92} but at higher temperatures the amount of the s-cis form will increase, the activation energy for the transition of s-trans to s-cis being relatively small. (An estimate of the energy difference between the two forms and the

activation energy for isomerisation, based on thermodynamic data, is 2.3 and 4.5 kcal.mole⁻¹ respectively;⁹³ an extended Hückel calculation, however, gives values of 9.5 and 0 respectively.⁹²⁾

It is presumed that the 30:70 ratio of products obtained from the reaction of tetramethyldiphosphine with butadiene is an indication of the proportion of s-cis to s-trans forms of butadiene present at the reaction temperature. The reaction was found to be catalysed by the radical initiator azobis(isobutyronitrile) (A.B.N.) and in the presence of this a 62% conversion of reactants was obtained after 6 hr. at 100°. Again no 1,2-addition product was found, and the ratio of cis:trans isomers had changed to 25:75 which is consistent with the lowering of the reaction temperature, although the effect of A.B.N. on the ratio was not investigated.

Two other possible reaction paths were considered: (a) an ionic mechanism and (b) a cyclic molecular addition mechanism. The ionic mechanism is discounted because of the absence of any 1,2-addition product. In studies of both the chlorination⁹⁴ and bromination⁹⁵ of butadiene it was found that an ionic reaction is characterised by a predominance of the 1,2- product. A cyclic molecular addition mechanism related to the Diels-Alder reaction⁹⁶ would give rise to the cis- isomer, and would require that the trans- isomer arises by thermal isomerisation (equ. 36).



A 66:33 mixture of the cis- and trans- isomers was heated in an n.m.r. tube for 3 hr. at 100-150° but there was no significant change in the isomer distribution. Further, it would be expected that cyclopentadiene would react more rapidly than butadiene as the double bonds in this compound are held in the necessary cisoid configuration.⁹⁶ After a mixture of tetramethyldiphosphine and cyclopentadiene had been heated for 4 hr. at 110°, the reactants were recovered. At 145-180° over 2 hr. a trace of an unidentifiable material was found.

The ¹H n.m.r. spectrum (220 MHz) of the cis:trans mixture gave the ratio of the isomers by integration of the vinylic peaks which were well separated. There is no general correlation of the chemical shift of vinylic protons with the geometry of symmetrical 1,2-disubstituted olefins.⁹⁷ The unequivocal assignment of the spectrum was permitted by comparison with that of the pure trans- isomer, which was prepared as described previously - Section I-3. Each absorption of the trans- isomer occurs at a higher field than that of the corresponding proton in the cis- isomer (see App. 1 - Table 5). The Figure below shows a comparison of the spectra of the trans-isomer (b) and the cis:trans mixture (a) which was obtained from the reaction of lithium dimethylphosphide and cis-1,4-dichlorobut-2-ene, but which is the same, except for the ratio, as that obtained from the reaction being described in this Section.

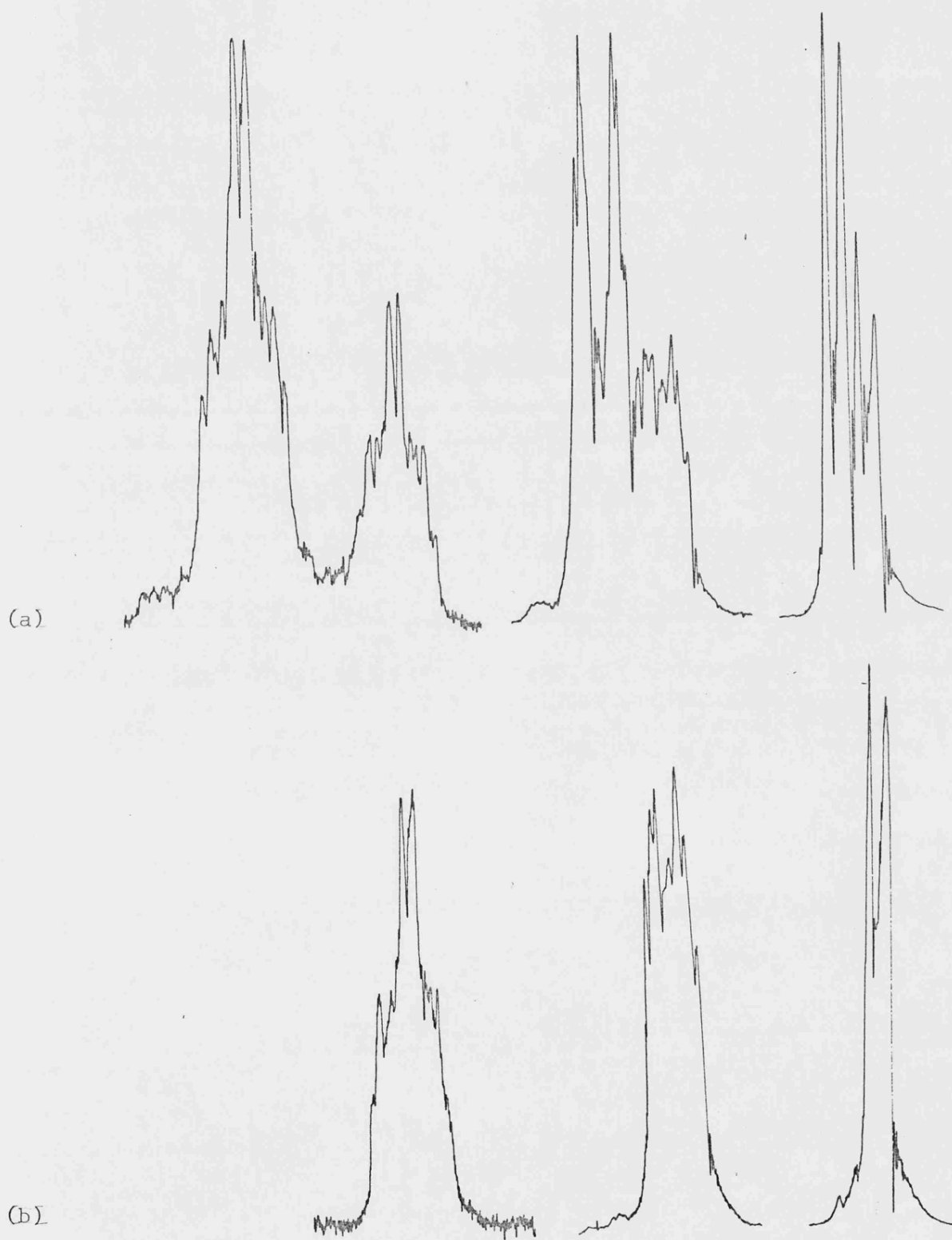


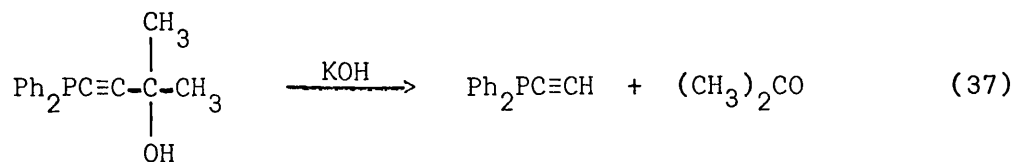
Figure: ^1H n.m.r. Spectra of (a) cis- and trans-1,4-Bis(dimethylphosphino)but-2-ene, and (b) trans-1,4-Bis(dimethylphosphino)but-2-ene.

Confirmation of the structure of the trans- isomer was obtained from its Raman and i.r. spectra, the key feature of which is the presence of a strong absorption at 1655 cm^{-1} in the Raman spectrum, and the absence of a band in this region of the i.r. spectrum. This alone identified a symmetrical trans-substituted olefin.⁹⁸ Assignments of most of the bands have been made utilising published vibrational data on tetramethyldiphosphine.^{98,99} (The spectra are given in App. 2 - Table 12).

The platinum(II) chloride complexes of the cis:trans mixture were separated by their different solubilities in chloroform. They are apparently polymeric and are almost insoluble in common organic solvents, though the cis- isomer complex is sufficiently soluble in chloroform to allow their separation. The two complexes were characterised by their i.r. spectra, details of which are given in App. 2 - Table 13.

5. Acetylenic Mono-phosphines

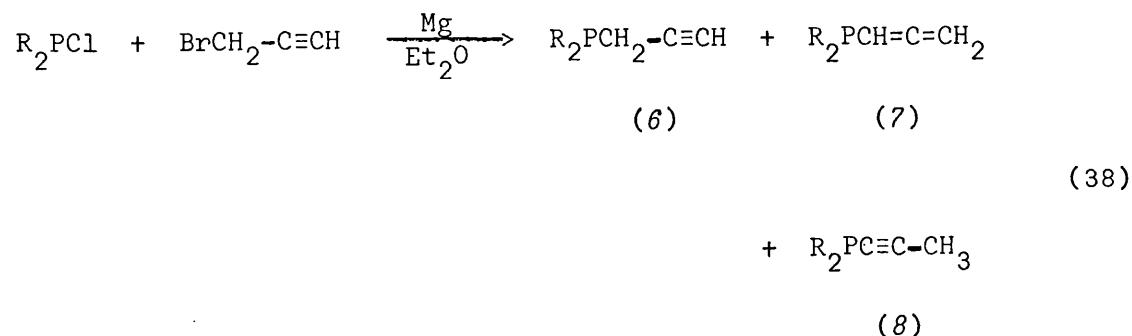
α -Acetylenic phosphines have been known for several years. Ethynyldiphenylphosphine was first prepared by Hartman¹⁸ from the methyl phosphonium salt of bis(diphenylphosphino)acetylene, and subsequently by Cadiot¹⁶ who used the route shown in equ. (37).



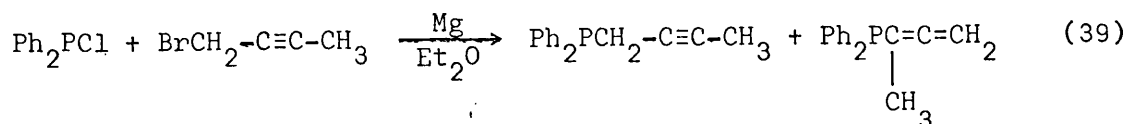
The analogous alkyl substituted ethynyl phosphines were prepared by Voskuil and Arens³¹ from the appropriate dialkylchlorophosphine and acetylenic-Grignard, and were subsequently examined by ^1H n.m.r.

spectroscopy.¹⁰⁰ The preparation of substituted α -acetylenic phosphines is the subject of a paper by Cadiot and co-workers¹⁰¹ in which they discuss the spectral properties of the phosphines. Again, the Grignard route using diphenylchlorophosphine was employed.

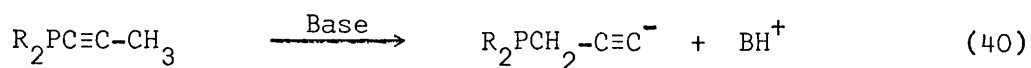
Attempts have been made to prepare β -acetylenic phosphines. The French workers reported¹⁰² that Voskuil had examined the reaction of chlorophosphines R_2PCl with the Grignard reagent of 3-bromoprop-1-yne. Three products were found: the β -acetylenic phosphine (6), the allenic phosphine (7), and the α -acetylenic phosphine (8) - equ. (38).



The proportions of the isomers vary according to the group R. It was shown by the use of a substituted prop-2-ynyl bromide, $BrCH_2-C\equiv C-CH_3$, that the reaction proceeds with an "inversion" of structure for the allenic and α -acetylenic phosphines; with this bromide the products were the but-2-ynyl- and 1-methylpropa-1,2-dienylphosphine (equ. 39).



This rearrangement could occur by attack on the γ -carbon atom, or by rearrangement of the Grignard reagent before the reaction. Voskuil is also reported to have observed a prototropic rearrangement of the phosphines.¹⁰² With a trace of base, a mixture of (6) and (7) was isomerised to (8), but in the presence of a greater than stoichiometric amount of a strong base, the equilibrium was found to favour isomer (6). Presumably this is because of the acidic proton in isomer (6) (equ. 40).



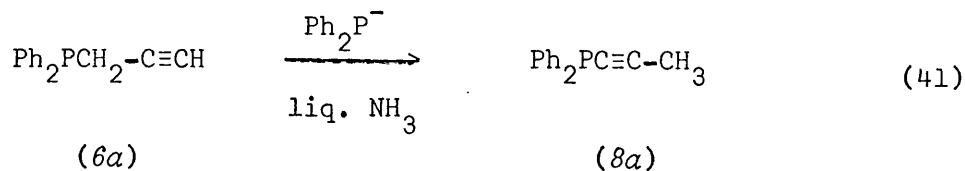
The mixtures of isomers from the Grignard reaction were used in a study of long range P-H coupling constants in n.m.r. spectroscopy,¹⁰³ and the paper describes the composition of the mixtures with various alkyl and aryl groups on the phosphorus. The reaction of prop-2-ynyl-Grignard reagents with chloroarsines has been studied¹⁰⁴ and an analogous mixture of isomers was found.

β -Acetylenic phosphines were required in this work (Series IV) for a study of their transition metal complexes. Mixtures of phosphines are not suitable for such work and an alternative preparation giving the pure isomers had to be found. The reaction of sodium diphenylphosphide with alk-2-ynyl halides was investigated.

The addition of 3-chloroprop-1-yne to sodium diphenylphosphide in liquid ammonia gave one isomer in good yield - diphenyl-

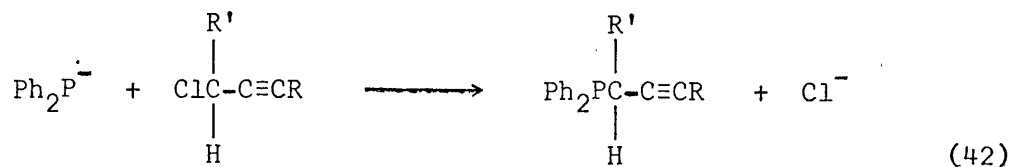
Examples of S_N2' reactions have been discussed,¹⁰⁵ although a recent paper suggests that only a few reactions have been demonstrated to proceed by this mechanism.¹⁰⁶ It has been suggested that some reactions of alk-2-ynyl halides are of this type.^{105,107}

The following observations are consistent with the first mechanism. (i) The reaction was carried out in tetrahydrofuran in which the phosphine acts as a weaker base. The mixture of isomers which was obtained was examined by 1H n.m.r. spectroscopy and was found to be the prop-2-ynylphosphine (6a), the allenylphosphine (7a), and the prop-1-ynylphosphine (8a) in the ratio 6:1:20. (ii) To avoid the presence of excess phosphide, which provides the basic medium, the reaction was carried out by reverse addition, i.e. a solution of sodium diphenylphosphide in tetrahydrofuran was added to 3-chloroprop-2-yne in tetrahydrofuran. Thus, in the absence of base, the pure prop-2-ynylphosphine (6a) was obtained in 64% yield. (iii) A sample of prop-2-ynylphosphine was added to a solution of sodium diphenylphosphide in liquid ammonia (the conditions of the original reaction). It was isomerised to the α -acetylenic phosphine.



(iv) If the reaction were proceeding by an S_N2' mechanism, methyl substituted prop-2-ynyl chlorides should give allenyl products with an "inverted" structure. However, both 3-chlorobut-

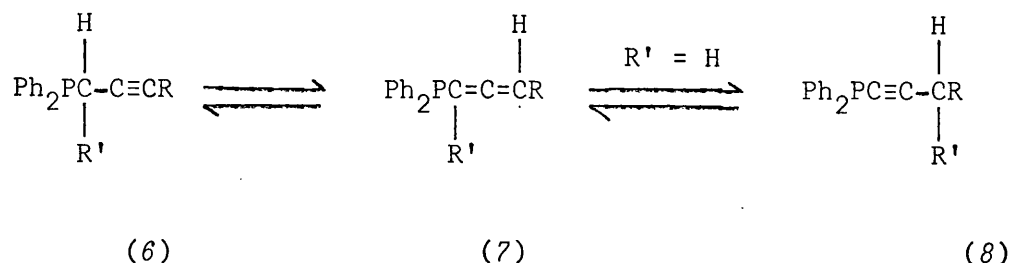
1-yne and 1-chlorobut-2-yne react with sodium diphenylphosphide in liquid ammonia to give the corresponding β -acetylenic phosphines, (6b) and (6c) respective (equ. 42).



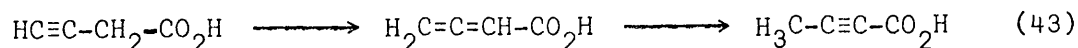
(6b) $\text{R} = \text{H}, \text{R}' = \text{Me}$

(6c) $\text{R} = \text{Me}, \text{R}' = \text{H}$

It might be expected that if the reaction were proceeding by mechanism (a), the rearranged α -isomers should be obtained since there was an excess of sodium diphenylphosphide present during the addition. This may be discussed in terms of the relative stabilities of the possible isomers in each system.

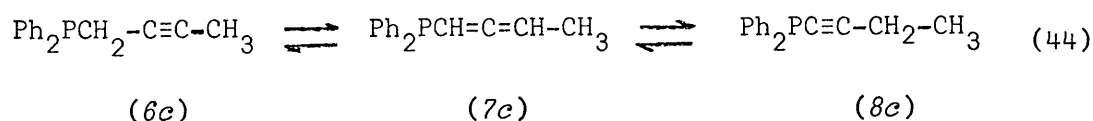


When $\text{R} = \text{R}' = \text{H}$ $[(6a) \rightleftharpoons (8a)]$, the α -acetylenic phosphine (8a) is stabilised by two effects (i) a d_π - p_π interaction between the orbitals of phosphorus and the acetylene group, and (ii) the known stabilising influence of a methyl group attached to an acetylene.^{108,109} Neither of these two effects operates in the β -isomer (6a). The observed rearrangement of (6a) \longrightarrow (8a) exactly parallels that of the corresponding carboxylic acids where the same effects can apply (equ. 43).¹¹⁰

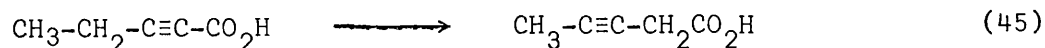


Considering the possible system where $\text{R} = \text{Me}$, $\text{R}' = \text{H}$

$[(6c) \rightleftharpoons (8c)]$, the delocalisation effect (i) will apply to the α -acetylenic phosphine (8c), whereas the interaction (ii) will operate in the β -isomer (6c), (equ. 44).



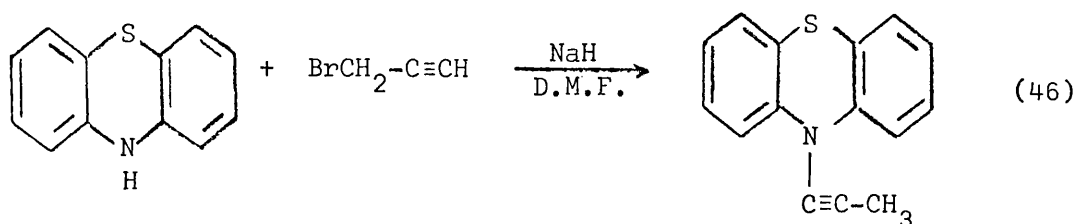
It would appear that the stabilisation of the acetylene group by a methyl substituent is more important than the stabilisation by phosphorus. Again, the same result is found in the analogous carboxylic acid system (equ. 45);¹⁰⁹ the stabilisation by a methyl group is more important than stabilisation by the acid group.



Finally, when $\text{R} = \text{H}$, $\text{R}' = \text{Me}$ (6b), a base catalysed prototropic rearrangement cannot give rise to an α -acetylene as this would involve the migration of Me^+ . The allene (7b) is apparently no more stable than the β -acetylenic phosphine (6b). However, on heating to ca 130° the crude product from the preparation of (6b), which was shown by ^1H n.m.r. spectroscopy to be mainly (6b), some of the allene was formed.

There are many examples of analogous base catalysed proto-

tropic rearrangements of acetylenes in the literature, although during some reactions of 3-bromoprop-1-yne the isomerisation was not observed. Thus, Gaudemar⁶⁶ described the reaction with various nucleophiles (R_2N^- , RO^- , $(RO_2C)_2CH$, RCO_2^-) to give prop-2-ynyl products. Other authors, however, found that under strongly basic conditions prop-2-ynyl amines did rearrange. Zaugg and co-workers obtained the prop-1-ynylamine when phenathiazine was treated with 3-bromoprop-1-yne in the presence of sodium hydride (equ. 46).



This reaction with aromatic amines was studied in greater detail by Dumont.¹¹² Using sodamide or butyl-lithium to prepare the amide he found that the prop-2-ynylamines could be obtained, but that these isomerised in the presence of strong base (potassium hydroxide or t-butoxide) to the prop-1-ynylamines. The isomerisation of diethylprop-2-ynylamine has been reported by Viehe who used aluminium oxide and potassamide at 50-80°. ¹¹³ There is also a brief report of an analogous rearrangement occurring in the corresponding thiyl compounds. ¹¹⁴

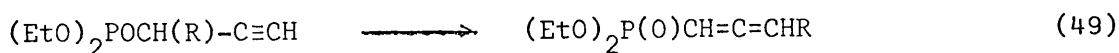
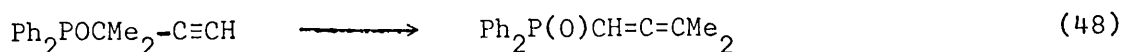
Prototropic rearrangements have been reported for phosphorus-containing compounds. Jacobson found that an Arbuzov reaction between triethyl phosphite and 3-bromoprop-1-yne gave diethyl prop-

1-ynylphosphonate (equ. 47).¹¹⁵



The reaction between 3-bromoprop-1-yne and sodium diethyl phosphonate gave the same product, although a little of the prop-2-ynyl phosphonate was detected.¹¹⁶ This latter observation was disputed by later workers¹¹⁷ who, on re-examination of the reaction using sodium dimethyl and diethyl phosphonates, found only the prop-1-ynyl products. On re-examination of the Arbuzov reaction (equ. 43) they found that whereas the prop-1-ynylphosphonate was obtained with triethyl phosphite, trimethyl phosphite gave the prop-2-ynyl isomer. Presumably this is due to the different basicities of the systems with the two phosphites.

The preparations of allenic phosphine oxides¹¹⁸ and phosphonates¹¹⁹ have been reported by a rearrangement mechanism (equ. 48 and 49).



The allenyl phosphonate, which is probably the intermediate in the Arbuzov and Michaelis-Nylen reactions described above, was found to rearrange spontaneously in the absence of solvent to the alk-1-ynyl-phosphonate.¹²⁰

Alk-2-ynyl bromides were found to react with sodium diphenyl-phosphide in some cases by attack on the halogen atom instead of the carbon atom. This is discussed in a previous section of this thesis (I-2).

II Preparation and Structure of Phosphine Complexes.

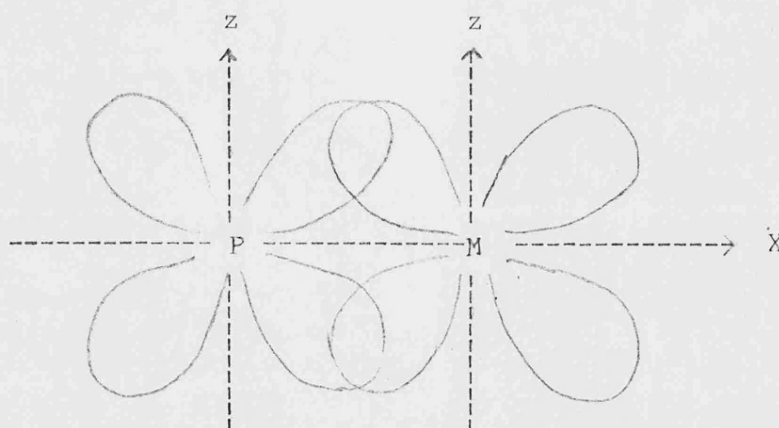
1. Introduction

Transition metal complexes with phosphorus and arsenic ligands have been extensively studied in recent years. In a review article Booth discusses in detail the complexes with each Group of transition metals in the Periodic Table, bringing out the various applications of these ligands.¹²¹

Ahrland, Chatt and Davies¹²² drew up a classification of metals based on the relative stabilities of their complexes with Group V elements, class (b) being those whose complexes follow the sequence $N \ll P > As > Sb > Bi$, while class (a) follow the sequence $N > P > As > Sb > Bi$. The division between the two classes is not a sharp one, but they found that the class (b) atoms were chiefly those of Group VIII. It is with metals in this class, palladium and platinum, that this thesis is concerned. Pearson later proposed a related classification based on the concept of hard and soft acids and bases.¹²³ Platinum and palladium come into the category of soft acids, and form strong complexes with soft bases, e.g. phosphine or arsine. Pearson points out that his principle is a useful statement of scientific facts but is not a theory in itself. For the underlying theories he suggests that the many aspects of chemical bonding need to be looked at.

The affinity of Chatt's class (b) metals for phosphorus has been explained by the ability of phosphorus to act as a π -acceptor as well as a σ -donor ligand. The vacant 3d orbitals on phosphorus are of the correct symmetry to interact with the

filled non-bonding d-orbitals of the metal.



The relative importance of this acceptor property will vary from one phosphine to another. In trifluorophosphine, PF_3 , where the electronegative fluorine atoms will reduce the σ -bonding effect of the phosphine, the π -effect probably plays a major role in the bonding; in fact, PF_3 has been likened to carbon monoxide as a ligand.¹²⁴ The class (b) metals have low oxidation states and a large number of electrons in the non-bonding d-orbitals, e.g. Pt(II) is d^8 , and it is likely that the acceptor property of the ligands is important in reducing the electron density on the metal. Recently, however, Venanzi has challenged this explanation, and prefers to assign the stability of the complexes to phosphorus having "an intrinsic property of forming strong platinum-phosphorus σ -bonds".¹²⁵ He does not offer an explanation of this property. Carty and Efraty have attempted to obtain a measure of the back bonding contribution by examining complexes of bis(diphenylphosphino)acetylene.¹²⁶ The Raman active $\nu(\text{C}\equiv\text{C})$ absorption of the ligand occurs at a lower than the normal range for disubstituted acetylenes. This they explain by the interaction of the acetylene orbitals and the empty d-

orbitals of the phosphorus. This interaction will be reduced, they argue, by any back donation from metal orbitals into the same orbitals on the phosphorus when a complex is formed. Shifts in frequency of about 40 cm^{-1} were observed in platinum(II) and palladium(II) complexes of the ligand.

Whatever the cause of the stabilising influence, phosphine ligands have been found useful for preparing a wide variety of platinum(II) and palladium(II) complexes. The general order of stability is found to be $\text{Pt} > \text{Pd}$, and this is reflected in the organometallic compounds that have been isolated. Metal alkyls of the type $\text{PtXR}(\text{PR}'_3)_2$, $\text{PtR}_2(\text{PR}'_3)_2$, $\text{PdXR}(\text{PEt}_3)_2$ and $\text{PdR}_2(\text{PEt}_3)_2$ have been prepared,^{127, 128} and acyl derivatives have been obtained by the action of carbon monoxide on these.¹²⁹ Olefin and acetylene complexes of palladium and platinum are known and this subject has been extensively reviewed by Bennett,¹³⁰ and more recently by Hartley¹³¹ and Italian workers.¹³²

A number of dihalogen compounds of platinum(II) and palladium(II) are known. These are either of the form $\text{MX}_2(\text{PR}_3)_2$, or $\text{MX}_2(\text{diphos})$, where "diphos" is a ditertiary phosphine, e.g. $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$. References to these compounds may be found in Tables VIII and IX of the review by Booth.¹²¹

Phosphines are useful for stabilising low oxidation states, and a number of complexes of platinum(0) and palladium(0) have been studied. Work has been carried out in this field by Malatesta¹³³ and Chatt,¹³⁴ and the subject has been amply reviewed by Ugo.¹³⁵ Metal(IV) complexes may be obtained by oxidising the corresponding metal(II) complex with halogens.¹³⁶

The complexes with which this thesis is concerned are the dichlorides of platinum(II) and palladium(II) with some unsaturated phosphorus ligands. The usual routes to compounds $(PR_3)_2MX_2$ are by the reaction of the phosphine directly with platinum(II) or palladium(II) chloride, or with a complex derived from these, e.g. sodium chloroplatinite, $Na_2PtCl_4 \cdot 4H_2O$, or bis(benzonitrile)-metal(II) chloride. The complexes may be obtained with a cis- or trans- arrangement of the ligands around the metal. In general, using monophosphines trans- complexes are obtained with palladium(II), and cis- complexes with platinum(II). Exceptions to this rule were found in this work; bis(diphenylpropynylphosphine)palladium(II) chlorides were obtained as the cis- isomers, and bis(allyldiphenylphosphine)platinum(II) chloride as a mixture of the two forms.

The following two Sections describe the structures of the complexes of unsaturated phosphines which have been obtained.

2. Complexes of Unsaturated Phosphines

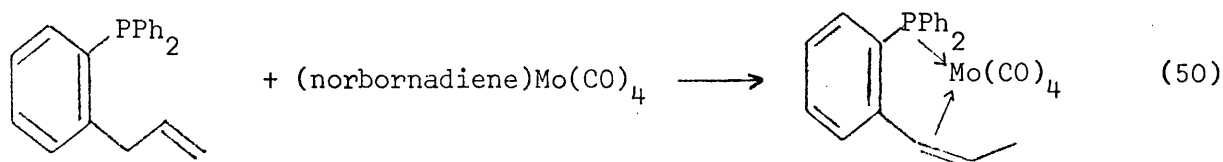
Platinum(II) and palladium(II) complexes of four series of unsaturated phosphines were examined. In all cases it was found that the ligand co-ordinated to the metal through the phosphorus, and only with certain ligands was there any bonding between the metal and the unsaturated unit.

Wu and Welch prepared silver(I) complexes of diphenylvinylphosphine (a phosphine of Series I - $R_2P(CH_2)_nCH:CH_2$ - with $R = Ph$, $n = 0$).¹³⁷ They obtained two complexes, 1:1 and 1:2, and concluded from spectroscopic data (i.r. and n.m.r.) that both the phosphorus and the vinyl group are co-ordinated to the metal.

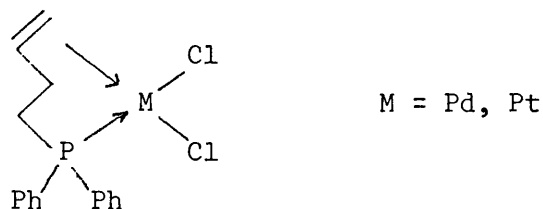
They suggested, however, that these complexes are monomeric with the two groups donating to the same metal, but this is unlikely for steric reasons, our work suggesting that a chain of four or five carbon atoms is required for a chelate complex of this kind. Wu and Welch based the monomeric structures on molecular weight determinations, but their interpretation of such measurements for ionic compounds must be questioned.

Complexes of another phosphine from Series I, pent-4-enyl-diphenylphosphine (I, R = Ph, n = 2), and the arsine analogue, have been studied by Bennett.¹³ With platinum(II) chloride the phosphine gives a monomeric non-ionic complex with both the phosphorus and olefin bonded to the same platinum atom. Dipent-4-enyldiphenylphosphine gives a complex in which one olefin group is bonded and the other is free; the free olefin does not displace the phosphorus. With palladium(II), and also mercury(II), pent-4-enyldiphenylphosphine gives a complex in which the double bond is not co-ordinated and to which was assigned a dimeric structure with chlorine bridges. This school also examined the complexes of ligands in which the carbon chain is made up in part by a benzene ring. The ligand with five carbon atoms in the chain, o-allyldiphenylphosphine, and the arsine, form complexes with a variety of metals (palladium(II),¹³⁸ platinum(II),^{138,139} rhodium(III),¹³⁹ copper(I) and silver(I),¹⁴⁰ manganese(I) and rhenium(I),¹⁴¹ and vanadium¹⁴²), and in all cases except with some silver and copper salts, co-ordination to the metal is from both the phosphorus and the double bond. Chromium(0), molybdenum(0) and tungsten(0) react with this phosphine to give

complexes of the isomeric diphenyl-o-cis-prop-2-enylphenylphosphine (equ. 50).^{14,15,143}



Issleib¹² prepared phosphines with one carbon atom less in the chain - but-3-enyldialkylphosphine where the alkyl group was ethyl or cyclohexyl. Again complexes with several metals were prepared. With platinum(II), palladium(II) and chromium(0) both the olefin and the phosphorus co-ordinated to the metal, whereas with nickel(II), silver(I) and copper(I), only the phosphorus formed a bond. We found that with the phenyl analogue, but-3-enyldiphenylphosphine, platinum(II) and palladium(II) chlorides gave chelate complexes with both functional groups co-ordinated (9).



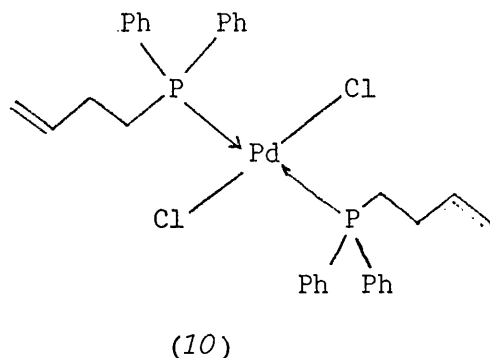
(9)

The evidence for assigning this structure to the complexes was spectroscopic. The absorption in the i.r. spectrum of the free ligand at 1639 cm^{-1} , which may be assigned to the $\nu(\text{C}:\text{C})$ vibration,⁹⁸ and the absorption at 995 and 909 cm^{-1} due to the vinylic hydrogen atoms, were absent in the complexes. New bands appeared at 1503 and

1525 cm^{-1} in the platinum and palladium complexes respectively. The shift in the i.r. frequency from about 1640 cm^{-1} has been generally used as a diagnostic tool to show the presence of a co-ordinated olefin.^{1,144} The cis-arrangements of the chlorine atoms were confirmed by absorptions in the far infrared region of the spectra at 398 and 330 cm^{-1} for $\nu(\text{Pt-Cl})$, and 325 and 298 cm^{-1} for $\nu(\text{Pd-Cl})$.¹⁴⁵ The ^1H n.m.r. spectrum of the platinum complex had absorptions which were shifted slightly up-field with respect to those in the free ligand. The olefinic protons of the ligand absorb at 4.28, 5.10 and 5.13 τ (with respect to T.M.S.), and those of the complex at 4.45, 5.20 and 5.26 τ . These changes are not as large as those found in Zeiss's salt, where the olefinic proton absorption is shifted from 4.59 τ in free ethylene to 5.59 τ .¹⁴⁶ Two effects determine the amount by which the signals are moved: the donor property of the olefin which, in reducing the electron density, causes a shift down-field, and the back donation from the platinum into the empty anti-bonding π -orbitals of the olefin which will cause a shift up-field. The net change will be a balance between these two effects and will vary from one complex to another. Platinum-hydrogen coupling was not observed as the sample was not sufficiently concentrated to allow these small bands to be identified above the background noise. The n.m.r. spectrum of the palladium complex could not be obtained because of the low solubility of the compound. The mass spectrum of the platinum complex showed a parent ion at m/e 504, which is expected for complex (9), $M = \text{Pt}$.

When the palladium complex - (9) $M = \text{Pd}$ - was prepared by the addition of the phosphine to sodium chloropalladite, a second product was obtained by fractional crystallisation. The i.r. spectrum

showed an unco-ordinated double bond [$\nu(\text{C}:\text{C})$ 1640 cm^{-1}], the far i.r. spectrum showed a trans-arrangement of the ligands about the metal [$\nu(\text{Pd}-\text{Cl})$ 351 cm^{-1}], and analytical data showed it to be $(\text{RPPH}_2)_2\text{PdCl}_2$. Structure (10) was assigned to this complex

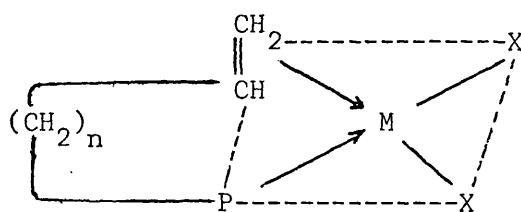


We found also, as did Issleib, that whereas but-3-enyldiethylphosphine forms a chelate complex with palladium(II) chloride, with platinum(II) chloride the reactants may be recovered unchanged.

Reducing the carbon chain by one atom has a great effect on the type of complex which is formed. Allyldiphenylphosphine with platinum (II) chloride and palladium(II) chlorides gives complexes of the type $(\text{CH}_2=\text{CH}-\text{CH}_2\text{PPh}_2)_2\text{MCl}_2$. No bonding between the olefin and the metal can be detected spectroscopically. Both free ligand and the complex have bands in their i.r. spectra at around 1640 cm^{-1} [$\nu(\text{C}:\text{C})$], 1000 and 920 cm^{-1} [$\delta(\text{:C-H})$], and their ^1H n.m.r. spectra are virtually identical. The compounds analysed correctly for 2:1 complexes. With allyldiethylphosphine, again the complexes had no co-ordination from the olefinic bond. The only complex of an allyl phosphine which has been reported in the literature is that between allyldiphenylphosphine and nickel(II) chloride.¹¹ Again, no chelation was found.

Reducing the number of carbon atoms further gives a vinyl phosphine, the only reported complex of which has already been discussed.

It appears, therefore, that for phosphines of Series I, whether there is co-ordination from the olefin as well as the phosphorus depends on the length of the carbon chain. Platinum(II) will form chelate complexes when the chain is four or five carbon atoms in length, but not if it is three. Palladium(II), however, will only give complexes in which the olefin is bonded if the number of carbon atoms in the chain is four, unless some rigidity is given to the chain by including an aromatic ring. The effect of the chain length is undoubtedly steric. For co-ordination between the metal and an olefin in square planar complexes the carbon chain has to be orientated so that the plane of the double bond is almost perpendicular to the plane of the metal and the other ligands.¹⁴⁷

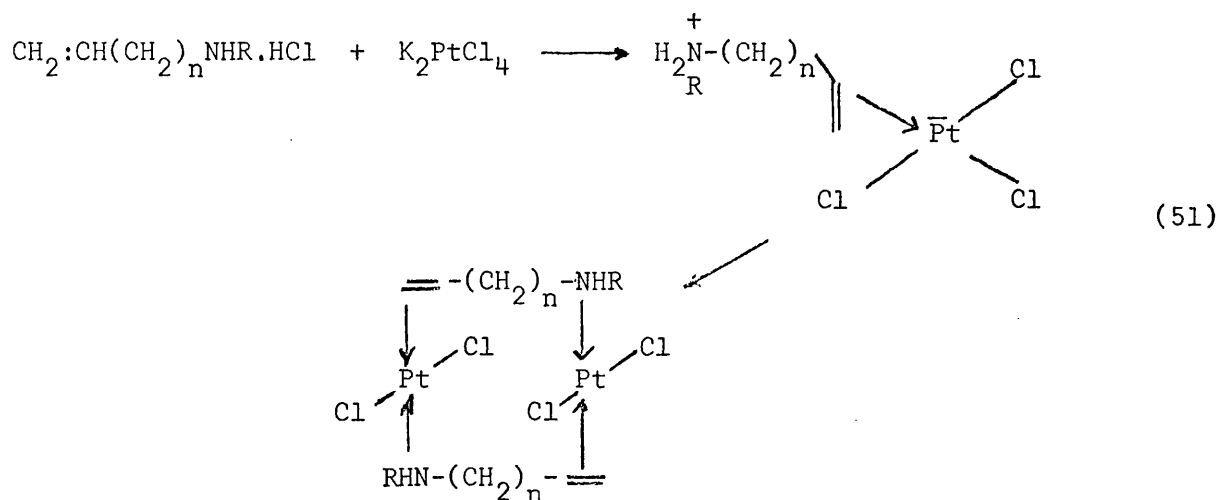


(11)

When $n = 1$ the chain, it appears, is too short to allow this orientation, but when $n = 2$ or 3 , this is possible.

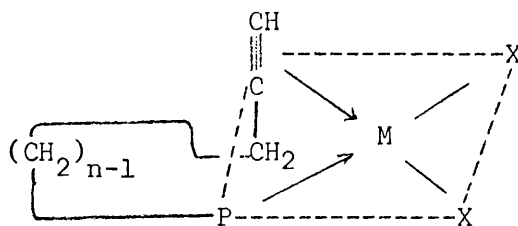
The analogous secondary amines, $\text{CH}_2:\text{CH}(\text{CH}_2)_n\text{NHR}$, have been studied by Venanzi and co-workers.^{148,149} They found that when $\text{R} = n\text{-octyl}$ and $n = 1, 2$ or 3 , platinum(II) complexes with both olefin and amine co-ordinated could be obtained by neutralising the product from the reaction of the amine hydrochloride and potassium chloroplatinite (equ. 51). These complexes, however, were polymeric. The complex formed by the direct addition of

allylamine to potassium chloroplatinite¹⁵⁰ is discussed later (Section III-1).



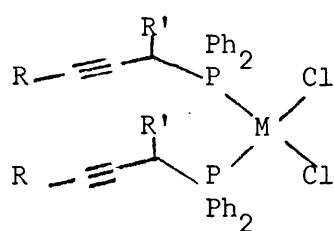
Goodall examined complexes of the corresponding but-3-enyl and pent-4-enyl sulphides¹⁵¹ and selenides.¹⁵² He found the same result as with the phosphorus containing ligands; both the pentenyl and butenyl ligands co-ordinate through the Group VI element and the olefin to platinum(II), but only the butenyl ligands co-ordinate in this way to palladium(II).

There are no examples of complexes of phosphines of Series II - $\text{R}_2\text{P}(\text{CH}_2)_n\text{C}\equiv\text{CH}$ - in the literature. For bonding to occur between platinum(II) and an acetylene group, the unsaturated group must be perpendicular to the plane of the metal and the other ligands,¹⁵³ just as in the case of an olefin. In addition, stable acetylenic complexes are obtained only with electron donating substituents. The steric restriction should mean that an even longer chain is needed for co-ordination from both the phosphorus and acetylene, as the final three carbon atoms of the chain must be almost linear (12).



(12)

Our attempts to prepare but-3-ynyldiphenylphosphine (II, R = Ph, n = 2) were not successful. With a shorter chain (n = 0, 1), the phosphines formed insoluble complexes with platinum(II) and palladium(II) chlorides. Diphenylprop-2-ynylphosphine reacted to give cis-bis(diphenylprop-2-ynylphosphine)metal(II) chlorides (13a). The complexes were identified by their i.r. spectra, which were the same as that of the free ligand. The far i.r. spectra had absorptions at 315 and 294 cm^{-1} in the platinum complex, and 309 and 292 cm^{-1} in the palladium complex, indicative of a cis- arrangement of the ligands.¹⁴⁵ This arrangement is unusual for palladium(II) halides with monophosphines. The elemental analyses showed the complexes to be 2:1.



(13)

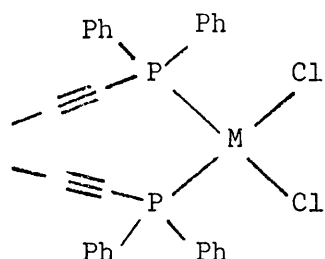
(a) M = Pd, Pt; R = R' = H

(b) M = Pd, Pt; R = H; R' = Me

(c) M = Pd, Pt; R = Me; R' = H

The corresponding complexes (13b, c) were obtained with methyl-substituted prop-2-ynyl phosphines (except that the palladium complexes had a trans- configuration). With diphenylprop-1-ynylphosphine platinum and palladium chlorides formed complexes.

(14a) and (14b). The cis- configurations were shown by their far i.r. spectra [$\nu(\text{Pt-Cl})$ 314 and 294 cm^{-1} ; $\nu(\text{PdCl}_2)$ 319 and 295 cm^{-1}]. The near i.r. spectra were almost identical to that of the free ligand.



(a) M = Pt

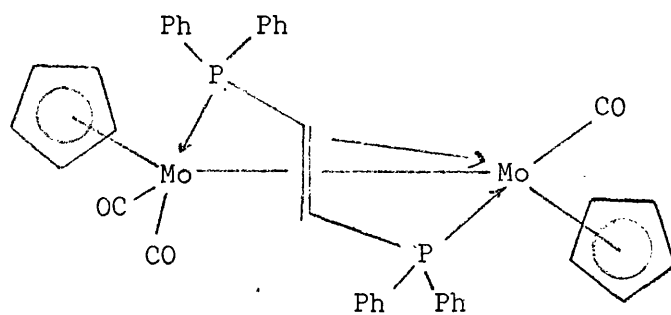
(b) M = Pd

(14)

Not suprisingly, no evidence of any acetylene-metal bond formation was found with these short-chain acetylenic phosphines.

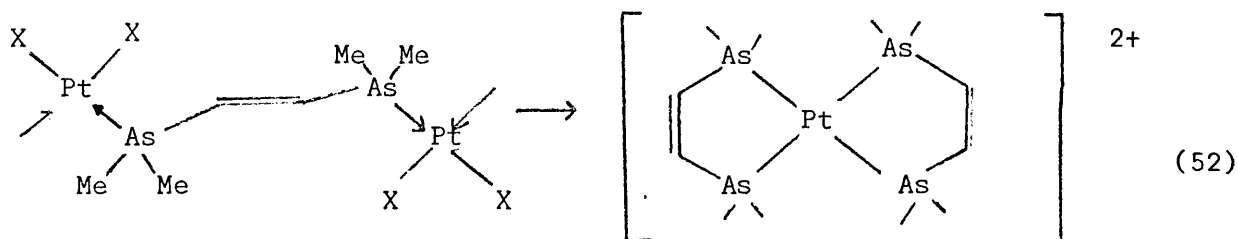
The complex which was isolated from the reaction of prop-2-ynyl-amine and platinum(II) chloride¹⁵⁴ is discussed later (Section III-1).

Some complexes of phosphines of Series III - $\text{R}_2\text{P}(\text{CH}_2)_n\text{CH}:\text{CH}(\text{CH}_2)_n\text{PR}_2$ - have been previously reported. Complexes of cis-bis(diphenylphosphino)ethylene (III, R = Ph, n = 0) with several metals have been studied¹⁵⁵⁻¹⁶⁰ but in no case did the double bond participate in the co-ordination. A complex with a novel structure involving bonding from the olefin to molybdenum has been reported by King and Kapoor, using trans-1,2-bis(diphenylphosphino)ethylene.¹⁶¹ The complex, prepared by irradiating a mixture of the ligand and the dimer of cyclopentadiene-molybdenum tricarbonyl, was assigned structure (15).



(45)

An interesting isomerisation was observed on irradiation of the platinum(II) chloride complex of the analogous trans-arsine ligand.¹⁶² The polymeric compound was isomerised to a complex of the cis-ligand (equ. 52).

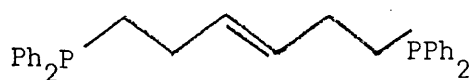
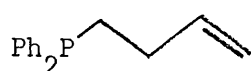


The complexes from the phosphines of Series III which were examined in this work were chiefly with trans-1,4-bis(diphenylphosphino)but-2-ene (III, trans, R = Ph, n = 1). With platinum(II), palladium(II) and nickel(II) there was no evidence of participation of the olefin in this or any other but-2-ene diphosphine. The structure of these complexes is discussed later (section II-3).

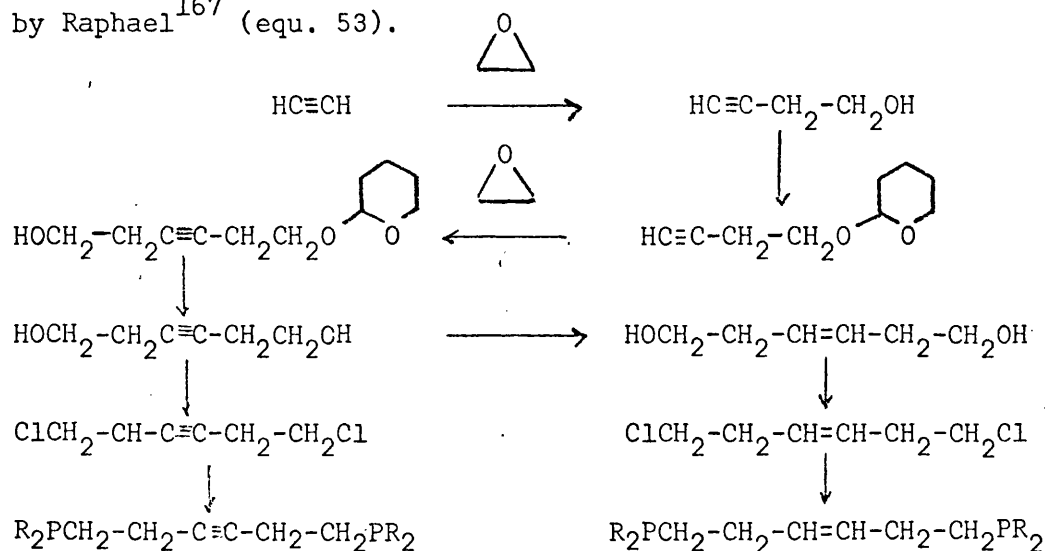
Phosphines of Series IV - $R_2P(CH_2)_n C \equiv C (CH_2)_n PR_2$ - were not studied in any depth. The phosphine (IV, R = Ph, n = 1), $Ph_2PCH_2.C \equiv C.CH_2PPh_2$, could not be obtained pure, and the next members of the Series, $Ph_2P(CH_2)_2 C \equiv C (CH_2)_2 PPh_2$, was only obtained

in a small yield. The platinum(II) complex of this phosphine could not be characterised. Carty and Efraty^{19,126,162-165} examined many complexes of $\text{Ph}_2\text{PC}\equiv\text{CPh}_2$ (IV, R = Ph, n = 0) but, not unexpectedly, no participation of the acetylene group in the bonding was observed.

From the work on the olefinic monophosphines, it would appear that whether or not there is co-ordination from the unsaturated unit depends, for steric reasons, on the chain length. If, therefore, phosphines from Series II-IV could be prepared with longer chains it may be possible to obtain complexes with both functional groups co-ordinated. For Series II a longer chain than those in Series I may be required (see structure 12), but the preparation of these phosphines is not easy. The next member of Series III above those examined, trans-1,6-bis(diphenylphosphino)hex-3-ene, may bond through the olefin as this is equivalent to the first member of Series I in which there is chelation:



An attempt was made to synthesise this ligand by a lengthy route starting with acetylene, described previously in part by Raphael¹⁶⁷ (equ. 53).



(53)

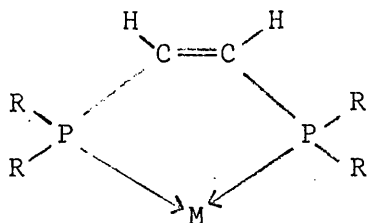
The acetylenic phosphine was prepared in this way, but it did not prove possible to carry out the reduction step on the alcohol to obtain the olefinic product. With Series IV an even longer chain may be required because of the linearity of the acetylene group.

It has been found that platinum(0) and palladium(0) complexes with olefins and acetylenes have the unsaturated group almost in the plane of the metal and the other ligands.¹⁶⁸ It may be possible, therefore, to form chelate complexes involving phosphorus and an unsaturated group with metals in this oxidation state when the chain is shorter than is necessary for metal(II) complexes. Initial experiments were carried out with the platinum(II) complex of 1,6-bis(diphenylphosphine)hex-3-yne, and the palladium(II) complex of allyldiphenylphosphine, using hydrazine for the reduction after the method of Chatt.¹⁶⁹ No characterisable product could be isolated from either reaction. A more attractive method might involve the reaction of the unsaturated phosphine with $(\text{Ph}_3\text{P})_3\text{Pt}$. This zero valent complex and $(\text{Ph}_3\text{P})_2\text{Pt}$ (olefin) have found general application in the synthesis of platinum(0) complexes.¹⁷⁰

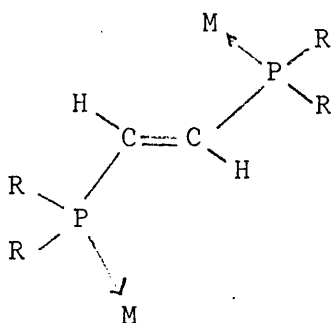
3. Complexes with But-2-enyl Diphosphines

Complexes of olefinic diphosphines which are capable of chelation through the two phosphorus atoms, e.g. cis-bis(diphenylphosphino)ethylene, have been extensively studied in recent years.¹⁵⁵⁻⁶⁰ The trans-isomer of this ligand, however,

has received little attention and only one complex of it has been reported.¹⁶¹ Complexes of equivalent arsines, trans-bis(dimethylarsino)ethylene and trans-bis(diphenylarsino)ethylene, have been reported with platinum,¹⁶² titanium,¹⁷¹ and rhodium.¹⁷² Unlike the cis- isomers, the trans- phosphines and arsines cannot form chelate complexes as the Group V atoms are too far apart; consequently, with the trans- ligands, complexes are obtained in which the donor atoms co-ordinate to different metal atoms.

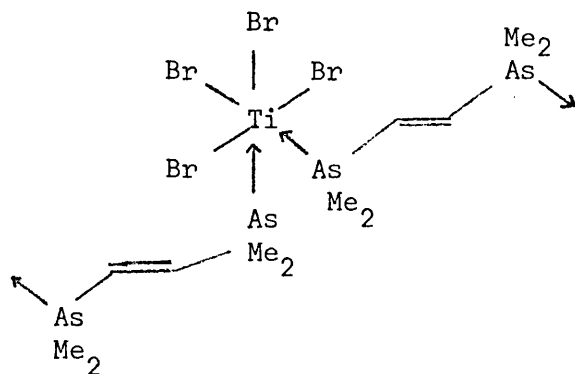


(16)



(17)

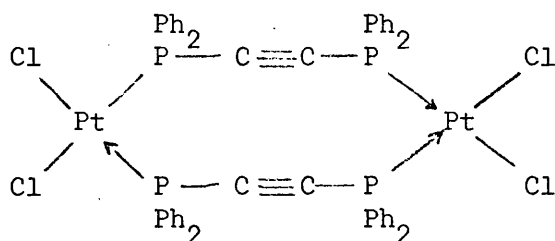
King and Kapoor obtained a complex between molybdenum and trans-1,2-bis(diphenylphosphino)ethylene with the novel structure described earlier (structure 15) in which two molybdenum atoms are bonded to the ligand.¹⁶¹ Less spectacular polymeric structures are proposed for complexes between trans-1,2-bis(dimethylarsino)-ethylene and platinum¹⁶² and titanium (18).¹⁷¹



(18)

A simple polymeric structure was also suggested for the complex between trans-1,2-bis(diphenylphosphino)ethylene and rhodium dicarbonyl chloride dimer.¹⁷²

Another phosphine which, because of its geometry, cannot give chelating complexes has been the subject of a series of papers by Carty and Efraty.^{19,126,163-166} Bis(diphenylphosphino)-ethylene acts as a bridging ligand with a variety of transition metals, a typical structure being for the complex with platinum (II) chloride (19).

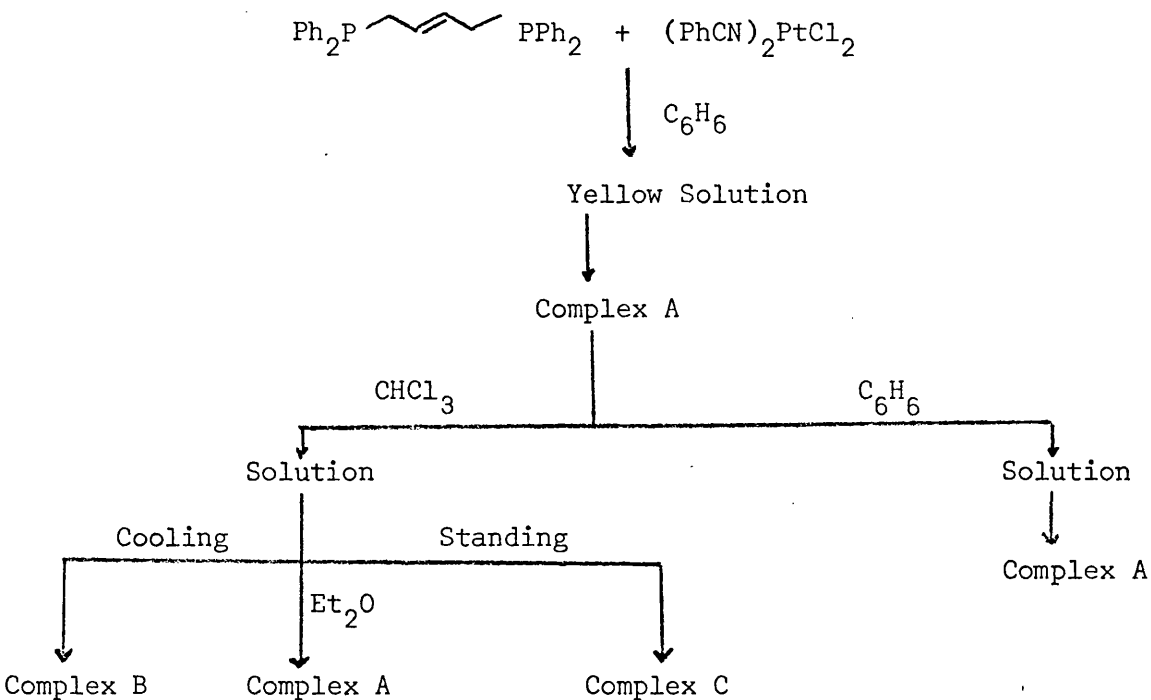


(19)

Polymeric complexes like those of the trans- ethylene diphosphines and diarsines were not found. The evidence for structure (19) is that linearity will not allow chelation, yet the analysis indicates a 1:1 complex; the osmometric molecular weight shows that the unit $M_2X_4(\text{ligand})_2$ is present; the i.r. and Raman spectra are consistent with that structure.

We have examined complexes of trans-1,4-bis(phosphino)-but-2-enes. The geometry of this type of ligand is such that chelation cannot occur by bonding from the two phosphorus atoms to the same metal, and the length of the chain makes it unlikely that the olefin could participate in the bonding (see section II-2).

Complexes of nickel(II), palladium(II) and platinum(II) with trans-1,4-bis(diphenylphosphino)but-2-ene have been prepared. Bis(benzonitrile)palladium(II) chloride was treated with the ligand in benzene and from the resulting solution was obtained a yellow complex - A. Complex A could be recovered unchanged from benzene, but on cooling a hot chloroform solution of A, an isomeric complex B was isolated. Complex A could be recovered from chloroform by rapid precipitation with ether. Complex B could be converted into A by extracting it with chloroform (in which it was barely soluble) and adding ether to the resulting solution, but from benzene it was recovered unchanged. A third isomer C was precipitated on allowing a chloroform solution of complex A to stand for a long time.



It would appear that the complexes are in equilibrium in a chloroform solution. Whereas complex A is readily soluble, complexes B and C

can only be taken into solution by prolonged extraction with the solvent. From a solution of B or C prepared in this way, A can be obtained.

The complexes, which all analyse as 1:1, were identified by differences in their i.r. spectra. The biggest differences are between 900 and 750 cm^{-1} . (Full details of the spectra are given in Appendix 2 - Table 8). In this region complex A has bands at 856 (medium) (with shoulders at 862 and 848 cm^{-1}) and 826 cm^{-1} (strong); complex B has 860 (strong), 831 (medium) and 790 cm^{-1} (strong); complex C has 858 (strong), 807 (medium) and 786 cm^{-1} (strong). The free ligand has a single strong band at 826 cm^{-1} . Other differences occur in the position of a band at 1117 cm^{-1} (weak) in the free ligand; in complex A it occurs at 1124 cm^{-1} (medium), in complex B at 1140 cm^{-1} (medium), and in complex C at 1130 cm^{-1} (medium). Absorptions of the free ligand at 988 (strong) and 970 cm^{-1} (weak) vary in intensity and position in the complexes; in complex A they occur at 976 (medium) and 970 cm^{-1} (medium), in B at 976 (weak) and 963 cm^{-1} (strong), and in C at 973 (strong) and 933 cm^{-1} (weak).

There are considerable differences in the far i.r. spectra of the three complexes. Complex A has a strong band at 354 cm^{-1} , and in the Raman spectrum there is a band at 306 cm^{-1} . This pattern of two bands, one i.r. active and one Raman active is characteristic of a trans- arrangement of the PdCl_2 unit.¹⁴⁴ Complex C has two strong bands in its far i.r. spectrum (313 and 287 cm^{-1}) which are also found in its Raman spectrum (315 and 298 cm^{-1}); this pattern is characteristic of a cis- arrangement of PdCl_2 . The third isomer, complex B, which has an i.r. spectrum more closely resembling that

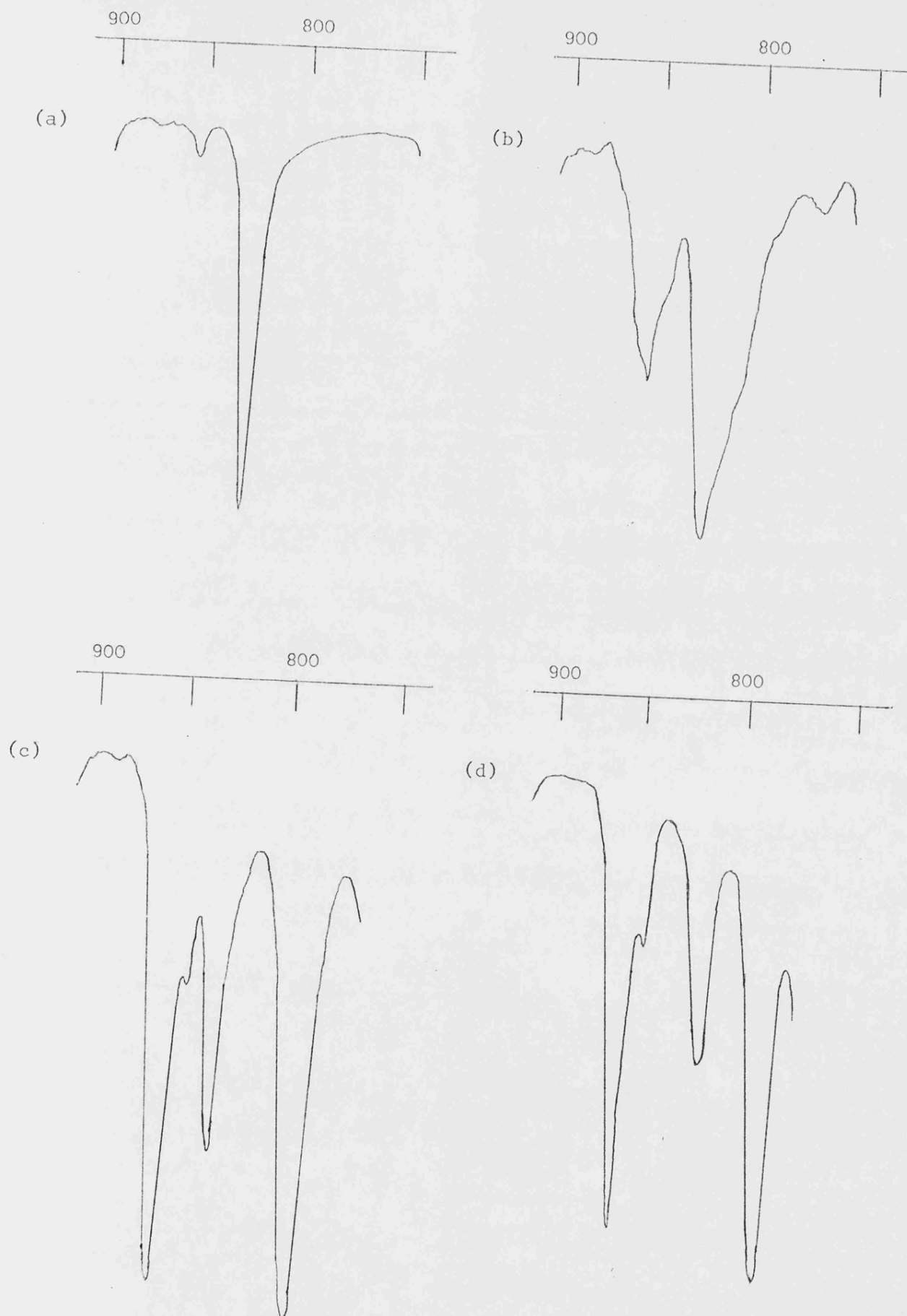


Figure: I.r. Spectra from 900-750 cm^{-1} of (a) trans-1,4-Bis(di-phenylphosphino)but-2-ene, (b) Complex A, (c) Complex B, and (d) Complex C.

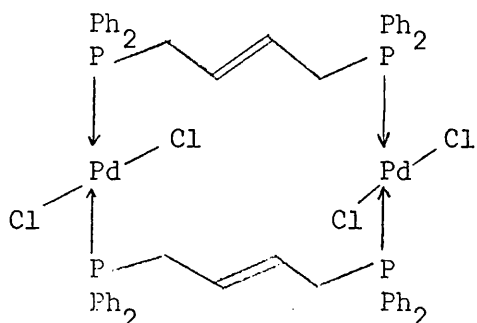
of C than A, has two absorptions in its far i.r. spectrum, but is not the same as C. There is a strong band at 353 cm^{-1} , and a band of medium intensity at 317 cm^{-1} . The Raman spectrum has only one strong absorption in that region, at 304 cm^{-1} .

The Raman spectra of all three isomers, and of the ligand, have a strong absorption at 1592 cm^{-1} which may be assigned to the $\nu(\text{C}:\text{C})$ vibration of the ligand. That there is no change on forming the complex is indicative of an absence of any contribution from the olefin in the bonding scheme. The only isomer which is sufficiently soluble to allow a ^1H n.m.r. spectrum to be recorded is complex A. The spectrum is virtually identical to that of the free ligand.

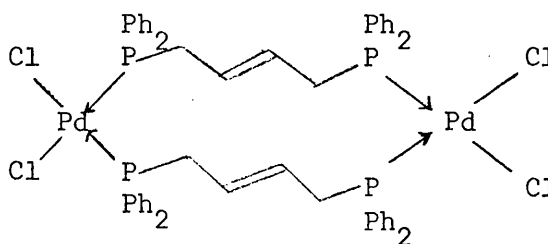
Osmometric molecular weight measurements on complex A gave a value of 845 in chloroform at 30° , and 990 in *o*-dichlorobenzene at 120° . The "monomeric" unit $(\text{Ph}_2\text{PCH}_2\text{CH}:\text{CHCH}_2\text{PPh}_2)\text{PdCl}_2$ has a molecular weight of 602, therefore these observed values do not determine the number of units per molecule. Complex B in *o*-dichlorobenzene at 120° had a value of 1060. A molecular weight determination on complex C by X-ray photographs of the crystal is being carried out, but unfortunately the data are not yet available.

Until some definite molecular weight data becomes available one can only speculate on the structures of A, B and C. The difference between A and C is clear from their far i.r. spectra; A has a trans- arrangement and C has a cis- arrangement of the ligands about the metal atom. The differences in the near i.r. will probably be due to the steric effect of these different

geometries on the phosphorus ligand, distortions giving rise to extra bands. It has not been possible to assign the changing bands in the region $900-750\text{ cm}^{-1}$. Tentative structures for A (20) and C (21) are shown below.



(20)



(21)

Complex B would appear to be somewhere between the two, with a trans-arrangement of ligands about the metal, but with the phosphines twisted into the same shape as those in the cis-complex. It is possible that the complexes are trimeric, or even high oligomers, the low molecular weight being due to dissociation in solution.

Two complexes, both 1:1, were isolated from the reaction of bis(benzonitrile)platinum(II) chloride with trans-1,4-bis(diphenylphosphino)but-2-ene. The less soluble isomer (D) has an i.r. spectrum identical to that of complex C, and the far i.r. spectrum has absorptions at 314 and 298 cm^{-1} , characteristic of cis- PtCl_2 . This complex is probably the platinum analogue of structure (21). The other more soluble isomer (E) again has a cis-arrangement of chlorine atoms, but the near

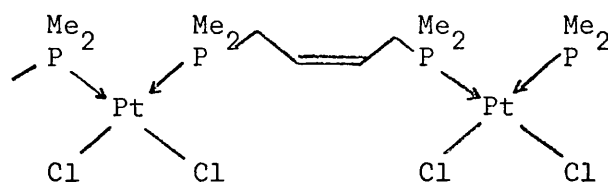
i.r. was identical to that of complex A. This complex probably has a structure the reverse of B - a cis- arrangement of ligands around the metal, but with phosphines twisted into the shape of those found in the palladium complex with the trans- arrangement.

With nickel(II) chloride, again two complexes were obtained. The differences in their i.r. spectra were again chiefly in the region $900-750\text{ cm}^{-1}$ and it is probable that structures similar to those for palladium are involved. Both complexes show a cis- arrangement of the ligands, and their colour (red) suggests square planar complexes. Only one isomer can be isolated from nickel(II) bromide and the ligand, but it is apparent from colour changes that the complex is different in the solid (green) and solution (brown).

trans-1,4-Bis(diethylphosphino)but-2-ene was prepared and the nickel(II), palladium(II) and platinum(II) complexes of this ligand were briefly examined. Only one complex of each metal could be isolated. The i.r. spectra of the complexes with all three metals were the same, and indicated that the double bond was not co-ordinated (App. 2 - Table 11).

Platinum(II) complexes of both cis- and trans-1,4-bis(dimethylphosphino)but-2-ene were obtained (see Section I-4). There was no evidence of isomerisation of each complex occurring. The far i.r. spectrum of each complex showed them both to have a cis- arrangement of ligands around the metal, and they probably have either structures equivalent to (21), or are long polymers (22). In general complexes with methyl substituted phosphines are more soluble than those with phenyl substituted phosphines,

however, in this case the "methyl" complexes are less soluble than most of the "phenyl" complexes (A-E). This suggests that whereas (A-E) form cyclic structures involving two or three monomer units, the "methyl" derivatives are polymeric.

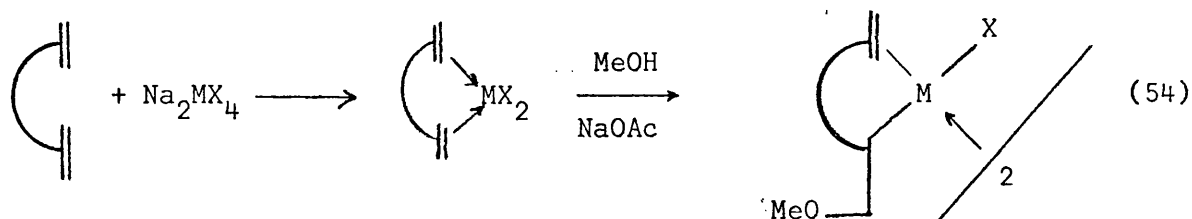


(22)

III Reactions of Complexes of Unsaturated Phosphines.

1. Introduction

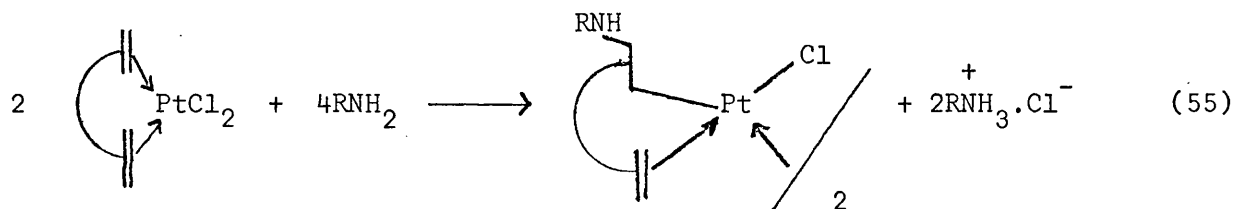
The first reaction involving nucleophilic attack of an olefin co-ordinated to platinum(II) was carried out many years ago.¹⁷³ In 1908 Hofman and von Narbutt investigated the reaction of dicyclopentadiene and potassium chloroplatinite in aqueous methanol; they obtained a complex the structure of which was not realised for almost fifty years until it was reprepared by Doyle and Jonassen.¹⁷⁴ Chatt and co-workers subsequently studied the reaction of the methoxide ion with a variety of co-ordinated diolefins including dicyclopentadiene on both platinum¹⁷⁵ and palladium.¹⁷⁶ They proposed the scheme shown in equ. (54).



Some decomposition of the palladium complex occurred in hot methanol, but this was overcome by carrying out the reaction at room temperature.¹⁷⁷ Hofman and von Narbutt found the reaction to be reversible with hydrochloric acid.¹⁷³

The stereochemistry of the reaction was studied by Stille and Morgan.¹⁷⁸ An examination by ¹H n.m.r. spectroscopy of the organic moiety obtained from the complex on reduction with sodium borohydride or deuteride indicated that the methoxy group attacked trans to the metal. This has been confirmed by an X-ray structure determination.¹⁷⁹

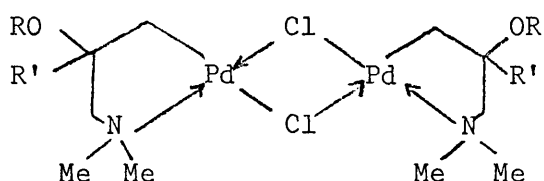
Reactions of a number of other nucleophiles with (diene)MX₂ have been reported; primary amines such as benzylamine or α-phenylethylamine, react with the platinum complex of 1,5-cyclooctadiene, norbornadiene, 4-vinylcyclohexene and 1,5-hexadiene, to give the corresponding halogen-bridged species (equ. 55).¹⁸⁰



Tsuiji carried out the reaction using diethylmalonate and ethyl-acetoacetate in the presence of base,¹⁸¹ and Lewis and co-workers examined the reactions of β-diketones with base and (diene)MX₂.¹⁸² A further variation was studied by Anderson and Burrenson who prepared complexes with acetate bridges instead of chlorine.¹⁸³

These reactions, and the reactions with mono-olefins, are discussed in detail in reviews by Hartley¹³¹ and White.¹⁸⁴

The reaction of allylamine with palladium(II) chloride in a neutral medium was examined by Cope and co-workers.¹⁸⁵ The product was formulated as structure (23). Although the reaction proceeded via the formation of an insoluble intermediate, this was not isolated.

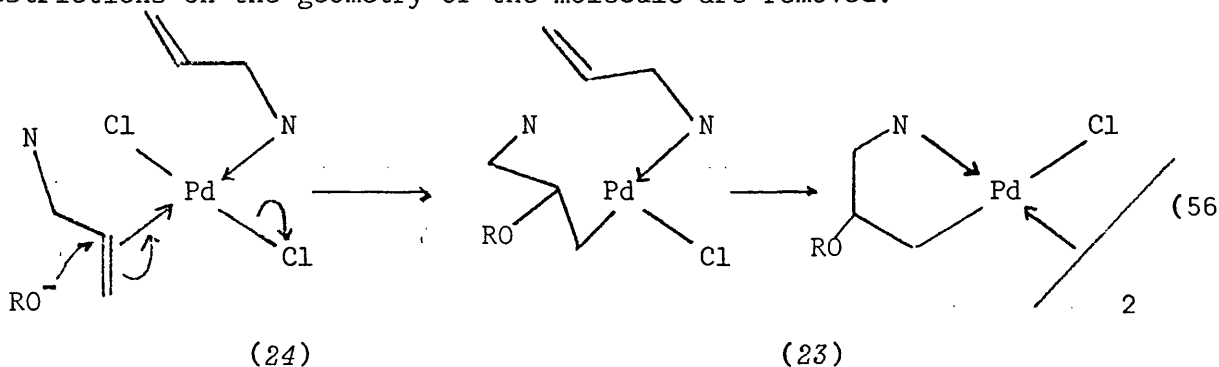


R = Me, Et, CH₂CH₂OH

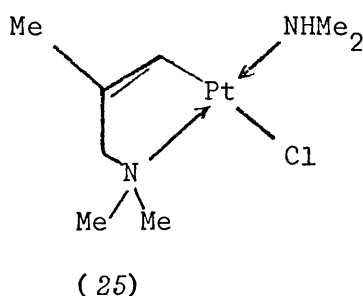
R' = H, Me

(23)

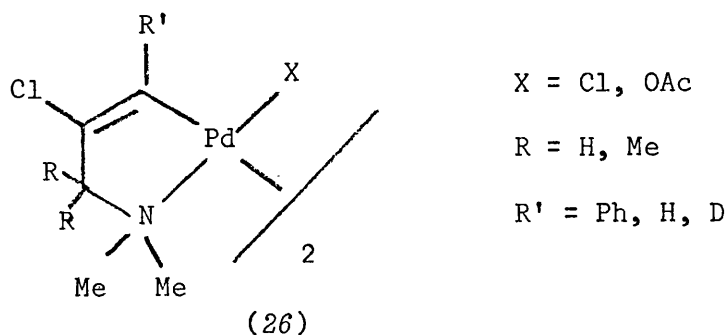
It has been suggested that the complex between platinum(II) chloride and the hydrochloride of allylamine involved co-ordination through the olefin and not the amine (equ. 51),^{148,149} and that neutralisation of this complex gives a dimeric complex in which both functional groups are co-ordinated to the metal. A possible mechanism for the formation of complex (23) is by attack of the alkoxide on this dimer (equ. 56). Bonding through the nitrogen to the same metal atom as the olefin is not likely in the intermediate (24) for the steric reasons already discussed (section II-2), but once the Pd-C σ -bond has been formed, restrictions on the geometry of the molecule are removed.



The speed with which the reaction proceeds is consistent with the intermediate (24) having a palladium-olefin bond. With platinum(II) chloride, dimethyl-2-methylallylamine gives a different complex,¹⁵⁰ the proposed structure of which is shown below (25). The mechanism for the formation of this complex is not clear, and further details of the reaction in the literature are awaited.



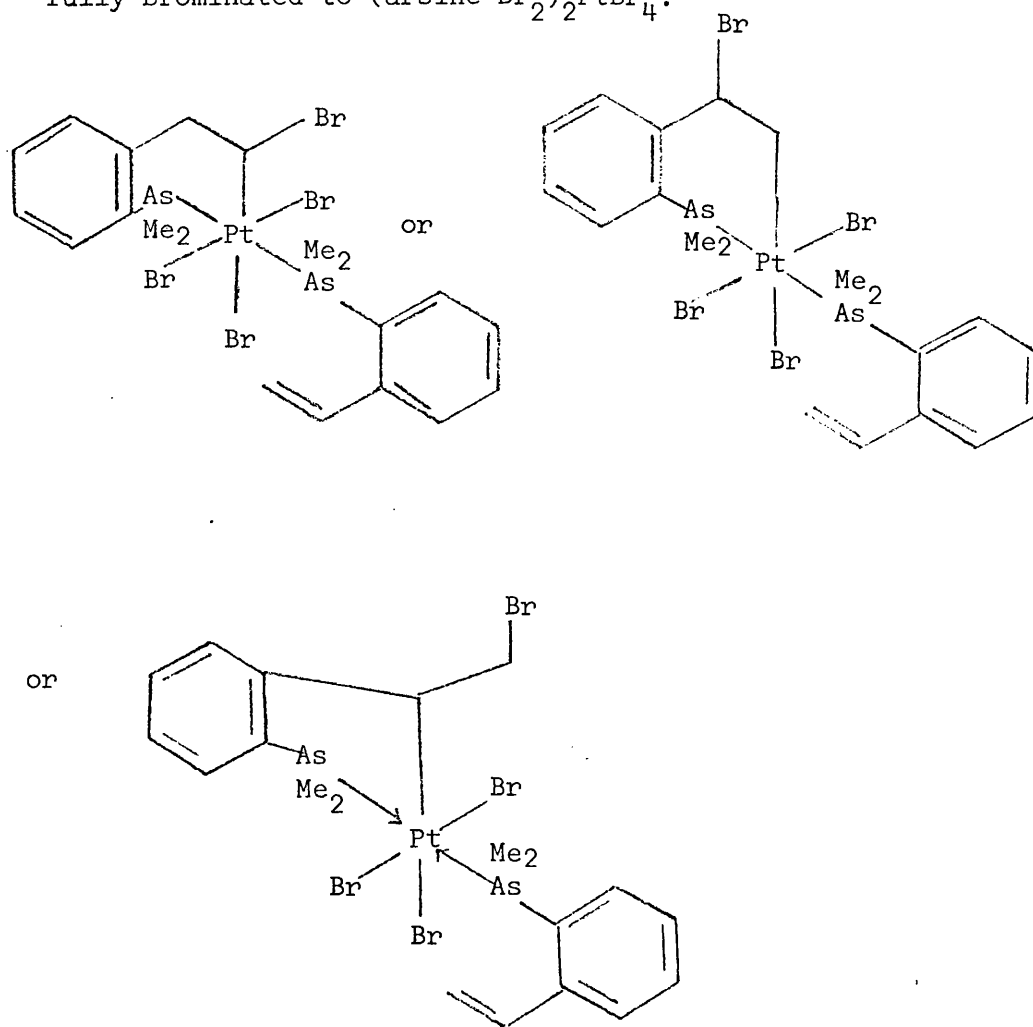
Chlorovinyl cyclic complexes with halogen bridges were obtained in analogous reactions by Yukawa and Tsutsumi.¹⁵⁴ Prop-2-ynylamines were reacted with palladium(II) chloride and lithium chloride to give complexes (26).



Presumably the reaction is proceeding by a mechanism similar to that shown in equation (56).

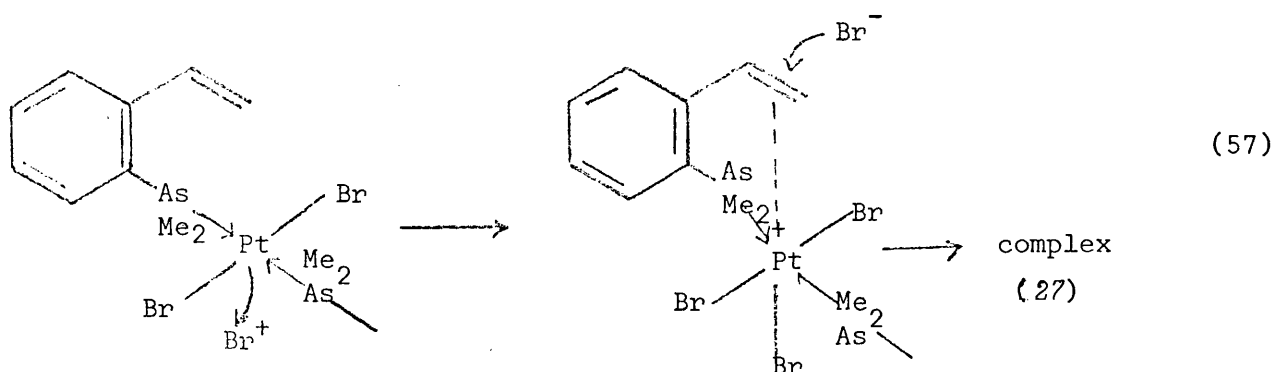
An interesting reaction involving bromine and an olefin in the environment of platinum has been described by Bennett.¹³⁹

Whereas the complexes of meta- and para-allylphenyldimethylarsine (and the styryl analogues), $(\text{arsine})_2\text{PtBr}_2$, react in the expected manner with three moles of bromine to give complexes of platinum(IV) with the olefins brominated, complexes of the ortho-arsines react differently. It is suggested that the reaction with the first mole of bromine gives a complex with structure (27) (for the styryl arsine), which is subsequently brominated at the remaining double bond, and then fully brominated to $(\text{arsine-Br}_2)_2\text{PtBr}_4$.

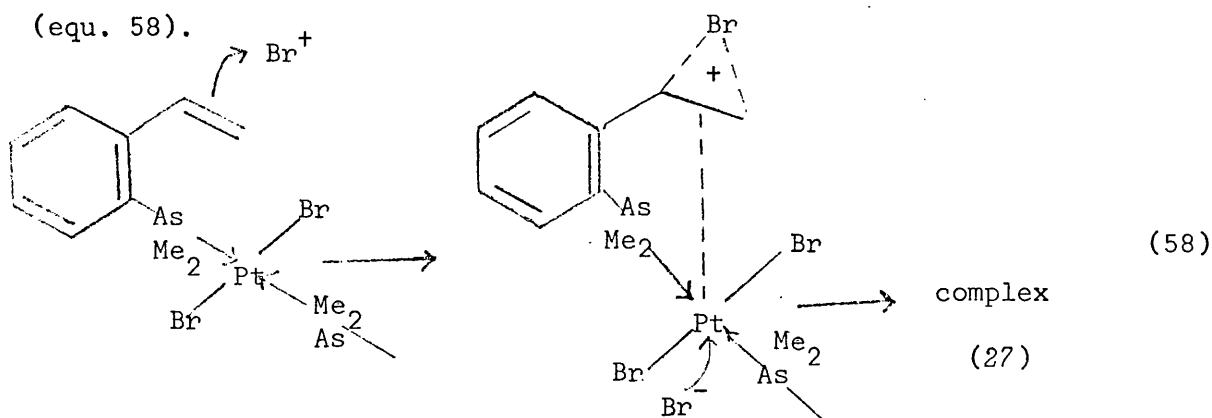


(27)

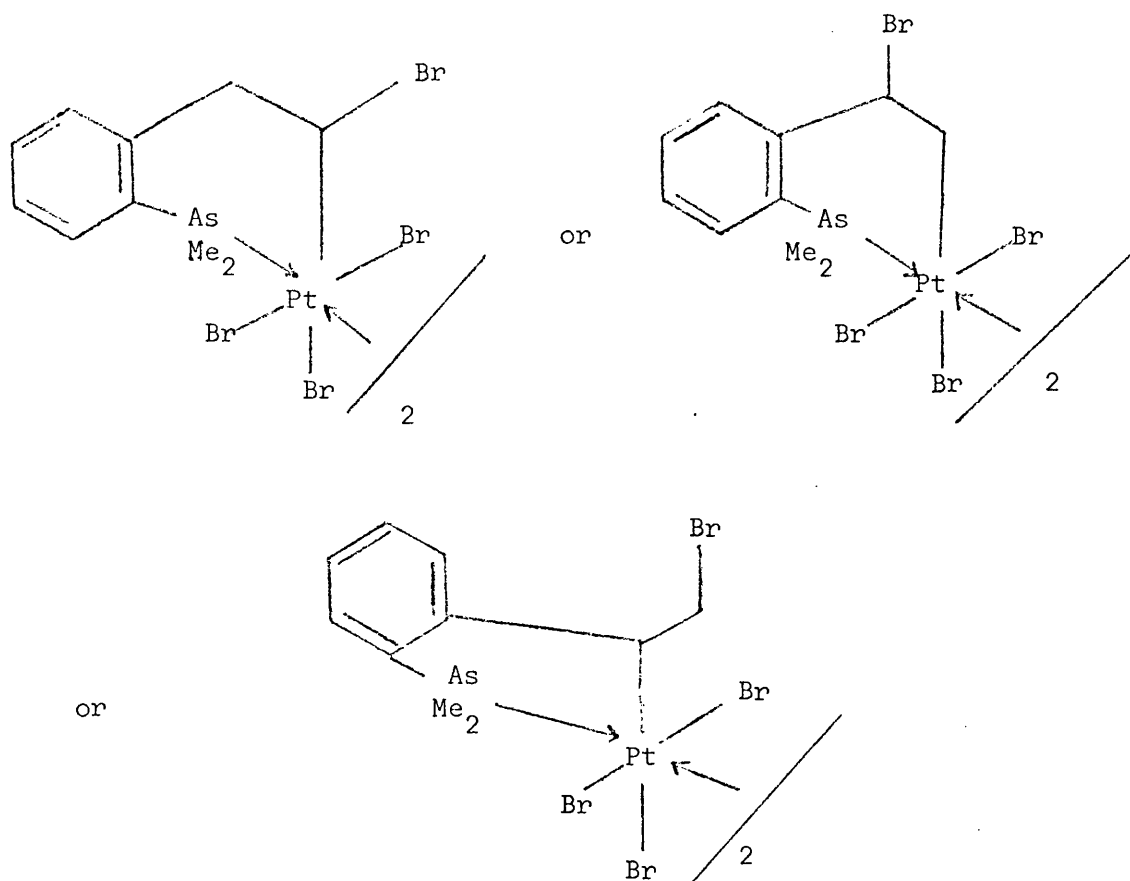
The mechanism which is proposed for this reaction is initial attack by Br^+ on the platinum giving a species which may be stabilised by interaction with the double bond. The double bond, now susceptible to nucleophilic attack, reacts with Br^- to give complex (27), (equ. 57).



An alternative mechanism would be electrophilic attack on the uncoordinated olefin by Br^+ giving an intermediate which can be stabilised by interaction with the metal, followed by attack on the metal by Br^- (equ. 58).

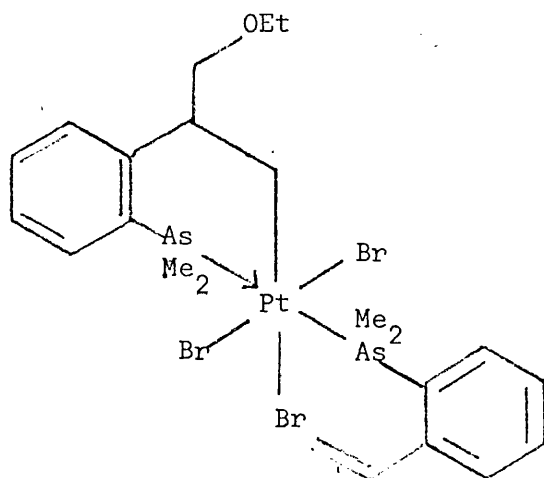


The reaction of bromine with the complexes in which the olefin is co-ordinated to platinum was subsequently described.¹⁸⁶ A complex of structure (28) was obtained, presumably by a similar mechanism of initial attack on either the olefin or the metal.



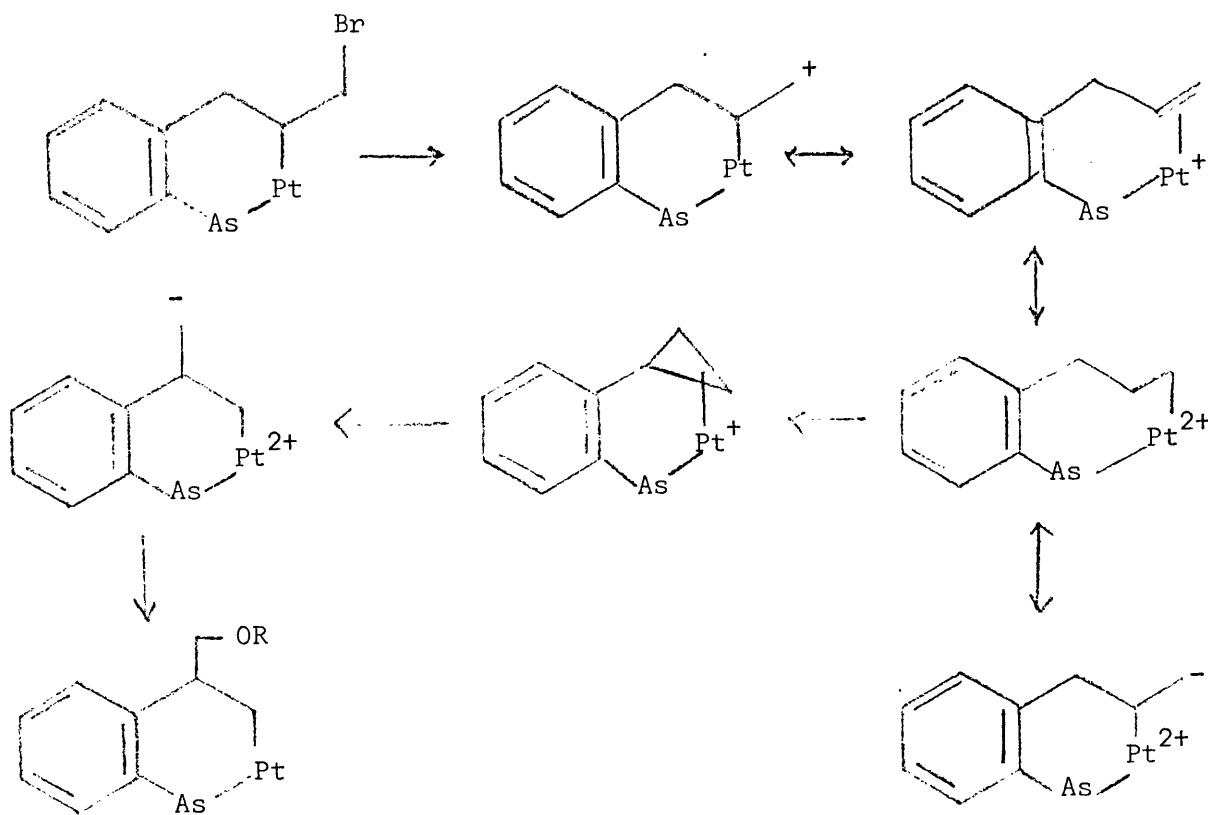
(28)

The reaction of complex (27) with primary alcohols involved replacement of the bromine attached to carbon with an alkoxy group. An X-ray structure of the product from the reaction of ethanol with the complex from o-allylphenylarsine showed that a rearrangement had taken place in the side chain of the ring (structure 29).¹⁸⁷

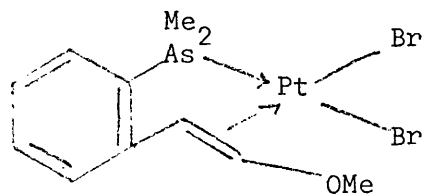


(29)

It is not known whether the rearrangement occurs during the first reaction of the complex $(\text{arsine})_2\text{PtBr}_2$ with bromine, or during the subsequent alcoholysis. White¹⁸⁴ suggests the mechanism shown in equation (59).

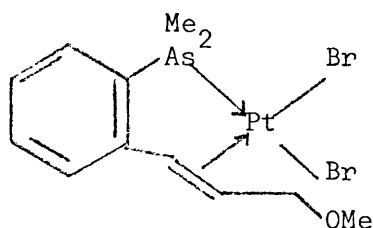


The attack of alcohol on complex (28) gives a product containing a co-ordinated vinyl ether (30).



(30)

The allylarsine analogue of complex (28) also gives a product with a co-ordinated double bond on reaction with alcohol, and Bennett proposed structure (31) for this.



(31)

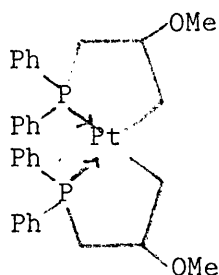
The following Sections describe nucleophilic attack by the methoxide ion on co-ordinated and unco-ordinated olefins and acetylenes of complexes of unsaturated phosphines.

2. Reaction of Nucleophiles with Unco-ordinated Olefins and Acetylenes.

Whereas unactivated olefins are not susceptible to nucleophilic attack,¹⁸⁸ olefins complexed to metals of low electron density [e.g. platinum(II)] react readily with nucleophiles to form σ -bonded complexes (Section III-1). We have found, however, that although the olefin is not co-ordinated to the metal in the platinum(II) chloride complex of allyldiphenylphosphine, it is susceptible to attack by the methoxide ion.¹⁸⁹

cis-Bis(allyldiphenylphosphine)platinum(II) chloride was shaken with sodium hydrogen carbonate in methanol to give a new complex (32).

The bands in the i.r. spectrum of the starting material at 1640, 1000 and 920 cm^{-1} due to the vinylic group⁹⁸ are absent in the spectrum of (32), and there are new bands at 2900, 2780 $[\nu(\text{C-H})]$, 1085, and 1072 cm^{-1} $[\nu(\text{C-O})]$ ⁹⁸ due to a methoxy group. The absence of any platinum-chlorine bonds was inferred from the far i.r. spectrum of (32), which had no strong absorptions, and was confirmed by elemental analysis. Structure (32) is assigned to the complex based on these observations.



(32)

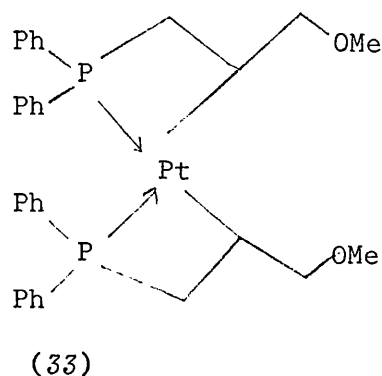
The retention of the cis- configuration of the phosphorus ligands about the central metal atom is suggested by the high dipole moment of the complex in benzene (5.2 D). The mass spectrum shows a parent ion at the calculated value of 708.

Because of the low solubility of the complex only unsatisfactory ^1H n.m.r. spectra with poor signal noise ratios could be obtained. The most prominent feature is a pair of lines of equal intensity centred at 6.8τ and separated at 4.5 Hz at 60 MHz and 17 Hz at 220 MHz, due to the methoxy protons. The difference in separation at different fields indicates that the signals are due to two methoxy groups in slightly different environments, and not due to spin-spin coupling. It is probable that two geometric isomers, differing in the arrangement of the methoxy groups (cis and trans with respect to the co-ordination plane of the platinum) are obtained, in the ratio 1:1.



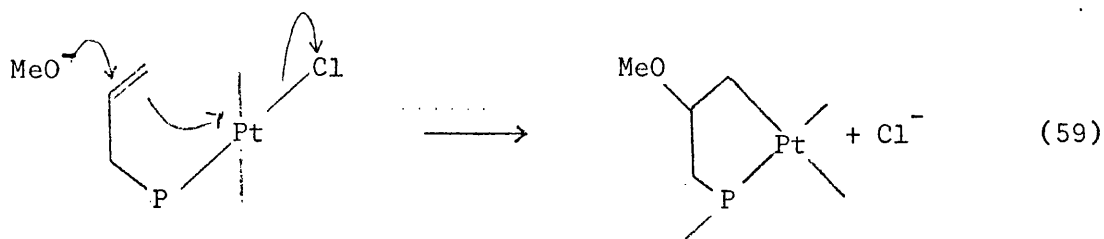
It is not surprising that details of the ring protons are not seen in the spectrum, as each has a different environment, and there will be considerable coupling between the ring protons, phosphorus, and platinum.

The possibility that a 4-membered ring complex (33) was formed by attack on the α -(terminal) carbon atom of the olefin was considered.



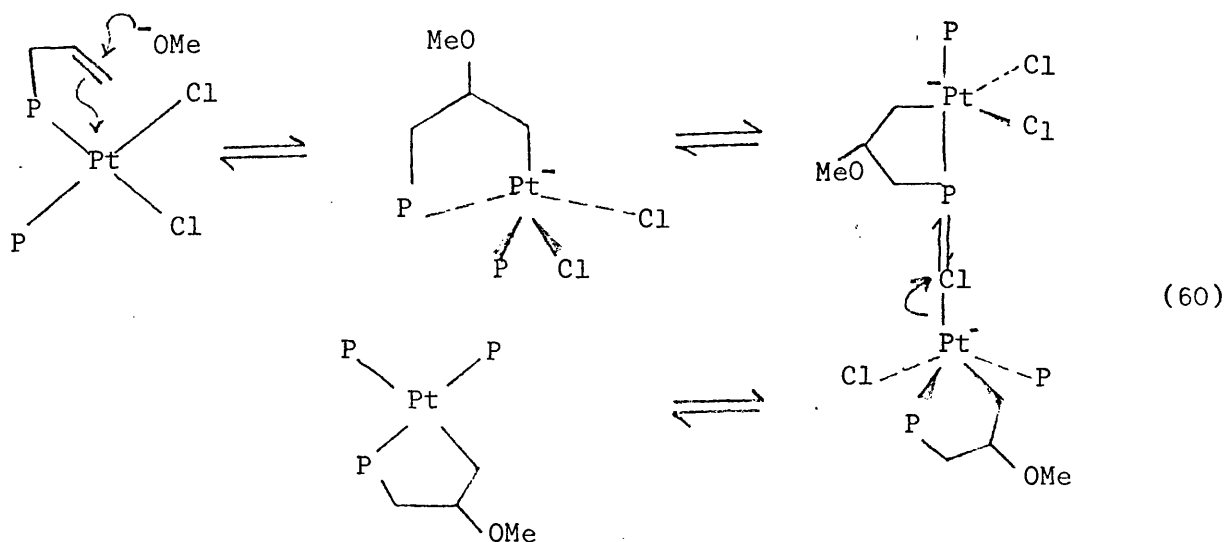
It is found that nucleophilic attack on mono-olefins co-ordinated to a metal occurs predominantly at the β -carbon atom. Thus, when propene is shaken with acetic acid in the presence of palladium(II) chloride, iso-propenyl acetate is obtained,¹⁹⁰ and with hydroxide ion, acetone is obtained in preference to propionaldehyde.² Attack on the β -carbon atom would lead to complex (32), and coupled with the steric preference for 5- rather than 4-membered rings, it is most likely that structure (32) is correct for this complex.

The ease with which complex (32) is formed is presumably due to the olefin being held in close proximity to the metal even though it is not initially co-ordinated to it.

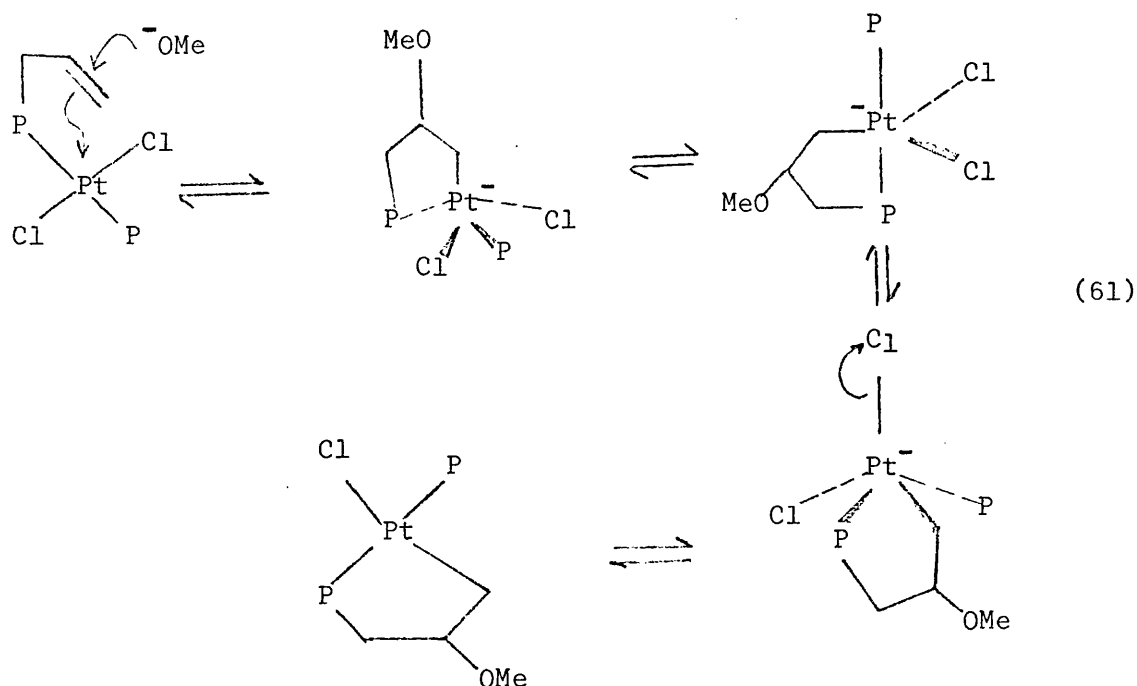


The second attack can occur from the same side or from the opposite side of the intermediate, giving rise to the cis and trans products described above.

It was found, however, that the attack of the methoxide did not take place with trans-bis(allyldiphenylphosphine)platinum(II) chloride, therefore it would appear that the cis arrangement of the ligands is essential for the reaction. This can be explained using theories on pseudo-rotation of a five co-ordinate intermediate.¹⁹¹ A group attacking a square planar structure must approach from above or below the plane to form a square-based pyramidal intermediate. Similarly, a group leaving an intermediate to give a square planar structure must depart from the apical position of a square-based pyramid. The intermediate must rearrange by pseudo-rotation through trigonal bipyramids and square-based pyramids to allow this to occur. There are, however, restrictions to the rotation; electronegative groups prefer to occupy axial positions of a trigonal bipyramid, and steric requirements of chelating groups must be considered. The sequence for the reaction of the cis complex described here is shown in equation (60).



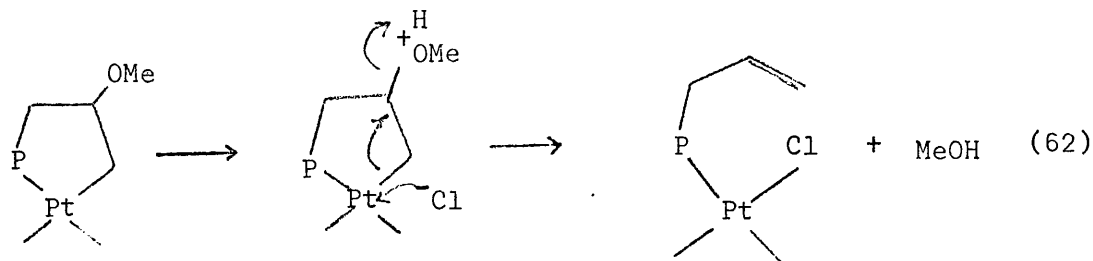
This sequence is satisfactory as the intermediate trigonal bipyramid does not involve having both electronegative chlorine atoms in equatorial positions, nor does the chelating group have to stretch between two equatorial positions. Now, consider the corresponding sequence for the trans complex undergoing a similar reaction, equ. (61).



The intermediate trigonal bipyramid needed to place the chlorine group in an apical position for elimination has the unfavourable arrangement of both electronegative groups equatorial, and the equilibrium will lie to the left.

It was found that the reaction sequence (60) was reversed

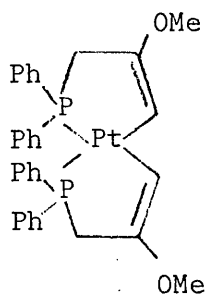
by the addition of hydrochloric acid (equ. 62), in a manner characteristic of β -methoxyalkyl platinum complexes (Section III-1).



The complex of allyldiethylphosphine and platinum(II) chloride gave an intractable product with methoxide. The palladium(II) complex of allyldiphenylphosphine has a trans arrangement of the ligands and, like the trans- platinum(II) complex, it was recovered unchanged from an attempted reaction with sodium hydrogen carbonate and methanol. Stronger base, sodium carbonate in hot methanol, caused the complex to decompose and to deposit palladium metal. Allyldiphenylphosphine itself was shaken with sodium hydrogen carbonate in methanol, but, as expected, the reactants were recovered unchanged. This confirms that the attack on the double bond is induced by the proximity of the metal.

Nucleophilic attack on acetylenes occurs more readily than attack on olefins,¹⁹² and cis-bis(diphenylprop-2-ynylphosphine)-platinum(II) chloride reacts with methoxide in a manner analogous to that of the allyl-phosphine complex to give the corresponding vinylic cyclic complex (34). Bands due to the acetylene group [$\nu(\equiv\text{C-H})$ 3225 cm^{-1} , $\nu(\text{C}\equiv\text{C})$ 2105 cm^{-1}] were absent in the spectrum

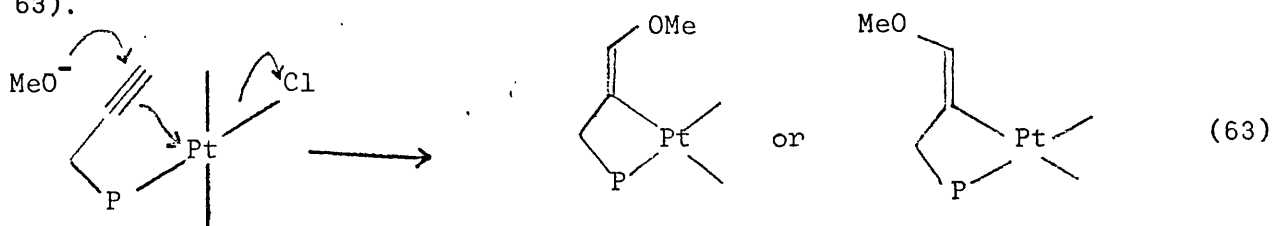
of complex (34), and the presence of a vinylic ether group was supported by a strong band at 1667 cm^{-1} [$\nu(\text{C}=\text{C})$], and a medium band at 1083 cm^{-1} [$\nu(\text{C}-\text{O})$]. The far i.r. spectrum of (34) showed no platinum-halogen bonds, and the elemental analysis supports the formulation (34).



(34)

The ^1H n.m.r. spectrum of (34) in benzene has a strong singlet at 6.93τ which is presumably due to the protons of the methoxy group. Isomerisation about the co-ordination plane of the platinum is not possible in this case and only one isomer would be expected. Again the ring protons are not resolved even at 220 MHz, due to the combined effects of low solubility and multiple coupling. The dipole moment of 6.7 D is indicative of the retention of cis arrangement of the phosphorus ligands around the metal.

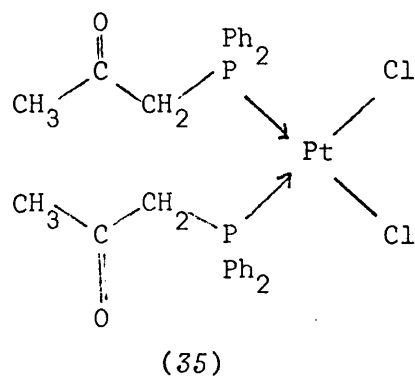
Complex (34) could have 4-membered instead of the proposed 5-membered rings by attack on the α -carbon atom of the chain (equ. 63).



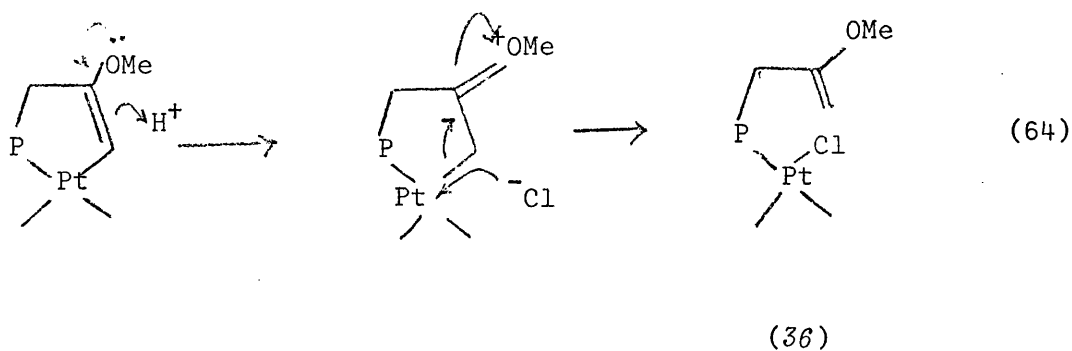
The formation of such a ring, however, is though to be unlikely for steric reasons. Further, if the above 4-membered ring compound were formed with the propynylphosphine complex, it might be expected that a mixture of isomers would be obtained. The fact that there is only one absorption in the ^1H n.m.r. spectrum for the methoxy group is not consistent with this.

Confirmation of structure (34) was obtained by the action of acid on the complex. Complex (34) reacts with hydrochloric acid in methanol to give a new complex (35). The i.r. spectrum of this compound has a strong band at 1704 cm^{-1} which is assigned to $\nu(\text{C}=\text{O})$, and the far i.r. spectrum has two strong bands at 312 and 290 cm^{-1} , which may be assigned to the cis- PtCl_2 . The ^1H n.m.r. spectrum of this complex shows a singlet at 7.72τ and a doublet with a coupling constant of 10.5 Hz at 6.22τ , as well as absorption due to aromatic protons at 2.40 - 2.93τ . The ratio of the non-aromatic protons is $3:2$.

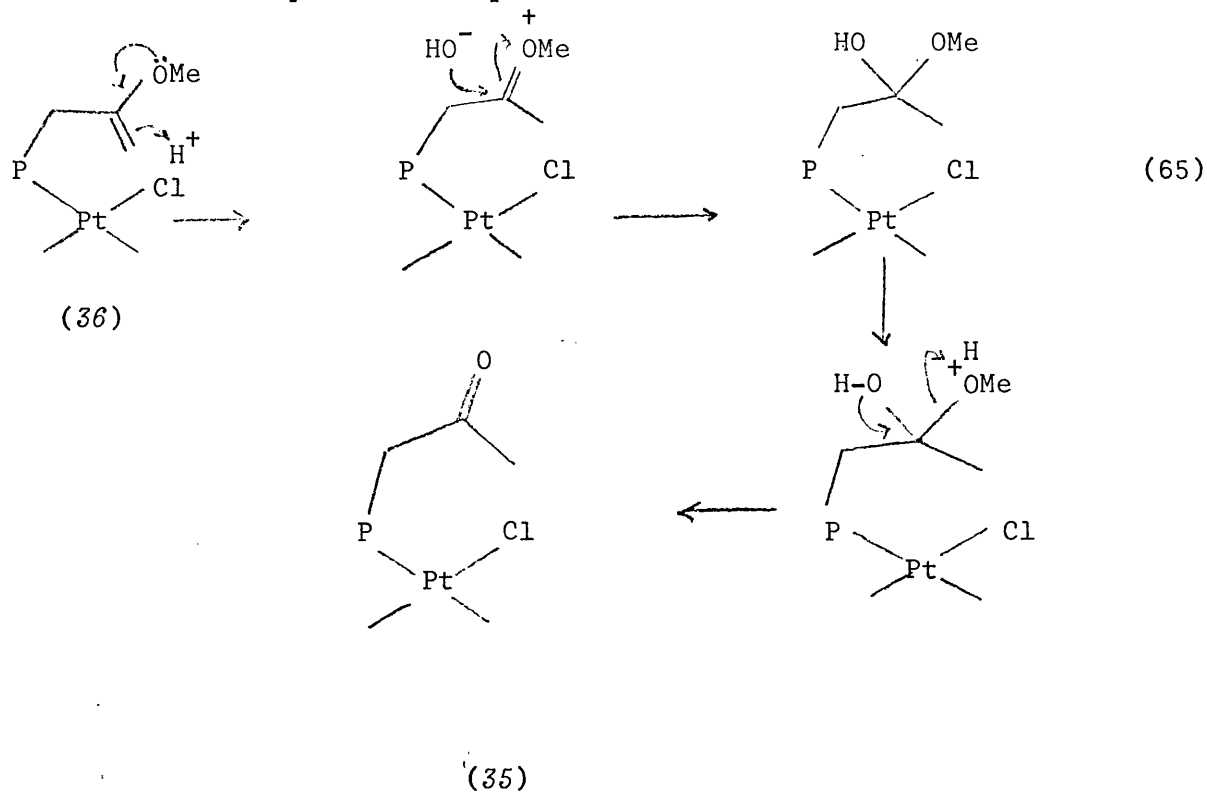
Consistent with this data is the structure shown below. No coupling is expected for the methyl group which, being next to a carbonyl group, absorbs at a lower field than that which is found for a paraffinic methyl. The methylene protons are coupled to phosphorus. The absence of any coupling between the two sets of protons eliminates the possibility of the oxygen being attached to the carbon atom next to the phosphorus.



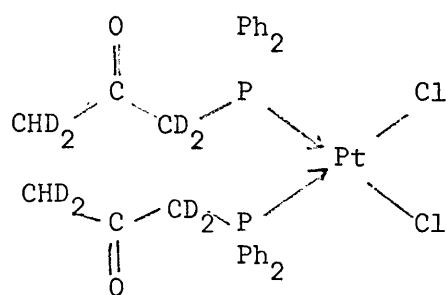
Complex (34) has a vinylic ether group and protonation in acid may occur at the carbon atom attached to the platinum. Attack by chloride would then lead to the intermediate (36) rather than elimination of methanol as occurs for the saturated ring complex (34) (equ. 64, cf. equ. 62).



The intermediate (36) still contains a vinylic ether group which is susceptible to acid hydrolysis.¹⁹³ Thus reaction on (36) would lead to the isolated complex (35) (equ. 65).

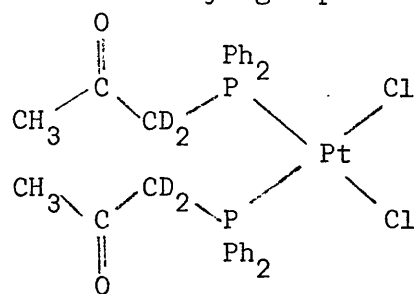


The unequivocal assignment by ^1H n.m.r. spectroscopy of the carbonyl group to the centre carbon atom of the chain labels this as the carbon to which the methoxy group was attached, ruling out a mechanism by equation (62). Structure (34) was further confirmed by carrying out the acid hydrolysis of (34) with deuterium chloride in deuterated methanol. The ^1H n.m.r. and i.r. spectra of the resulting complex showed it to be (37).



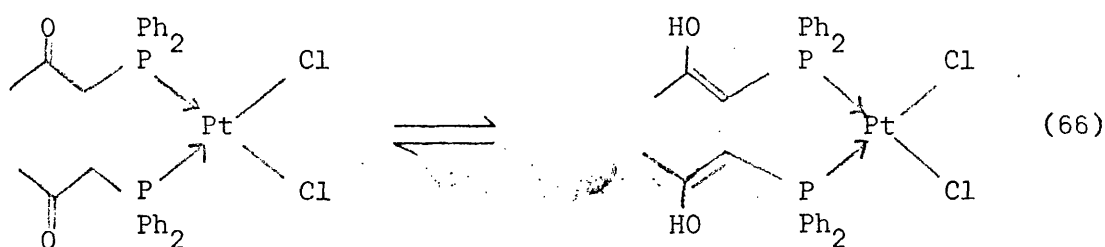
(37)

That deuteration of only the α -carbon atom is caused by an exchange reaction between the initial product and the solvent was demonstrated by treating complex (35) with DCl in MeOD. Compound (38) was obtained, and no exchange on the methyl group of the chain occurred.



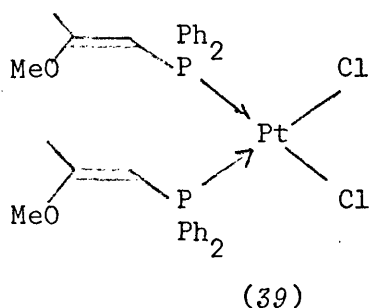
(38)

The mechanism for such an exchange is by enolisation, and the enol involving the carbon atom adjacent to the phosphorus will be favoured because of the electron withdrawing effect of the hetero atom (equ. 66).



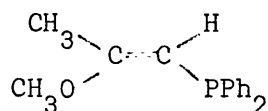
The deuterium on the terminal methyl group in (37), therefore, cannot have been obtained by an exchange reaction. This is supported by the fact that one hydrogen atom remains on this carbon atom. Thus it is established that the platinum-carbon bond in complex (34) is indeed to this γ -carbon atom of the chain, and deuterium incorporation is through the breaking of such a bond, followed by hydrolysis of the resulting vinylic ether group between the β and γ -carbons (equ. 64 and 65).

cis-Bis(diphenylprop-1-ynylphosphine)platinum(II) chloride also reacts with methoxide under the same mild conditions of sodium hydrogen carbonate in methanol. The strong band at 2190 cm^{-1} [$\nu(\text{C}\equiv\text{C})$] in the i.r. spectrum of the starting complex is absent in that of the product, and new bands appear at 1600 cm^{-1} (strong) [$\nu(\text{C}=\text{C})$], 1093 cm^{-1} [$\nu(\text{C}-\text{O})$], and 858 cm^{-1} [$\delta(\text{C}=\text{H})$]. The far i.r. spectrum showed two strong bands at 302 and 278 cm^{-1} , indicative of terminal cis- PtCl_2 . Structure (39) was assigned to this complex on the basis of this data, the ^1H n.m.r. spectrum, and its elemental analysis.

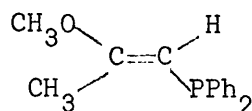


The ^1H n.m.r. spectrum in chloroform at 220 MHz consists of a multiplet due to the aromatic protons at 2.3-2.9 τ (20H), a doublet ($J_{\text{P,H}}$ 14 Hz) at 5.22 τ (2H) due to a vinylic proton, a singlet at 6.78 τ (6H) which may be assigned to methoxy groups, and a singlet at 8.25 τ (6H) which is consistent with a methyl group attached to a double bond.

The addition of nucleophiles to acetylenes normally gives products resulting from trans addition. Archibald reported the addition of lithium diphenylphosphide to phenylacetylenic compounds,^{54,55} and Truce has studied the addition of mercaptides to alkynes;⁵⁸ in both cases trans products resulted. A phosphine with the geometry (40) would result from trans addition, whereas cis addition would give the phosphine (41).



(40)



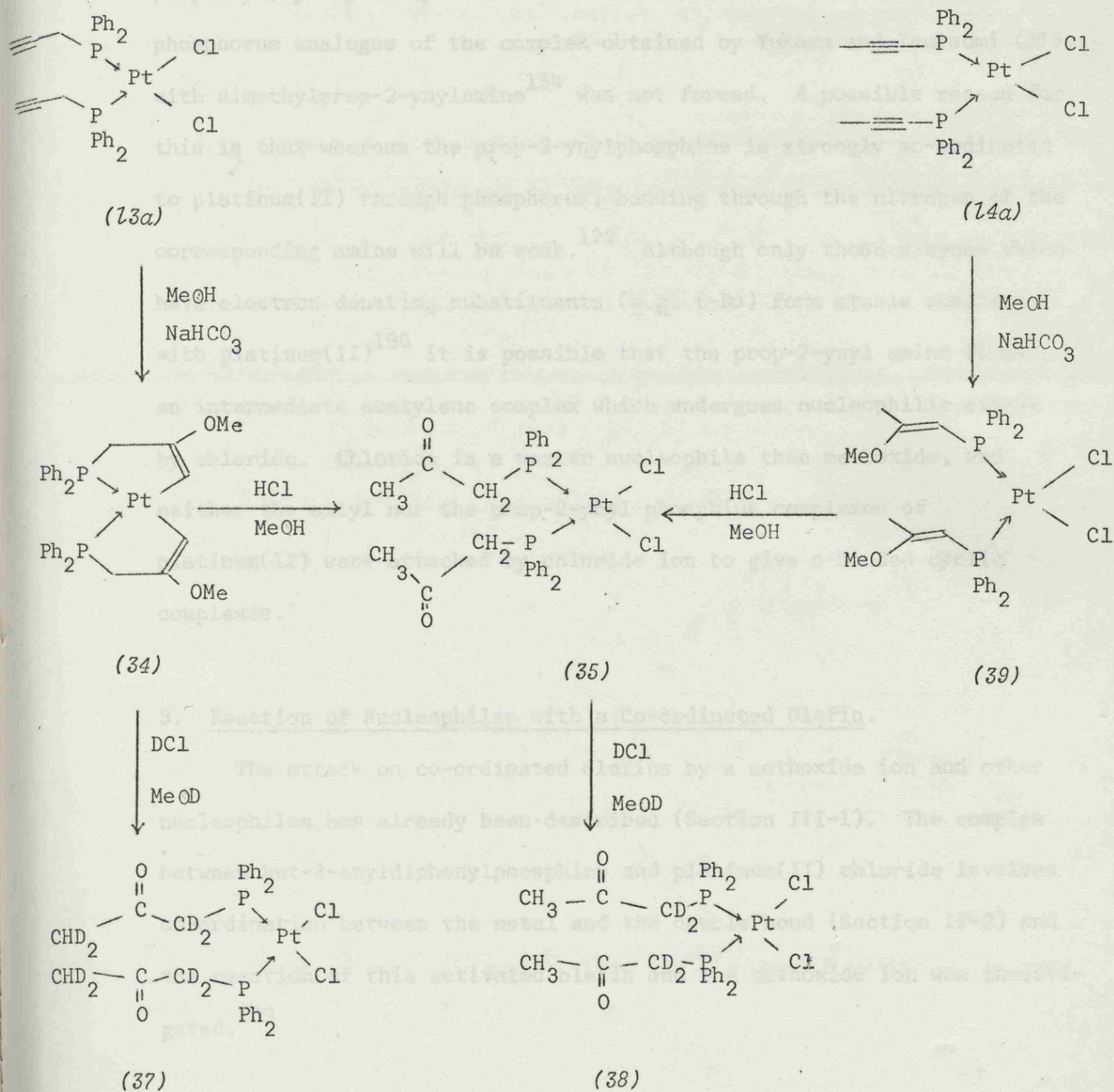
(41)

According to Dyer,¹⁹⁴ the ^1H n.m.r. spectrum of the cis-addition product (41) would be expected to show coupling between the vinylic proton and the methyl group trans- to it, while coupling between the vinylic proton and a methyl group in the cis- position (40), would be very small. That no such coupling is observed in the ^1H n.m.r. spectrum of complex (39) supports the suggestion that the ligands have the geometry (40). Jackman,¹⁹⁵ however, disagrees with this and suggested that the coupling in the cis- compound (40) should be greater than that in the trans- (41).

The position of the methoxy group was demonstrated by acid hydrolysis; treatment of a methanol solution of (39) with hydrochloric

acid gave complex (35), which was identified by its i.r. and ^1H n.m.r. spectra. This labels the β -carbon atom as the one bearing the methoxy group in structure (39). Complex (39) has a vinylic ether group, and the mechanism for the hydrolysis to the complex of the ketonic complex will be that shown previously in equation (65).

Inter-relationship of Complexes of Diphenylprop-1-ynyl- and Diphenylprop-2-ynylphosphine



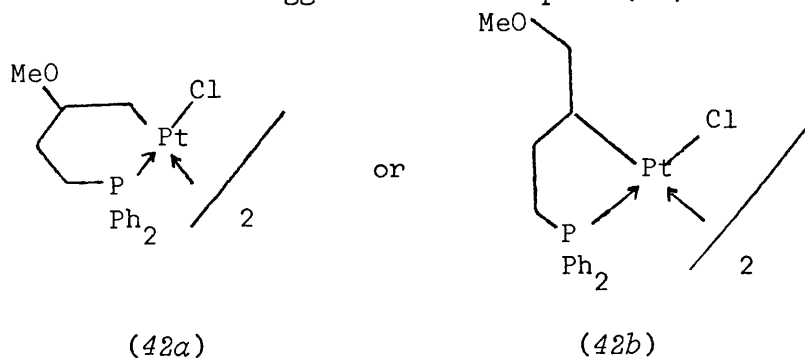
That methanol does not add across the triple bond of the free ligand was shown by recovery of the phosphine after it had been shaken with sodium hydrogen carbonate in methanol. It would appear, therefore, that the platinum has the effect of reducing the electron density of the acetylenic group sufficiently to make it susceptible to nucleophilic attack though there is no direct bonding between the two.

Prop-2-ynylphosphine was added to a solution of sodium chloroplatinite and lithium chloride in methanol. The complex cis-bis(diphenylprop-2-ynylphosphine)platinum(II) chloride (*3a*) was obtained. A phosphorus analogue of the complex obtained by Yukawa and Tsutsumi (26) with dimethylprop-2-ynylamine¹⁵⁴ was not formed. A possible reason for this is that whereas the prop-2-ynylphosphine is strongly co-ordinated to platinum(II) through phosphorus, bonding through the nitrogen of the corresponding amine will be weak.¹²² Although only those alkynes which have electron donating substituents (e.g. *t*-Bu) form stable complexes with platinum(II)¹⁹⁶ it is possible that the prop-2-ynyl amine forms an intermediate acetylene complex which undergoes nucleophilic attack by chloride. Chloride is a weaker nucleophile than methoxide, and neither the allyl nor the prop-2-ynyl phosphine complexes of platinum(II) were attacked by chloride ion to give σ -bonded cyclic complexes.

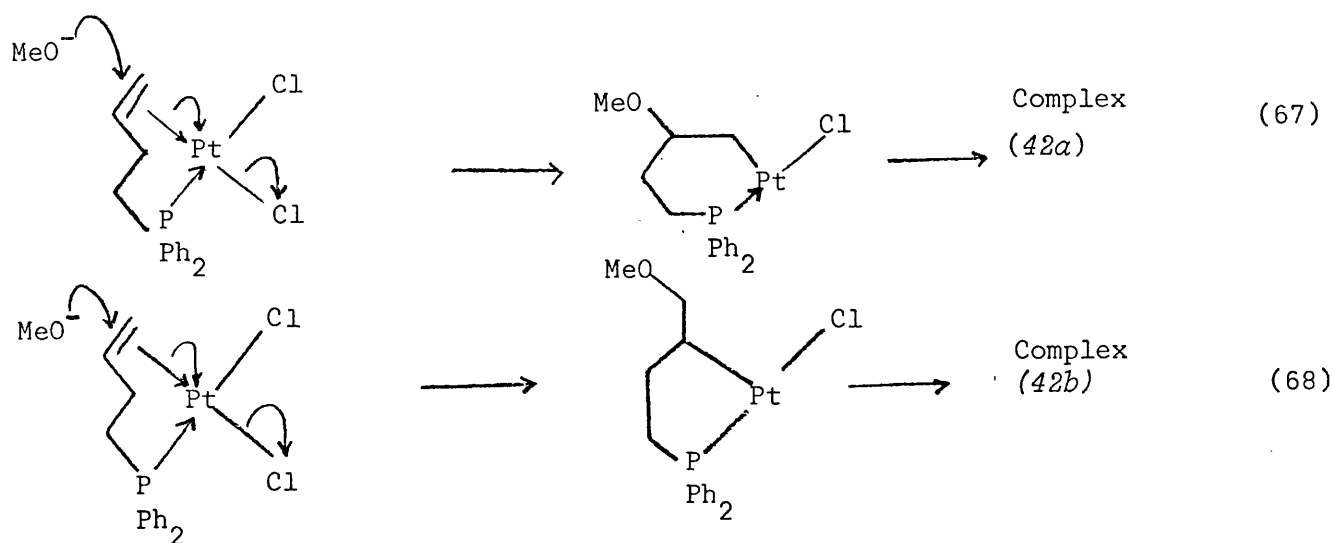
3. Reaction of Nucleophiles with a Co-ordinated Olefin.

The attack on co-ordinated olefins by a methoxide ion and other nucleophiles has already been described (Section III-1). The complex between but-3-enyldiphenylphosphine and platinum(II) chloride involves co-ordination between the metal and the double bond (Section II-2) and the reaction of this activated olefin and the methoxide ion was investigated.¹⁸⁹

The complex 1,2,5-trihapto-but-3-enyldiphenylphosphineplatinum(II) chloride (9) was treated with sodium hydrogen carbonate in methanol. A white complex (42) was obtained. The bands in the i.r. spectrum of (9) which are associated with the co-ordinated double bond are absent in the spectrum of (42), and there is a strong new band at 1095 cm^{-1} which may be assigned to a $\nu(\text{C-O})$ vibration. The far i.r. spectrum showed two broad absorptions at 271 and 240 cm^{-1} which is characteristic of bridging chlorine atoms.¹⁴⁵ It is suggested that complex (42) has the structure shown below.



The alternative structures depend on whether attack by the methoxide ion is at the β - or α -carbon atom (equ. 67 and 68).



The ^1H n.m.r. spectrum of (42) is complex and does not permit assignment of either of these structures.

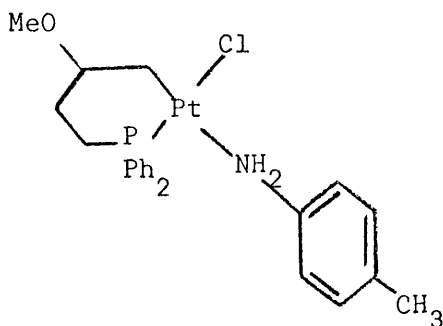
A similar reaction with an unspecified phosphine has been reported recently by Brooks and Nyholm.¹⁹⁷

Chatt and co-workers¹⁹⁸ assigned a band at around 1200 cm^{-1} in the i.r. spectrum to the CH_2 rocking vibration in the systems $\text{Pt-CH}_2\text{-X}$. There is a band of medium intensity at 1198 cm^{-1} in the i.r. spectrum of (42) which is not present in the spectrum of the starting complex. If this is due to such a vibration then it would confirm the structure of the complex as (42a), but it would be expected that this band would occur in a similar position in the i.r. spectrum of complex (32). The only band in this region of the spectrum of (32), however, is a weak absorption at 1210 cm^{-1} .

It was pointed out earlier (Section III-2) that nucleophilic attack on co-ordinated mono-olefins such as propene occurs predominantly at the β -carbon atom. Such an attack on complex (9) would lead to (42a). It is probable that 5- and 6-membered rings would have similar substabilities,¹⁹⁹ and so there should be no steric restrictions on the formation of either. The more likely of the two structures, therefore, is (42a), arising from the probable β -attack.

Complex (42) reacts with hydrochloric acid in the same way as complex (32), reforming the starting material.

Dinuclear chlorine bridged platinum(II) complexes undergo bridge cleavage reactions with amines and other donor ligands.²⁰⁰ Complex (42) reacts with p-toluidene to give a complex with one strong band in its far i.r. spectrum, at 287 cm^{-1} [$\nu(\text{Pt-Cl})$]. The near i.r. spectrum shows very few changes from that of (42). There are additional bands at 3419 cm^{-1} [$\nu(\text{N-H})$] and 826 cm^{-1} (para di-substituted benzene). Structure (43) is assigned to this complex.



(43)

Phosphorus is favoured as the trans- ligand to the chlorine because of the frequency of the $\nu(\text{Pt-Cl})$ vibration. It was found that the $\nu(\text{Pt-Cl})$ absorption in trans- PtClMeP_2 occurs at around 270 cm^{-1} , while in the cis-isomers it occurs at around 290 cm^{-1} .²⁰¹ The ^1H n.m.r. spectrum of (43) could not be obtained because of its low solubility in the normal range of solvents.

This Section of the project could well be extended and other nucleophiles used. Preliminary experiments were carried out with ammonia and benzylamine, with encouraging results, and hydroxide and other oxygen based nucleophiles could be used. A reaction which may lend itself to investigation may be that of another olefin with the co-ordinated double bond. Different, new, products may be obtained by treating complex (42) with non-mineral acids. This reaction with the ring compound (36) could lead to reactions being carried out on vinylic ether leaving the ring intact. Similarly, reactions with different nucleophiles could be carried out on the unco-ordinated double bond of cis-bis(allyldiphenylphosphine)platinum(II) chloride. Only complexes with platinum(II) and palladium(II) chlorides have been examined, and another extension of the project would be to examine the complexes of unsaturated phosphines with other metals.

PART C - EXPERIMENTAL

I. Introduction

So that a sequence of reactions leading to the examination of a particular complex may be easily followed, the experimental section has been arranged differently to the previous section. The divisions in "Results and Discussion" deal with the various facets of the project, but if the "Experimental" were to be so arranged it would be repetitive, and it would prove difficult to find the preparations of the phosphine and complex associated with a given reaction product. Each division, therefore, is based on a particular type of phosphine, e.g. "Monophosphines - Allyl". The preparations of the phosphines are described first, in the order of phenyl, ethyl and methyl, followed by the complexes, nickel, palladium then platinum, next reactions of the complexes, and finally experiments to characterise the reaction products.

II. General Techniques

All the preparations of the phosphines were carried out in an atmosphere of dry nitrogen using air-free solvents. Where appropriate, the solvents were dried as follows: benzene, pentane and ether by standing over sodium wire, tetrahydrofuran (THF) by distillation from sodium diphenylketyl. Pyridine was dried by distillation from potassium hydroxide. Thionyl chloride was purified by distillation from triphenylphosphite.²⁰²

Elemental analyses, and the physical techniques outlined below, were carried out by the appropriate departments of the Petrochemical & Polymer Laboratory.

^1H n.m.r. spectra were obtained using a Perkin-Elmer R10 or Varian HR220 instrument and are recorded in Appendix 1.

I.r. spectra were obtained using a Grubb Parsons Spectromaster Mk. 1, Perkin-Elmer 137, 157, 257 Spectrophotometer, or Hilger Watts Infragraph H1200 instrument. The far infrared region of the spectrum was obtained using a Grubb Parsons DM4 spectrometer. The spectra are recorded in Appendix 2.

Mass spectra were obtained using an A.E.I. MS9 or MS12 instrument and are recorded in Appendix 3.

Raman spectra were obtained by Dr. D.M. Adams (Leicester University) using a Coderg spectrometer, and are recorded in Appendix 2.

Melting points were recorded on a Kofler hotstage apparatus and are uncorrected.

III. Preparation of Starting Materials.

1. Preparation of Tetra-alkyldiphosphine.

(a) Tetramethyldiphosphine.³⁷ - Preparation of tetramethyl-
diphosphine disulphide. Bromomethane (346 g., 3.6 mole) in ether (200 ml.) was added dropwise to a suspension of magnesium turnings (88.3 g., 3.6 mole) in ether (750 ml.) at such a rate to keep the flask just above room temperature. A "dricold" condenser was used to prevent the bromomethane evaporating. The reaction was initiated with a crystal of iodine. The mixture was stirred overnight, more ether (750 ml.) was added, and the flask was cooled to $-10 - -20^{\circ}$.

Thiophosphoryl chloride (189 g., 1.1 mole) was added during 2 hr. at such a rate to keep the mixture at $3-5^{\circ}$. A thick white suspension was formed. The mixture was warmed at 30° for 1 hr. and allowed to stand overnight, before being poured slowly on to ice (6 l.) and conc. sulphuric acid (40 ml.). The white solid was recrystallised from a 3:1 toluene:ethanol mixture to give tetramethyldiphosphine disulphide (60 g., 59% yield), m.p. $224-230^{\circ}$ (lit.³⁷ m.p. $228-229^{\circ}$).

Reduction of tetramethyldiphosphine disulphide. Iron powder (B.D.H. "Reduced with Hydrogen") (258 g., 5 mole) was added to tetramethyldiphosphine disulphide (60 g., 0.32 mole) in a 250 ml. round-bottomed flask fitted with distillation head, condenser and Perkin triangle, and the mass was heated with a free flame. As the disulphide melted, the diphosphine began to distil at 140° . The product (35 g., 90% yield) was ampouled under nitrogen. Lit b.p.³⁷ 138° .

(b) Tetraethyldiphosphine.³⁷ - Preparation of tetraethyl-
diphosphine disulphide. Bromoethane (545 g., 5 mole) was added slowly to a suspension of magnesium turnings (121.5 g., 5 mole) in ether (1 l.) at a rate just sufficient to keep the solvent boiling. The reaction was initiated with dibromoethane. The mixture was refluxed for a further $\frac{1}{2}$ hr., stirred overnight, and was cooled to 0° . Thiophosphoryl chloride (265 g., 1.75 mole) was added at such a rate that the temperature of the mixture was $5-6^{\circ}$. Dry THF (1.5 l.) was added slowly and the suspension was stirred overnight, then heated at $40-45^{\circ}$ for $2\frac{1}{2}$ hr. After being cooled to room temperature, the slurry was poured on to ice (7 l.) to which conc. sulphuric acid

(50 ml.) had been added. The ethereal layer was separated and washed with water. The water layer and washing were extracted with ether (3 x 250 ml.). The combined ethereal extracts were dried over anhydrous sodium sulphate and evaporated under reduced pressure to give a pale yellow solid. Recrystallisation from methanol gave tetraethyldiphosphine disulphide (92 g., 50% yield), m.p. 77-79° (lit.³⁷ m.p. 77-78°).

Reduction of tetraethyldiphosphine disulphide. Iron powder (110 g., 1.97 mole) and tetraethyldiphosphine disulphide (50 g., 0.21 mole) were heated, using a free flame. Diethylphosphine (0.5 g.; b.p. 78-84°) and tetraethyldiphosphine (26.4 g., 72% yield), b.p. 218-220° (lit.³⁷ b.p. 220-221°) were obtained. The phosphines were ampouled under nitrogen.

2. Preparation of Metal Phosphides.

(a) Sodium Diphenylphosphide in Liquid Ammonia. - A typical preparation using Hewertson and Watson's method³² would be:

Sodium (4.6 g., 0.2 mole) was dissolved in liquid ammonia (300 ml.) at -76°. Triphenylphosphine was added during 20 min. and the mixture was stirred for 1 hr. Ammonium chloride (5.35 g., 0.1 mole) was added during 15 min., and the mixture was stirred for a further 1 hr. An orange solution was obtained.

(b) Lithium Dialkylphosphide in THF. - A typical preparation using Hewertson and Taylor's method⁷² would be: Tetra-alkyldiphosphine (0.13 mole) was added to a suspension of lithium flakes (1.88 g., 0.26 mole) in dry THF (250 ml.). Naphthalene (1.65 g., 0.013 mole) was added and the mixture, which became dark green after $\frac{1}{4}$ hr., was stirred overnight at room temperature. All the lithium was used. A green solution was obtained.

3. Preparation of Bis(benzonitrile)metal(II) Chloride.

(a) Bis(benzonitrile)palladium(II) Chloride.²⁰³ - Palladium(II) chloride (10 g., 0.057 mole) was heated in benzonitrile (125 ml.), boiling under reflux, for 1 hr. The hot orange solution which was formed was filtered through a kieselguhr pad, and was allowed to cool. The resulting orange crystals were washed with benzene, then ether, and dried. The product, bis(benzonitrile)palladium(II) chloride (20.9 g., 96% yield), was identified by comparison of its i.r. spectrum (App. 2 - Table 1) with that of an authentic sample.

(b) Bis(benzonitrile)platinum(II) Chloride. - Platinum(II) chloride (15 g., 0.056 mole) and benzonitrile (250 ml.) were stirred for 2 hr. at 120°. The orange solution was filtered while hot, and on cooling gave yellow crystals which were washed well with petroleum-ether (b.p. 60-80°) and dried. The product, bis(benzonitrile)platinum(II) chloride (23 g., 87% yield), was identified by comparison of its i.r. spectrum (App. 2 - Table 1) with that of an authentic sample.

IV. Monophosphines - Allyl.

1. Preparation of Phosphines.

(a) Allyldiphenylphosphine. - (i) Sodium diphenylphosphide (0.25 mole) was prepared using sodium (11.5 g., 0.5 mole), triphenylphosphine (65.5 g., 0.25 mole) and ammonium chloride (13.3 g., 0.25 mole) in liquid ammonia (1 l.) [III-2(a)]. Allyl chloride (19.1 g., 0.25 mole) in ether (25 ml.) was added during $\frac{1}{2}$ hr. at -76°. The solution progressively paled to a cream colour. The ammonia was allowed to evaporate overnight and the residue extracted with water (500 ml.) and ether (4 x 250 ml.). The combined ether extracts were dried over anhydrous sodium sulphate and the solvent was removed by distillation at atmospheric pressure. The residual oil was distilled under reduced pressure to give allyl-

diphenylphosphine, b.p. 131-134°/1.7 mm. (39.7 g., 70% yield). Lit.¹¹ b.p. 102-103°/0.45 mm. The ¹H n.m.r. (App. 1 - Table 1) and i.r. (App. 2 - Table 2) spectra were consistent with the structure.

The phosphine was further characterised as its methiodide, m.p. 147-148° (Found: C, 52.2; H, 4.9; I, 34.5. C₁₆H₁₈IP requires C, 51.7; H, 5.0; I, 34.8%).

(ii) Allyl bromide (12.1 g., 0.1 mole) in ether (10 ml.) was added dropwise to sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) during $\frac{1}{4}$ hr. at -76°. The mixture became colourless. After the ammonia had evaporated, the residue was worked-up with ether and water in the usual way. Distillation gave allyldiphenylphosphine, b.p. 99-103°/0.2 mm. (15.95 g., 70% yield), which was identified by its ¹H n.m.r. spectrum (App. 1 - Table 1) and i.r. spectrum (App. 2 - Table 2).

(b) Allyldiethylphosphine. - Lithium diethylphosphide (0.2 mole) in dry THF (250 ml.) was prepared as described in Section III-2(b), from lithium (1.38 g., 0.2 mole), naphthalene (1.3 g., 0.01 mole) and tetraethylphosphine, prepared in situ³² from diethylchlorophosphine (24.9 g., 0.2 mole) and lithium (1.38 g., 0.2 mole). The green solution was cooled to around -40° and allyl chloride (15.3 g., 0.2 mole) in THF (10 ml.) was added dropwise. The colour, which became orange then progressively paled to yellow, was completely discharged when the mixture warmed to room temperature. The solvent was removed under reduced pressure and the residue extracted with ether and water. The ethereal extracts were dried over anhydrous sodium sulphate and distilled. Allyldiethylphosphine (19.2 g., 74% yield; b.p. 62-72°/50 mm.) was obtained as a colourless oil, and was ampouled under nitrogen. The product was identified by its ¹H n.m.r. (App. 1 - Table 1) and i.r. (App. 2 - Table 2) spectra.

The phosphine was further characterised as its methiodide, m.p. 189-192° (Found: C, 35.1; H, 6.7. $C_8H_{18}IP$ requires C, 35.3; H, 6.7%).

2. Preparation of Palladium(II) Chloride Complexes.

(a) Allyldiphenylphosphine. - (i) Bis(benzonitrile)palladium(II) chloride (2.3 g., 6 mmole) was dissolved in boiling benzene (150 ml.) and the solution was filtered hot. Allyldiphenylphosphine (2.7 g., 12 mmole) in benzene (10 ml.) was added dropwise. After refluxing for 1 hr., the solution was cooled, filtered, and evaporated to small bulk. A yellow solid precipitated on standing. This was recrystallised from benzene-ethanol to give yellow crystals (1.7 g.) of trans-bis(allyldiphenylphosphine)palladium(II) chloride, m.p. 189-191° (Found: C, 57.5; H, 5.0; Cl, 11.0. $C_{30}H_{30}Cl_2P_2Pd$ requires C, 57.2; H, 4.8; Cl, 11.2%). The complex was characterised as the trans-isomer by its far i.r. spectrum (App. 2 - Table 4). The 1H n.m.r. of the complex is recorded in App. 1 - Table 1.

(ii) Allyldiphenylphosphine (2.91 g., 13 mmole) in methanol (10 ml.) was added dropwise to sodium chloropalladite (2.2 g., 6 mmole) in water (5 ml.) and methanol (40 ml.). A yellow precipitate was formed immediately. This redissolved on stirring, then a yellow solid was precipitated. Recrystallisation from ethanol-benzene gave trans-bis(allyldiphenylphosphine)palladium(II) chloride, m.p. 187-189°, 3.2 g. (Found: C, 57.5; H, 4.9; Cl, 10.8. $C_{30}H_{30}Cl_2P_2Pd$ requires C, 57.2; H, 4.8; Cl, 11.2%).

(iii) Sodium chloropalladite (2.7 g., 7.3 mmole) was dissolved in water (5 ml.) and the solution diluted with a methanol solution (40 ml.) of lithium chloride (10 g.). Allyldiphenylphosphine (1.65 g., 7.3 mmole) in methanol (5 ml.) was added dropwise. A yellow solid

was immediately formed. This dissolved on stirring and the complex precipitated on standing. It was shown by i.r. spectroscopy to be identical to the products from the previous preparations.

(b) Allyldiethylphosphine. - (i) Allyldiethylphosphine (2.45 g., 19 mmole) was added to a solution of bis(benzonitrile)palladium(II) chloride (3.45 g., 9 mmole) in benzene (100 ml.) boiling under reflux. After boiling for $\frac{1}{2}$ hr., the orange solution was filtered, cooled and evaporated to a small bulk. Crystallisation was eventually induced by removal of all the solvent, cooling, and shaking the residual oil. Recrystallisation from ethanol gave yellow trans-bis(allyldiethylphosphine)palladium(II) chloride, m.p. 144-147° (Found: C, 38.2; H, 7.0. $C_{14}H_{30}Cl_2P_2Pd$ requires C, 38.4; H, 6.9%), identified by its i.r. spectrum (app. 2 - Tables 2 and 4).

(ii) Allyldiethylphosphine (1.65 g., 12.7 mole) was added to sodium chloropalladite (2.3 g., 6.3 mmole) in water (5 ml.) and ethanol (15 ml.). A yellow precipitate immediately formed. This was shown by i.r. spectroscopy to be identical to the complex described above.

3. Preparation of Platinum(II) Chloride Complexes.

(a) Allyldiphenylphosphine. - (i) Allyldiphenylphosphine (4.75 g., 21 mmole) was added to a solution of bis(benzonitrile)-platinum(II) chloride (4.95 g., 11 mmole) in benzene (300 ml.) boiling under reflux. After $\frac{1}{2}$ hr. the solution was filtered, allowed to cool, and on evaporation to dryness gave a yellow oil which solidified on treatment with warm methanol. Recrystallisation from ethanol-benzene gave two fractions, (a) yellow crystals of trans-bis(allyldiphenylphosphine)platinum(II) chloride (0.28 g.), m.p. 173-176° (Found: C, 50.0; H, 4.35. $C_{30}H_{30}Cl_2P_2Pt$ requires C, 50.1; H, 4.2%), and (b) the white cis-isomer contaminated with a

little of the trans-. This was further recrystallised from ethanol-benzene to give cis-(allyldiphenylphosphine)platinum(II) chloride (2.2 g.), m.p. 185-188° (Found: C, 49.9; H, 4.0. $C_{30}H_{30}Cl_2P_2Pt$ requires C, 50.1; H, 4.2%). The complexes were identified by their i.r. spectra (App. 2 - Tables 2, 4).

(ii) Allyldiphenylphosphine (2.56 g., 11 mmole) in methanol (5 ml.) was added to sodium chloroplatinite (2.6 g., 5.5 mmole) in water (5 ml.) and methanol (45 ml.). A grey precipitate was obtained. Recrystallisation from ethanol and treatment with charcoal gave white crystals of cis-bis(allyldiphenylphosphine)-platinum(II) chloride, m.p. 188-192° (Found: C, 50.5; H, 4.7; Cl, 10.0. $C_{30}H_{30}Cl_2P_2Pt$ requires C, 50.1; H, 4.2; Cl, 9.9%).

(iii) Sodium chloroplatinite (2.98 g., 6 mmole) in water (5 ml.) was treated with lithium chloride (10 g.) in methanol (45 ml.). Addition of allyldiphenylphosphine (1.48 g., 6 mmole) gave a white precipitate which was recrystallised from ethanol to give cis-bis(allyldiphenylphosphine)platinum(II) chloride, identical to the above samples.

(b) Allyldiethylphosphine. - (i) Allyldiethylphosphine (1.95 g., 15 mmole) was added to a suspension of bis(benzonitrile)-platinum(II) chloride (3.3 g., 7 mmole) in benzene (100 ml.). The resulting solution was stirred at reflux for $\frac{3}{4}$ hr., filtered and evaporated to small bulk. White crystals (1 g.) of cis-bis(allyldiethylphosphine)platinum(II) chloride, m.p. 146-148° (Found: C, 32.3; H, 6.0; Cl, 12.9. $C_{14}H_{30}Cl_2P_2Pt$ requires C, 31.9; H, 5.7; Cl, 13.4%), were deposited on standing.

(ii) Allyldiethylphosphine (2.05 g., 16 mmole) was added dropwise to sodium chloroplatinite (3.6 g., 8 mmole) in water

(5 ml.) and methanol (10 ml.). A small amount of an oily solid was formed. On standing in the refrigerator, the solution gave a small amount of a pale yellow solid which had an i.r. spectrum identical to the compound described above (App. 2 - Tables 2, 4).

4. Reactions with Methoxide

(a) cis-Bis(allyldiphenylphosphine)platinum(II) Chloride. -

A suspension of cis-bis(allyldiphenylphosphine)platinum(II) chloride (2 g., 2.7 mmole) and sodium hydrogen carbonate (0.48 g., 5.4 mmole) in methanol (50 ml.) was shaken over a weekend. Recrystallisation of the resulting white solid from benzene gave cis-bis(1,4-dihapto-2-methoxypropyldiphenylphosphine)platinum(II)²⁰⁴ (32), m.p. 224° (Found: C, 54.5; H, 5.2; P, 8.8; Pt, 27.6. $C_{32}H_{36}O_2P_2Pt$ requires C, 54.2; H, 5.1; P, 8.8; Pt 27.5%). The dipole moment of the complex in benzene at 25° was found to be 5.2 D. The complex was identified by its i.r. (App. 2 - Table 6) and mass (App. 3) spectra.

(b) trans-Bis(allyldiphenylphosphine)platinum(II) Chloride. -

(i) The complex (0.28 g., 3.9 mmole) and sodium hydrogen carbonate (0.07 g., 7.8 mmole) were shaken overnight in methanol (25 ml.). The platinum complex (0.26 g.) was recovered unchanged.

(ii) Sodium methoxide (7 mmole) in benzene (5 ml.) was added to the platinum complex (0.26 g., 3.5 mmole) in benzene (3 ml.) and the mixture was stirred over a weekend. The red solution was filtered and was evaporated to dryness to give a red oil. It did not prove possible to crystallise this oil.

(c) cis-Bis(allyldiphenylphosphine)palladium(II) Chloride. -

(i) A suspension of the palladium complex (0.63 g., 1 mmole) and sodium hydrogen carbonate (0.16 g., 2 mmole) in methanol (30 ml.)

was shaken over a weekend. A residue of starting material was obtained. No identifiable product could be isolated from the solution.

(ii) cis-Bis(allyldiphenylphosphine)palladium(II) chloride (0.63 g., 1 mmole) and sodium carbonate (0.25 g., 2.4 mmole) were suspended in methanol (70 ml.) and the mixture was warmed. A black powder, apparently metallic palladium, was deposited. No complex could be obtained from the reaction mixture.

(iii) A suspension of the palladium complex (0.63 g., 1 mmole) and sodium acetate (0.27 g., 2 mmole) in methanol (20 ml.) was shaken overnight. The starting material was recovered unchanged.

(d) Allyldiphenylphosphine. - Allyldiphenylphosphine (1.65 g., 7.3 mmole) was added to a suspension of sodium hydrogen carbonate (0.62 g., 7.3 mmole) in methanol (20 ml.) and the mixture was stirred overnight. The solvent was removed and the residue was worked-up with ether and water. The ethereal extracts, after drying over anhydrous sodium sulphate, gave allyldiphenylphosphine on evaporation.

(e) cis-Bis(allyldiethylphosphine)platinum(II) Chloride. - The platinum complex (1 g., 1.9 mmole) and sodium hydrogen carbonate (0.3 g., 3.8 g.) were shaken overnight in methanol (50 ml.). The resulting solution was filtered and evaporated to dryness. The residue was extracted with chloroform and water, and the chloroform layer was evaporated to give an oil which could not be crystallised. The i.r. spectrum of this oil showed that a free olefinic group was still present.

5. Reactions of Complex (32).

(a) Reaction with Hydrochloric Acid. - (i) The complex (0.3 g., 0.42 mmole) was dissolved in benzene (20 ml.) and the solution

was diluted with methanol (60 ml.). Concentrated hydrochloric acid (5 ml.) was added dropwise. The mixture was stirred for $\frac{1}{2}$ hr., then was evaporated to dryness. The residue was recrystallised from methanol to give white crystals of cis-bis(allyldiphenylphosphine)-platinum(II) chloride (Found: C, 50.7; H, 4.1; Cl, 10.0. $C_{30}H_{30}Cl_2P_2Pt$ requires C, 50.1; H, 4.2; Cl, 9.9%).

(ii) The complex (0.1 g., 0.14 mmole) was dissolved in carbon tetrachloride (5 ml.) and concentrated hydrochloric acid (5 ml.) was added. The residue obtained on evaporation was recrystallised from methanol to give cis-bis(allyldiphenylphosphine)platinum(II) chloride.

V. Monophosphines - Propynyl.

1. Preparation of Phosphines.

(a) Preparation of Acetylenic Halides. - (i) 3-Chloroprop-1-yne. Thionyl chloride (5.81 g., 0.714 mole) was added dropwise to a stirred mixture of prop-1-yn-3-ol (40 g., 0.715 mole) and pyridine (0.5 ml.) at 0° . The mixture was stirred overnight, then heated at 50° for 2 hr. Distillation gave 3-chloroprop-1-yne (38.8 g., 72.5% yield), b.p. 56.5° (lit.²⁰⁵ b.p. 57.5°).

(ii) 1-Chlorobut-2-yne. 1,3-Dichlorobut-2-ene (250 g., 2 mole) was heated in a refluxing solution of sodium carbonate (125 g.) in water (1.25 l.) for 3 hr.²⁰⁶ The cooled solution was extracted with ether (5 x 250 ml.) and the combined ether extracts were dried over anhydrous magnesium sulphate. Distillation gave 3-chlorobut-2-en-1-ol (151 g., 70% yield), b.p. $55-58^\circ/7-8$ mm. (lit.²⁰⁶ b.p. $58-60^\circ/8$ mm.).

3-Chlorobut-2-en-1-ol (151 g., 1.4 mole) was added dropwise to a suspension of sodamide (3.2 mole) in liquid ammonia (2.5 l.)²⁰⁷

and the mixture stirred overnight. Ammonium chloride (166 g., 3.2 mole) was added, the solvent was allowed to evaporate, and the residue was extracted with ether (5 x 250 ml.). After being dried over anhydrous magnesium sulphate, the solution was distilled to give but-2-yn-1-ol (77.6 g., 78% yield), b.p. 50-54°/8 mm. (lit.²⁰⁶ b.p. 55°/8 mm.).

Thionyl chloride (59.5 g., 0.5 mole) was added to but-2-yn-1-ol (35 g., 0.5 mole) and pyridine (0.5 ml.) at 0°. After being heated at 70° for 3 hr., the mixture was distilled to give 1-chlorobut-2-yne (38.7 g., 87% yield), b.p. 100-103° (lit.²⁰⁸ b.p. 104-106°).

(iii) 1-Bromobut-2-yne.²⁰⁹ Bromine (48 g., 0.3 mole) was added at 0° to a stirred solution of triphenylphosphite (92.5 g., 0.3 mole) in ether (150 ml.). The resulting suspension was stirred for a further 2 hr. at room temperature before the solvent was decanted off. The solid was washed with ether (3 x 100 ml.) and dried. A solution of but-2-yn-1-ol (14 g., 0.2 mole) [V-1(a)(ii)] in pyridine (19.5 g., 0.25 mole) was added to 0° to the stirred solid, and the mixture was stirred for 2 hr. Volatile products were distilled in vacuo to a trap at -76°. 1-Bromobut-2-yne (5.1 g., 19% yield) was obtained.

(iv) 3-Chlorobut-1-yne.²¹⁰ Thionyl chloride (178.5 g., 1.5 mole) was added to a stirred solution of but-1-yn-3-ol (105 g., 1.5 mole), obtained from the commercially available aqueous solution, and pyridine (1.5 ml.) at 0°. The mixture was stirred at 70° for 3 hr. and distilled to give 3-chlorobut-1-yne (83.4 g., 63% yield), b.p. 66-68° (lit.²¹⁰ b.p. 68.5°).

(v) 3-Bromobut-1-yne.²⁰⁹ Bromine (68.8 g., 0.43 mole) was added dropwise to a stirred solution of triphenylphosphite (139 g., 0.45 mole) in ether (150 ml.) at 0°. After being stirred for 2 hr., the solvent was decanted off and the residue was washed with ether (2 x 100 ml.) and dried. But-1-yn-3-ol (14 g., 0.2 mole) in pyridine (19.5 g., 0.25 mole) was added dropwise at 0° to the stirred solid. The mixture was stirred for 2 hr. and the volatile products distilled under vacuum to a trap at -76°. Redistillation gave 3-bromobut-1-yne (16.8 g., 63% yield), b.p. 34-37°/98-99 mm. (lit.²⁰⁹ b.p. 43-45°/100 mm.).

(b) Reaction of 3-Chloroprop-1-yne with Sodium Diphenylphosphide. - (i) Reaction in liquid ammonia. Preparation of diphenylprop-1-ynylphosphine (β_a). Sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III-2(a)] was treated dropwise with a solution of 3-chloroprop-1-yne (7.45 g., 0.1 mole) in ether (5 ml.) during 10 min. There was an immediate exothermic reaction, the orange colour of the phosphide solution becoming progressively paler. The ammonia was allowed to evaporate overnight and the resulting residue was extracted with water (200 ml.) and ether (4 x 100 ml.). The ether extracts were dried over anhydrous sodium sulphate and the solvent was removed by distillation at atmospheric pressure. Vacuum distillation of the residue gave diphenylprop-1-ynylphosphine (β_a) as a viscous liquid (17 g., 78% yield), b.p. 105-107°/0.01 mm. (lit.¹⁰¹ b.p. 143°/0.1 mm.).

The product was identified by its ¹H n.m.r. (App. 1 - Table 2) and i.r. (App. 2 - Table 3) spectra.

The same product was obtained in 90% yield when the reaction was carried out at -40° instead of -76°.

(ii) Reaction in THF. Sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) was prepared as described in III-2(a), and the solvent was allowed to evaporate. THF (200 ml.) was added and the mixture was heated for $\frac{1}{2}$ hr. at 70° to remove any traces of ammonia, before being cooled to -40° . 3-Chloroprop-1-yne (7.45 g., 0.1 mole) in THF (5 ml.) was added dropwise during the 10 min. The red solution became paler, turned brown, and on warming to room temperature over 2 hr. it became almost black. The solvent was removed by distillation at reduced pressure and the residue worked-up with ether and water as above. The distillate, b.p. $106-111^{\circ}/0.01$ mm., was shown by its ^1H n.m.r. spectrum (App. 1 - Table 2) to be a mixture of diphenylprop-1-ynylphosphine (8a), diphenylprop-2-ynylphosphine (6a), and diphenylpropa-1,2-dienylphosphine (7a) in the ratio 20:6:1. (Total yield of $(\text{C}_6\text{H}_5)_2\text{PC}_3\text{H}_3$ 7.8 g., 35%).

(iii) Reaction in THF by reverse addition. Preparation of diphenylprop-2-ynylphosphine (6a). Sodium diphenylphosphide (0.1 mole) in THF (300 ml.) was prepared as described above. It was transferred to a dropping funnel and added dropwise to a stirred solution of 3-chloroprop-1-yne (7.7 g., 0.103 mole) in THF (100 ml.) at -40° . The orange colour of the phosphide solution was discharged as it mixed with the halide solution. Work-up as above, followed by distillation of the residue, gave diphenylprop-2-ynylphosphine (6a) (14.4 g., 64% yield), b.p. $110-116^{\circ}/0.01$ mm., identified by its ^1H n.m.r. (App. 1 - Table 2) and i.r. (App. 2 - Table 3) spectra.

(iv) Reaction of diphenylprop-2-ynylphosphine with sodium diphenylphosphide. Diphenylprop-2-ynylphosphine (6a) (1.4 g., 6.3 mmole) was added to a stirred solution of sodium diphenylphosphide (11 mmole) in liquid ammonia (25 ml.) at -76° , and the mixture was stirred for 3 hr. Ammonium chloride (0.6 g., 11 mmole) was added to destroy the sodium diphenylphosphide, and ammonia was allowed to evaporate overnight. The usual work-up with ether and water was carried out, and the resulting viscous liquid was examined by ^1H n.m.r. and i.r. spectroscopy. It was found to be a mixture of diphenylphosphine (from the phosphide) and diphenylprop-1-ynylphosphine (8a).

(c) Reaction of 3-Bromoprop-1-yne with Sodium Diphenylphosphide. - (i) 3-Bromoprop-1-yne (11.9 g., 0.1 mole) in ether (10 ml.) was added dropwise during 10 min. to a stirred solution of sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III-2(a)] at -76° . The colour of the solution progressively paled from orange to cream. The ammonia was allowed to evaporate, and the residue extracted with ether and water. The ethereal extract, after drying, was distilled to leave an orange oil containing a little solid. Attempted distillation of this residue gave a viscous liquid, b.p. $107-109^{\circ}/0.01$ mm. (1.5 g.) (i.r.: App. 2 - Table 5), which solidified on prolonged standing and evolved ammonia. The undistillable residue solidified on cooling. It was triturated with ethanol, and recrystallisation from propanol gave bis(diphenylphosphino)amine (7.3 g.), colourless needles, m.p. $138-139^{\circ}$ (lit.⁶⁰ m.p. 152° - from benzene) (Found: C, 74.6; H, 5.6; N, 3.4. Calc. for $\text{C}_{24}\text{H}_{21}\text{NP}_2$: C, 74.9; H, 5.5;

N, 3.6%). The compound was further characterised by its mass spectrum (App. 3). An accurate mass measurement on the parent ion - found: 385.1155; calculated for $C_{24}H_{21}NP_2$: 385.1148. The solid from the distillate had an identical i.r. spectrum (App. 2 - Table 5) to the above product. Total yield 8.3 g., 42%.

(ii) 3-Bromoprop-1-yne (0.43 g., 4 mmole) was condensed on to sodium diphenylphosphide (2.1 mmole) in liquid ammonia (5 ml.) contained in a flask connected to a vacuum line (App. 4 - Figure 1) and cooled to -196° . The mixture was allowed to warm to -40° and was stirred for 2 hr. The colour changed from dark orange to pale yellow. The volatile products and the solvent were condensed into a trap at -196° . The fraction which passed through a trap at -47° was collected in a trap at -196° and was shown by mass spectroscopy to be propyne (m/e 40, 39, 38, 37, 36) and ammonia.

(d) Reaction of 1-Chlorobut-2-yne with Sodium Diphenylphosphide. - 1-Chlorobut-2-yne (8.85 g., 0.1 mole) in ether (10 ml.) was added to a solution of sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III-2(a)]. The solvent was allowed to evaporate, and the residue was worked-up with ether and water. Distillation of the ether extracts gave but-2-ynyl-diphenylphosphine (6c) (15.3 g., 64% yield), b.p. $105-115^{\circ}/0.01$ mm. The phosphine was identified by its 1H n.m.r. (App. 1 - Table 2) and i.r. (App. 2 - Table 3) spectra.

(e) Reaction of 1-Bromobut-2-yne with Sodium Diphenylphosphide. - 1-Bromobut-2-yne (5.1 g., 0.038 mole) in ether (5

ml.) was added dropwise to a solution of sodium diphenylphosphide (0.038 mole) in liquid ammonia (150 ml.) at -76° . A rapid exothermic reaction occurred and the mixture became very pale yellow. After the usual work-up a sample of the crude product was shown to have an identical ^1H n.m.r. spectrum to that of but-2-ynyldiphenylphosphine (*6c*) (85% yield).

(f) Reaction of 3-Chlorobut-1-yne with Sodium Diphenylphosphide. - 3-Chlorobut-1-yne (8.85 g., 0.1 mole) in ether (5 ml.) was added to a solution of sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) at -76° . The residue obtained on evaporation of the solvent was worked-up with water (200 ml.) and ether (5 x 50 ml.). The ^1H n.m.r. spectrum of the crude product showed only the prop-2-ynyl phosphine. Fractional distillation gave (a) b.p. $94-97^{\circ}/0.01$ mm., 1-methylprop-2-ynyldiphenylphosphine (*6b*) (7.76 g., 33% yield), and (b) b.p. $100-104^{\circ}/0.01$ mm., a mixture of the acetylenic phosphine (*6b*) and 1-methylpropa-1,2-dienyldiphenylphosphine (*7b*) (3.08 g., 13% yield) in the ratio 3.7:1. The products were identified by their ^1H n.m.r. (App. 1 - Table 2) and i.r. (App. 2 - Table 3) spectra.

(g) Reaction of 3-Bromobut-1-yne with Sodium Diphenylphosphide. - 3-Bromobut-1-yne (14.2 g., 0.105 mole) in ether (10 ml.) was added dropwise to a stirred solution of sodium diphenylphosphide (0.105 mole) in liquid ammonia (300 ml.) at -76° . The mixture became pale yellow. The usual work-up gave a golden oil, the i.r. spectrum of which was identical to that of diphenylphosphinoamine (App. 2 - Table 5). The

oil was suspended in aqueous caustic soda (200 ml., 2%) and oxidised with hydrogen peroxide. After stirring for one day, the alkaline water solution was decanted from the residual oil. Acidification gave diphenylphosphinic acid (5.1 g., 45% yield), m.p. 192-194° (lit.²¹¹ m.p. 195-196°).

2. Preparation of Palladium(II) Chloride Complexes.

(a) Diphenylprop-1-ynylphosphine (8a). - (i) The phosphine (1.72 g., 7.8 mmole) was added to bis(benzonitrile)palladium (II) chloride (1.5 g., 4 mmole) in boiling benzene (100 ml.). A yellow precipitate was formed immediately. The mixture was boiled for $\frac{1}{2}$ hr., cooled and the solid was filtered off. It was washed well with benzene, ethanol then ether, and was dried to give trans-bis(diphenylprop-1-ynylphosphine)palladium(II) chloride (14b), m.p. 200-205° (decomp.) (Found: C, 59.0; H, 4.2. $C_{30}H_{26}Cl_2P_2Pd$ requires C, 57.6%, H, 4.2%). The complex was identified by its i.r. spectrum (App. 2 - Tables 3, 4).

(ii) The phosphine (8a) (3.1 g., 14 mmole) in methanol (5 ml.) was added to a solution of sodium chloropalladite (2.53 g., 7 mmole) in water (5 ml.) and methanol (45 ml.). Immediately a yellow precipitate of trans-bis(diphenylprop-1-ynylphosphine)-palladium(II) chloride (14b) was formed. (Found: C, 56.3; H, 3.8. $C_{30}H_{26}Cl_2P_2Pd$ requires C, 57.6; H, 4.2%). The complex had an identical i.r. spectrum to the one described above.

(b) Diphenylprop-2-ynylphosphine (6a). - The phosphine (2.4 g., 10.7 mmole) was added to a boiling solution of bis(benzonitrile)palladium(II) chloride (2.04 g., 5.3 mmole) in benzene (100 ml.). A yellow precipitate was formed immediately. This was washed with benzene, ethanol and ether, and dried to give cis-bis(diphenylprop-2-ynylphosphine)palladium(II) chloride

(13a), m.p. 163-166° (Found: C, 57.6; H, 4.1. $C_{30}H_{26}Cl_2P_2Pd$ requires C, 57.6; H, 4.2%), identified by its i.r. spectrum (App. 2 - Tables 3, 4).

(c) But-2-ynyldiphenylphosphine (6c). - The phosphine (2.0 g., 8.4 mmole) was added to bis(benzonitrile)palladium(II) chloride (1.62 g., 4.2 mmole) in boiling benzene (100 ml.). The solution was boiled for 1 hr., cooled and was evaporated to small bulk. The yellow solid which slowly precipitated was washed with benzene, ethanol and ether, and was dried, to give trans-bis-(but-2-ynyldiphenylphosphine)palladium(II) chloride (13c), m.p. 221-225° (decomp.) (Found: C, 58.5; H, 4.6. $C_{32}H_{30}Cl_2P_2Pd$ requires C, 58.8; H, 4.6%). The product was identified by its i.r. spectrum (App. 2 - Tables 3, 4).

(d) 1-Methylprop-2-ynyldiphenylphosphine (6b). - The phosphine (2.0 g., 8.4 mmole) was added to bis(benzonitrile)-palladium(II) chloride (1.53 g., 4 mmole) in boiling benzene (100 ml.), and the mixture boiled for a further $\frac{1}{2}$ hr. A fine yellow precipitate was formed. This was removed by filtration and the filtrate was evaporated to small bulk. Yellow crystals of trans-bis(1-methylprop-2-ynyldiphenylphosphine)palladium(II) chloride (13b), m.p. 106-110° (Found: C, 63.0, H, 5.1. $C_{32}H_{30}Cl_2P_2Pd$ requires C, 58.8; H, 4.6%), were obtained on cooling. The complex was shown to have a trans-configuration by i.r. spectroscopy (App. 2 - Tables 3, 4).

3. Preparation of Platinum(II) Chloride Complexes.

(a) Diphenylprop-1-ynylphosphine (8a). - The phosphine (1.85 g., 8.2 mmole) was added to bis(benzonitrile)platinum(II) chloride (1.88 g., 4 mmole) in boiling benzene (50 ml.) and the

mixture boiled for 1 hr. The white precipitate, which was formed immediately, was washed with benzene, ethanol, then ether, and was dried. It was shown by its i.r. spectrum (App. 2 - Tables 3, 4) to be cis-bis(diphenylprop-1-ynylphosphine)platinum(II) chloride (14a), m.p. 271-272° (decomp.) (Found: C, 50.9; H, 3.7. $C_{30}H_{26}Cl_2P_2Pt$ requires C, 50.4; H, 3.7%).

(b) Diphenylprop-2-ynylphosphine (6a). - (i) To a boiling solution of bis(benzonitrile)platinum(II) chloride (3.1 g., 6.6 mmole) in benzene (150 ml.) was added diphenylprop-2-ynylphosphine (3.0 g., 13.4 mmole). After boiling for 1 hr., the mixture was cooled and the white solid which was formed on adding the phosphine was filtered off. It was washed with benzene, ethanol and ether, and was shown to be cis-bis(diphenylprop-2-ynylphosphine)platinum(II) chloride (13a), m.p. 198-200° (decomp.) (Found: C, 51.1; H, 3.7. $C_{30}H_{26}Cl_2P_2Pt$ requires C, 50.4; H, 3.7%) by its i.r. spectrum (App. 2 - Tables 3, 4).

(ii) Diphenylprop-2-ynylphosphine (6a) (1.7 g., 7.6 mmole) was added to a solution of sodium chloroplatinite (3.46 g., 3.6 mmole) in water (5 ml.) and methanol (45 ml.) to which lithium chloride (10 g.) had been added. A white precipitate was formed immediately. The mixture was stirred for 1 hr., then filtered. The residue was recrystallised from benzene, and was shown by a comparison of its i.r. spectrum to be identical to the above complex.

(c) But-2-ynyldiphenylphosphine (6c). - To a boiling solution of bis(benzonitrile)platinum(II) chloride (1.95 g., 4.1 mmole) in benzene (50 ml.) was added but-2-ynyldiphenylphosphine (2.0 g., 8.4 mmole). The resulting red solution was refluxed

for 1 hr., was filtered, and after cooling was evaporated to small bulk. The resulting red oil, after trituration with warm benzene and cyclohexane, gave colourless crystals of cis-bis(but-2-ynyldiphenylphosphine)platinum(II) chloride (13a), m.p. 190-192° (Found: C, 49.2; H, 4.4. $C_{32}H_{30}Cl_2P_2Pt$ requires C, 51.8; H, 4.1%), i.r. (App. 2 - Tables 3, 4).

(d) 1-Methylprop-2-ynyldiphenylphosphine (6b). - The phosphine (1.52 g., 6.4 mmole) was added to a boiling solution of bis(benzonitrile)platinum(II) chloride (1.4 g., 3 mmole) in benzene (50 ml.), and the solution was boiled for a further 1 hr. The small amount of white solid that was formed was removed by filtration and the filtrate was evaporated to small bulk. Addition of petroleum-ether (b.p. 60-80°) gave colourless crystals of cis-bis(1-methylprop-2-ynyldiphenylphosphine)platinum(II) chloride (13b), m.p. 172-176° (Found: C, 52.4; H, 4.2. $C_{32}H_{30}Cl_2P_2Pt$ requires C, 51.8; H, 4.1%). The complex was identified by its i.r. spectrum (App. 2 - Tables 3, 4).

4. Preparation of Mercury(II) Chloride Complexes.

(a) Diphenylprop-1-ynylphosphine (8a). - The phosphine (5.9 g., 26 mmole) in ethanol (5 ml.) was added to an ethanolic solution of mercury(II) chloride (7.06 g., 26 mmole). A white oil was formed immediately. On trituration with ethanol this gave colourless diphenylprop-1-ynylphosphine-mercury(II) chloride, m.p. 175-177° (decomp.) (Found: C, 36.9; H, 2.7. $C_{15}H_{13}Cl_2HgP$ requires C, 36.3; H, 2.6%). The complex was identified by its i.r. spectrum (App. 2 - Table 3).

5. Reactions with Methoxide.

(a) cis-Bis(diphenylprop-1-ynylphosphine)platinum(II)

Chloride (14a). - The complex (1.0 g., 1.4 mmole) was shaken overnight in a suspension of sodium hydrogen carbonate (0.24 g., 2.8 mmole) in methanol (50 ml.). The resulting white solid, after being washed well with water, methanol and ether gave cis-bis(diphenyl-2-methoxyprop-1-enylphosphine)platinum(II) chloride (39), m.p. 170-178° (decomp.) (Found: C, 49.9; H, 3.9. $C_{32}H_{34}ClO_2P_2Pt$ requires C, 49.4; H, 4.4%). The complex was identified by its i.r. spectrum (App. 2 - Tables 4, 6).

(b) cis-Bis(diphenylprop-2-ynylphosphine)platinum(II)

Chloride (13a) - The complex (1.0 g., 1.4 mmole) and sodium hydrogen carbonate (0.24 g., 2.8 mmole) were shaken overnight in methanol (50 ml.). The mixture was filtered to remove a white residue of starting material, and the resulting yellow solution was evaporated to dryness. The residue was dissolved in benzene and after filtration the solution was evaporated to small bulk, warmed, and was treated with cyclohexane. Orange crystals of cis-bis(1,4-dihapto-diphenyl-2-methoxyprop-2-enylphosphine)platinum(II) chloride (34), m.p. 202-205° (Found: C, 55.1; H, 4.8. $C_{32}H_{32}O_2P_2Pt$ requires C, 54.5; H, 4.6%), were obtained, identified by its i.r. spectrum (App. 2 - Table 6).

(c) Diphenylprop-1-ynylphosphine (8a). - The phosphine (1.62 g., 7.2 mmole) was added to a suspension of sodium hydrogen carbonate (0.6 g., 7.2 mmole) in methanol (10 ml.) and the mixture was stirred overnight. The solvent was removed and the residue was extracted with water and ether. The ether extracts gave diphenylprop-1-ynylphosphine (8a) unchanged.

(d) Diphenylprop-2-ynylphosphine (6a). - The phosphine (1.3 g., 5.8 mmole) was added to a suspension of sodium hydrogen carbonate (0.5 g., 5.8 mmole) in methanol (25 ml.), and the mixture was stirred over the weekend. The solvent was removed, and the residue was worked-up with ether and water. Unchanged diphenylprop-2-ynylphosphine (6a) was obtained from the ether extract.

6. Reactions of Complex (39).

(a) Reaction with Hydrochloric Acid. - The platinum complex (39) (0.25 g., 0.32 mmole) was dissolved in a minimum volume of chloroform (5 ml.) and the solution was diluted with methanol (15 ml.). Concentrated hydrochloric acid (2 ml.) was added dropwise. After standing for 1 hr., the solution was evaporated to small bulk, and deposited white crystals of cis-bis(diphenyl-2-oxopropylphosphine)-platinum(II) chloride (35), m.p. 194-196° (Found: C, 47.6; H, 4.1. $C_{30}H_{30}Cl_2O_2P_2Pt$ requires C, 48.0; H, 4.0%). The complex was identified by its 1H n.m.r. (App. 1 - Table 3) and i.r. (App. 2 - Tables 4, 7) spectra.

7. Reactions of Complex (34).

(a) Reaction with Hydrochloric Acid. - The platinum complex (34) (0.2 g., 0.28 mmole) was dissolved in methanol (10 ml.), and concentrated hydrochloric acid (5 ml.) was added dropwise. After the mixture had been standing for 1 hr., the solvent was removed and the residue was washed well with ethanol, benzene then ether and dried, to give cis-bis(diphenyl-2-oxopropylphosphine)platinum(II) chloride (35), m.p. 200-205° (decomp.) (Found: C, 48.4; H, 4.0. $C_{30}H_{30}Cl_2O_2P_2Pt$ requires C, 48.0; H, 4.0%). The complex was identified by its 1H n.m.r. (App. 1 - Table 3) and i.r. (App. 2 - Tables 4, 7) spectra.

(b) Reaction with Deuterium Chloride.- The platinum complex (34) (0.25 g., 0.35 mmole) was dissolved in benzene (3 ml.) and methanol (10 ml.), both solvents deuterated, and deuterium chloride solution (2.5 ml.; 20% in D₂O) was added dropwise. The solution was reduced to small bulk, and the white solid (37) which was precipitated was examined by ¹H n.m.r. (App. 1 - Table 3) and i.r. (App. 2 - Tables 4, 7) spectroscopy. The structure of the product is discussed in the "Results and Discussion" (Section III - 2).

(c) Reaction of Complex (35) with Deuterium Chloride.- The platinum complex (35) (0.05 g., 0.07 mmole) was dissolved in benzene (4 ml.) and chloroform (2 ml.), both solvents being fully deuterated, and deuterium chloride (1 ml.) was added dropwise. The mixture was stirred for 1 hr., and the solvent was partially removed. The precipitate (38) which was formed was filtered off, was washed with methanol and ether, and dried. It was examined by ¹H n.m.r. (App. 1 - Table 3) and i.r. (App. 2 - Tables 4,7) spectroscopy. Its structure is discussed in Part B Section III - 2.

VI Monophosphines - Butenyl.

1. Preparation of Phosphines.

(a) Preparation of 1-Chlorobut-3-ene.- Allyl chloride (172 g., 2.25 mole) in ether (300 ml.) was added to magnesium (60 g., 2.67 mole) in ether (1 l.) over 4 hr. at -15°. The temperature was raised to 0° and more ether (1 l.) was added. Formaldehyde, formed by thermal decomposition of paraformaldehyde (100 g.) at 180-200°, was blown into the reaction mixture with a stream of nitrogen.²¹² The reaction mixture was stirred for 1 hr. at room temperature, then poured into a saturated solution of ammonium chloride in water (600 ml.) and ammonia (20 ml.; \bar{d} 0.880). The

mixture was stirred and was allowed to stand over the weekend.

The resulting white slurry was extracted with ether, and the extracts dried over anhydrous sodium sulphate before distillation.

But-3-en-1-ol (62.7 g., 39% yield) b.p. 114-115° (lit.²¹² b.p. 113°), was obtained.

Thionyl chloride (59.5 g., 0.5 mole) was added dropwise to but-3-en-1-ol (36 g., 0.5 mole) and pyridine (0.4 ml.) at 0°.²¹³ The mixture was heated at 70° for 3 hr. , and was distilled to give 1-chlorobut-3-ene (35 g., 77% yield), b.p. 73-74° (lit.²¹³ b.p. 73-74°).

(b) Preparation of But-3-enyldiphenylphosphine. - 1-Chlorobut-3-ene (9.05 g., 0.1 mole) in ether (5 ml.) was added dropwise during 10 min. to a stirred solution of sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III - 2(a)] at -76°. The mixture became pale yellow. Evaporation of the solvent gave a cream oil which was extracted with water (200 ml.) and ether (100 + 5 x 50 ml.). Distillation of the ether extract gave but-3-enyldiphenylphosphine (21.0 g., 88% yield), b.p. 101-103°/0.15 mm. The ¹H n.m.r. (App. 1 - Table 4) and i.r. (App. 2 - Table 2) spectra were consistent with the proposed structure. The phosphine was characterised as its oxide, m.p. 223-225° (Found C, 75.5; H, 6.5; P, 12.0. C₁₆H₁₇OP requires C, 75.0; H, 6.7; P, 12.1%).

(c) Preparation of But-3-enyldiethylphosphine. - 1-Chlorobut-3-ene (12.7 g., 0.14 mole) in THF (10 ml.) was added to a solution of lithium diethylphosphide (0.14 mole) in THF (250 ml.) [III - 2(b)] at 0°. The solution became almost colourless. The solvent was removed under reduced pressure and the residue extracted with water (200 ml.) and ether (6 x 50 ml.). The ether

extracts were dried over anhydrous sodium sulphate and distilled to give but-3-enyldiphenylphosphine (13.5 g., 67% yield), b.p. 26-27°/0.4-0.5 mm. (lit.¹² b.p. 170-172°). The ¹H n.m.r. (App. 1 - Table 4) and i.r. (App. 2 - Table 2) spectra were consistent with the proposed structure. The phosphine was characterised as its ethiodide, m.p. 191-192° (lit.¹² m.p. 189-191°) (Found: C, 37.6; H, 7.5. C₉H₂₀IP requires C, 37.8; H, 7.1%).

2. Preparation of Palladium(II) Chloride Complexes.

(a) But-3-enyldiphenylphosphine. - The phosphine (1.55 g., 6.45 mmole) was added to a boiling solution of bis(benzonitrile)-palladium(II) chloride (2.48 g., 6.45 mmole) in benzene (100 ml.). A yellow precipitate of 1,2,5-trihapto-but-3-enyldiphenylphosphine-palladium(II) chloride (9), m.p. 210-212° (decomp.) (Found: C, 45.8; H, 4.0. C₁₆H₁₇Cl₂PPd requires C, 46.0; H, 4.1%) was obtained. The structure was confirmed by its i.r. spectrum (App. 2 - Tables 2, 4).

(ii) The phosphine (1.1 g., 4.6 mmole) in benzene (5 ml.) was added dropwise to a stirred solution of sodium chloropalladite (1.7 g., 4.6 mmole) in water (5 ml.) and methanol (45 ml.), to give a yellow solid. Recrystallisation from ethanol-benzene gave a residue of 1,2,5-trihapto-but-3-enyldiphenylphosphinepalladium(II) chloride (9), m.p. 210-212° (decomp.) (Found: C, 46.2; H, 4.2. C₁₆H₁₇Cl₂PPd requires C, 46.0; H, 4.1%), and from the solution trans-bis(but-3-enyldiphenylphosphine)palladium(II) chloride (10), m.p. 150° (Found: C, 57.5; H, 5.1; Cl, 11.1. C₃₂H₃₄Cl₂P₂Pd requires C, 58.5; H, 5.2; Cl, 10.8%). The complex was identified by its i.r. (App. 2 - Tables 2, 4) spectrum.

(b) But-3-enyldiethylphosphine. - The phosphine (1.25 g., 8.7 mmole) was added to a boiling solution of bis(benzonitrile)-palladium(II) chloride (3.33 g., 8.7 mmole) in benzene (100 ml.). The solution was boiled for a further 1 hr., was filtered, and was allowed to cool. Yellow crystals of 1,2,5-trihapto-but-3-enyldiethylphosphinepalladium(II) chloride, m.p. 176-180° (decomp.) (lit.¹² m.p. 168-170°) (Found: C, 29.5; H, 5.7. $C_8H_{17}Cl_2PPd$ requires C, 29.8; H, 5.3%) was obtained. The i.r. spectrum (App. 2 - Tables 2, 4) showed that the $\nu(C:C)$ band in the free ligand was absent in the complex, and a new band appeared at 1503 cm^{-1} .

3. Preparation of Platinum(II) Chloride Complexes.

(a) But-3-enyldiphenylphosphine. - (i) The phosphine (3.2 g., 13.5 mmole) was added to a boiling solution of bis(benzonitrile)-platinum(II) chloride (6.15 g., 13.5 mmole) in benzene (300 ml.). A white precipitate was immediately formed. The mixture was boiled under reflux for 1 hr., was cooled and was filtered. The residue was washed with benzene, ethanol then ether, and dried. Recrystallisation from chloroform-ether gave 1,2,5-trihapto-but-3-enyldiphenylphosphineplatinum(II) chloride (g), m.p. 241-246° (decomp.) (Found: C, 37.1; H, 3.2. $C_{16}H_{17}Cl_2P_2Pt$ requires C, 37.8; H, 3.4%). The complex was identified by its i.r. (App. 2 - Tables 2, 4), 1H n.m.r. (App. 1 - Table 4) and mass (App. 3) spectra.

(ii) The phosphine (1.25 g., 5.2 mmole) in methanol (5 ml.) was added dropwise to a stirred solution of sodium chloroplatinite (2.37 g., 5.2 mmole) in water (5 ml.) and methanol (45 ml.). The mixture was stirred for 1 hr., and the solid which was formed was filtered off. Recrystallisation from ethanol gave a product which had an identical i.r. spectrum to the sample prepared from bis(benzonitrile)platinum(II) chloride.

(b) But-3-enyldiethylphosphine. - The phosphine (1.15 g., 8 mmole) was added to a boiling solution of bis(benzonitrile)-platinum(II) chloride (3.77 g., 8 mmole) in benzene (100 ml.). After boiling under reflux for 1 hr., the solution was cooled and evaporated to small bulk. Yellow crystals of the starting platinum compound were obtained, (identified by its i.r. spectrum).

4. Reactions with Methoxide.

(a) Platinum Complex of But-3-enyldiphenylphosphine. - A suspension of the complex, 1,2,5-trihapto-but-3-enyldiphenylphosphineplatinum(II) chloride (9), (1.0 g., 2 mmole) and sodium hydrogen carbonate (0.16 g., 2 mmole) in methanol (50 ml.) was shaken for 36 hr., and the resulting mixture was filtered. The residue was extracted with benzene and the solution was filtered. Evaporation to small bulk gave an oil which, on treatment with ethanol-benzene, gave white crystals (42), m.p. 166-170° (decomp.) (Found: C, 40.8; H, 3.9. $C_{34}H_{40}Cl_2O_2P_2Pt_2$ requires C, 40.7; H, 4.0%). The complex was examined by i.r. (App. 2 - Table 6) spectroscopy. Possible structures are discussed in Section B III - 3.

(b) Palladium Complex of But-3-enyldiphenylphosphine. - A suspension of the palladium complex (0.8 g., 1.9 mmole) and sodium hydrogen carbonate (0.16 g., 1.9 mmole) in methanol (50 ml.) was shaken. The yellow complex at once began to darken, and after $\frac{1}{2}$ hr. it was completely black. No identifiable complex could be isolated from the reaction mixture.

(c) But-3-enyldiphenylphosphine. - The phosphine (4.15 g., 17 mmole) was added to a suspension of sodium hydrogen carbonate (1.45 g., 17 mmole) in methanol (25 ml.), and the mixture was stirred over the weekend. The solvent was removed and the residue

was worked up with ether and water. The starting material was recovered from the ether extracts, as shown by its i.r. spectrum.

5. Reactions of Complex (42).

(a) Reaction with Hydrochloric Acid.- The complex (42) (0.15 g.) in benzene (5 ml.) and methanol (10 ml.) was treated with concentrated hydrochloric acid (2 ml.). Evaporation of the solution to small bulk gave white crystals of 1,2,5-trihapto-but-3-enyldiphenylphosphine, which was identified by its i.r. spectrum.

(b) Reaction with p-Toluidene.- The amine (0.1 g., 1 mmole) in benzene (3 ml.) was added to a warm solution of complex (42) (0.5 g., 0.5 mmole) in benzene (8 ml.). After standing overnight, the mixture was evaporated to dryness and the residual red oil, on treatment with hot methanol gave a white solid (43), m.p. 230-238° (decomp.) (Found: C, 47.0; H, 4.4; N, 2.5. $C_{24}H_{29}ClNOPPt$ requires C, 47.3; H, 4.8; N, 2.3%). The complex was identified by its i.r. spectrum (App. 2 - Table 6).

VII Diphosphines - Butenyl.

1. Preparation of Phosphines.

(a) Preparation of cis-1,4-Dichlorobut-2-ene²¹⁴ - Thionyl chloride (248 g., 2.08 mole) in chloroform (150 ml.) was added to a mixture of pyridine (0.5 ml.) and but-2-en-1,4-diol (88 g., 1 mole) (85% cis- and 15% trans- by g.l.c.) at 0°. After heating at 70° for 3 hr., the mixture was distilled to give cis-1,4-dichlorobut-2-ene (79.2 g., 75% yield based on cis-diol), b.p. 66°/20 mm. (lit.²¹³ b.p. 55-60°/12 mm.). G.l.c. on a 6 ft. "Carbowax" column showed the absence of the trans-isomer.

(B) Preparation of trans-1,4-Bis(diphenylphosphine)but-

2-ene.- (i) trans-1,4-Dichlorobut-2-ene (31.25 g., 0.25 mole) in THF (100 ml.) was added to a solution of sodium diphenylphosphide (0.5 mole) in THF (1 l.), obtained by preparing the phosphide in liquid ammonia (1.5 l.) [III - 2(a)], allowing the solvent to evaporate, then adding THF. The mixture, which became a pale yellow, was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure and the solid residue washed with water and cold methanol. Recrystallisation under nitrogen from propanol gave white crystals of trans-1,4-bis(diphenylphosphino)but-2-ene (77 g., 79% yield), m.p. 126-128° (Found: C, 79.5; H, 6.2; P, 14.7. $C_{28}H_{26}P_2$ requires C, 79.2; H, 6.2; P, 14.6%). The product was characterised by 1H n.m.r. (App. 1 - Table 5), i.r. (App. 2 - Table 8) and mass (App. 3) spectroscopy. It was further characterised as the dimethiodide, m.p. 266-268° (Found: C, 51.2; H, 4.6; I, 36.6; P, 9.0. $C_{30}H_{32}I_2P_2$ requires C, 50.9; H, 4.5; I, 35.8; P, 8.7%), and the dioxide (1H n.m.r.: App. 1 - Table 6; i.r.: App. 2 - Table 10; mass spectrum: App. 3), m.p. 246-248° (Found: C, 73.1; H, 5.8; P, 13.7. $C_{28}H_{26}O_2P_2$ requires C, 73.7; H, 5.7; P, 13.6%).

(ii) trans-1,4-Dichlorobut-2-ene (6.2 g., 0.05 mole) in ether (15 ml.) was added dropwise during 10 min. to sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III - 2(a)] at -76°. The mixture became colourless. The solvent was allowed to evaporate and the residue was washed with petroleum-ether (b.p. 60-80°), water and methanol. The product (20 g., 95% yield) was shown to be trans-1,4-bis(diphenylphosphino)-but-2-ene by

comparison of its i.r. spectrum with that of the above sample.

The same product was obtained in 95% yield when the above reaction was carried out in refluxing liquid ammonia, and in 92% yield when the dichlorobut-2-ene was added in a large volume (50 ml.) of ether.

(iii) Sodium diphenylphosphide (0.1 mole) was prepared in liquid ammonia (300 ml.) in the usual way, and the ammonia allowed to evaporate. Ether (300 ml.) was added and the mixture was cooled to 0° . trans-1,4-Dichlorobut-2-ene (6.2 g., 0.05 mole) was added dropwise during 10 min. The solvent was removed and the residue was washed with water then methanol. trans-1,4-Bis(diphenylphosphino)but-2-ene (17 g., 80% yield) was identified by its i.r. spectrum.

(iv) trans-1,4-Dichlorobut-2-ene (0.12 g., 1 mmole) was added to sodium diphenylphosphide (2.1 mmole) in liquid ammonia (5 ml.) contained in a flask connected to a vacuum line (App. 4 - Figure 1) and cooled to -196° . The mixture was allowed to warm to -40° and was stirred for 2 hr. Any volatile products and the solvent were condensed into a liquid nitrogen trap. Mass spectroscopy of a sample showed it to contain only ammonia and benzene, the latter being formed during the preparation of the sodium diphenylphosphide.

(v) trans-1,4-Dibromobut-2-ene (8.2 g., 0.038 mole) in ether (25 ml.) was added to sodium diphenylphosphide (0.076 mole) in liquid ammonia (300 ml.) [III - 2(a)] at -76° . The usual work-up gave trans-1,4-bis(diphenylphosphino)but-2-ene (5 g., 31% yield).

(vi) trans-1,4-Dibromobut-2-ene (0.2 g., 1 mmole) in ether (1 ml.) was added to sodium diphenylphosphide (2.1 mmole) in liquid ammonia (5 ml.) contained in a flask connected to a vacuum line and cooled to -196° . The mixture was allowed to warm to -40° and was stirred for 2 hr. The mass spectrum of the volatile products showed the presence of ammonia, ether, and butadiene. The solid residue was suspended in aqueous methanol and was allowed to stand in the air for 3 days. Three pellets of caustic soda were added, and the mixture was filtered. Acidification of the filtrate gave diphenylphosphinic acid (0.15 g., 33% yield), m.p. $190-195^{\circ}$ (lit.²¹¹ m.p. $195-196^{\circ}$).

(c) Attempted Preparation of cis-1,4-Bis(diphenylphosphino)-but-2-ene. - (i) cis-1,4-Dichlorobut-2-ene (6.2 g., 0.05 mole) in ether (20 ml.) was added dropwise during 15 mins. to sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III - 2(a)] at -76° . The solvent was allowed to evaporate to leave a red oil which was extracted with water and benzene. Evaporation of the benzene extracts gave a red oil which would not crystallise. Hydrogen peroxide (11.5 ml.; 100 vol.) in acetone (15 ml.) was added dropwise to a cooled solution of the oil in acetone (200 ml.). The solvent was removed and the residue recrystallised from benzene. As the product was found to contain some peroxide (i.r. spectrum), a benzene solution was extracted with a saturated solution of sodium metabisulphite (4 x 100 ml.). After being dried over anhydrous sodium sulphate, the solvent was removed. Recrystallisation from benzene gave cis-1,4-bis(diphenylphosphino)but-2-ene dioxide (13 g., 28% yield), still containing some peroxide (i.r. - App. 2 - Table 10). (Found: C, 71.7; H, 5.8; P, 14.1. $C_{28}H_{26}O_2P_2 \cdot \frac{1}{4}H_2O_2$ requires C, 72.3; H, 5.7; P, 13.3%). The 1H n.m.r. spectrum of

the dioxide is recorded in App. 1 - Table 6, and the mass spectrum in App. 3.

(ii) The reaction of cis-1,4-dichlorobut-2-ene with sodium diphenylphosphide in THF, using the same quantities of reactants as in (i), also gave a red oil which would not crystallise.

(iii) A solution of trichlorosilane (3.55 g., 0.026 mole) in benzene (15 ml.) was added to a solution of cis-1,4-bis(diphenylphosphino)but-2-ene dioxide (12 g., 0.026 mole) in benzene (500 ml.) and triethylamine (2.65 g., 0.026 mole) during 20 min.⁵³ A white precipitate was formed. After being heated under reflux for 20 hr. , the mixture was cooled to 0° and aqueous caustic soda added (100 ml.; 10%). The benzene layer was removed and was washed with an aqueous solution of sodium chloride (4 x 100 ml.). It was dried over anhydrous sodium sulphate, and was evaporated to dryness. The dioxide (9 g.) was recovered.

(d) Preparation of trans-1,4-Bis(diethylphosphino)but-2-ene.- Tetraethyldiphosphine (18 g., 0.1 mole) was added to a suspension of lithium flakes (2.6 g., 0.4 mole) in THF (150 ml.). The mixture was boiled for 20 hr. , was filtered, and was cooled to -60°. trans-1,4-Dichlorobut-2-ene (12.5 g., 0.1 mole) in THF (10 ml.) was added dropwise. The yellow solution turned brown. The usual work up gave trans-1,4-bis(diphenylphosphino) but-2-ene (7 g., 30% yield), b.p. 88-90°/0.2 mm. The phosphine was identified by its i.r. (App. 2 - Table 11) spectrum, and was further characterised as the diethiodide, m.p. 193-196° (decomp.) (Found: C, 35.5; H, 6.8; I, 46.9; P, 11.7. $C_{16}H_{36}I_2P_2$ requires C, 35.3; H, 6.7; I, 46.6; P, 11.4%).

(e) Preparation of trans-1,4-bis(dimethylphosphino)but-2-ene. -

trans-1,4-Dichlorobut-2-ene (10.6 g., 0.085 mole) in THF (10 ml.) was added to a solution of lithium dimethylphosphide (0.17 mole) in THF (250 ml.), prepared as described in III - 2(b), except biphenyl was used as catalyst instead of naphthalene. The blue solution turned orange then the colour progressively faded, but never disappeared. The usual work-up gave trans-1,4-bis(dimethylphosphino)but-2-ene (8.3 g., 55% yield), b.p. $81-84^{\circ}/8-9$ mm. The product was identified by its ^1H n.m.r. (App. 1 - Table 5) and i.r. (App. 2 - Table 12) spectra. It was further characterised as its dimethiodide, m.p. $271-274^{\circ}$ (decomp.) (Found: C, 25.6; H, 5.4. $\text{C}_{10}\text{H}_{24}\text{I}_2\text{P}_2$ requires C, 26.1; H, 5.2%).

(f) Preparation of cis-1,4-bis(dimethylphosphino)but-2-ene.-

(i) cis-1,4-Dichlorobut-2-ene (12.1 g., 0.09 mole) in THF (10 ml.) was added dropwise to a solution of lithium dimethylphosphide (0.18 mole) in THF (200 ml.) [III - 2(b)] at -40° . The solution became pale yellow. Pentane (100 ml.) was added and the mixture was filtered. Distillation of the filtrate gave 1,4-bis(dimethylphosphino)but-2-ene (6.65 g., 38%), b.p. $55-57^{\circ}/2$ mm. The ^1H n.m.r. spectrum (App. 1 - Table 5) of the product showed it to be a mixture of the cis- and trans- isomers in the ratio 66:33.

(ii) i-Propyl bromide (1.11 g., 0.009 mole) was added to a solution of lithium dimethylphosphide (0.22 mole) in THF (200 ml.) [III - 2 (b)] containing lithium naphthalenide (0.009 mole). The mixture was cooled to -40° and cis-1,4-dichlorobut-2-ene (13.75 g., 0.11 mole) was added dropwise. The mixture immediately became orange, then progressively turned a pale yellow. The solvent was removed and the residue was worked-up in the usual way with ether

and water. Distillation of the ethereal extracts gave 1,4-Bis(dimethylphosphino)but-2-ene (8.55 g., 48.5% yield), b.p. $52^{\circ}/1$ mm. The ^1H n.m.r. spectrum of the product showed it to be a mixture of cis- and trans- isomers in the ratio 85:15.

(g) Reaction of Tetramethyldiphosphine and Butadiene. -

(i) Tetramethyldiphosphine (3.37 g., 27.6 mmole) was purified by trap-to-trap distillation using a vacuum line (App. 4 - Figure 1), and transferred to a stainless steel bomb. Butadiene (27.9 mmole) was condensed into the bomb which was then sealed. It was heated for 6 hr. at 100° and opened on to the line; butadiene (22.4 mmole) was recovered. This was distilled back into the bomb which was reheated for 4 hr. at 105° , then 3 hr. at $120-140^{\circ}$. After being cooled to -76° , the bomb was reopened on to the line and was allowed to warm to -43° . Butadiene (14.9 mmole, 53% of the reactant) was recovered. The bomb was allowed to warm to room temperature and unreacted tetramethyldiphosphine (1.77 g., 14.5 mmole, 52%) was collected. The bomb was heated to ca. 50° and the slightly volatile 1,4-bis(dimethylphosphino)but-2-ene [identified by its mass spectrum (App. 3)] was pumped in to the line. The ^1H n.m.r. spectrum (App. 1 - Table 5) showed a cis:trans ratio of 30:70. The product was further characterised as the mixed methiodides, m.p. $257-265^{\circ}$ (decomp.) (Found: C, 25.9; H, 5.3; I, 54.7; P, 13.3. $\text{C}_{10}\text{H}_{24}\text{I}_2\text{P}_2$ requires C, 26.1; H, 5.25; I, 55.1; P, 13.5%.

(ii) Azobis(isobutyronitrile) (0.25 g., 1.4 mmole) in acetone (5 ml.) was put in a stainless steel bomb, and the solvent was removed under vacuum. Tetramethyldiphosphine (1.77 g., 14.5 mmole) and butadiene (15.5 mmole) were added via a vacuum line and the bomb was sealed. After being heated for 6 hr. at 100° the bomb was

opened on to the line; butadiene (5.9 mmole) was recovered. The product (1.25 g., 7.1 mmole, 74% based on butadiene used) was identified by its ^1H n.m.r. spectrum to be a mixture of cis- and trans-1,4-Bis(dimethylphosphino)but-2-ene in the ratio 25:75.

It was further characterised as its mixed methiodide, m.p. $259-269^\circ$ (decomp.) (Found: C, 25.7; H, 5.5. $\text{C}_{10}\text{H}_{24}\text{I}_2\text{P}_2$ requires C, 26.1; H, 5.25%).

(h) Attempted Isomerisation of cis-1,4-Bis(dimethylphosphino)-

But-2-ene. - (i) A mixture of cis- and trans-1,4-bis(dimethylphosphino)but-2-ene (2.85 g., 16 mmole) in the ratio 85:15 [VII - 1(f)(ii)] was added to a suspension of sodamide (16 mmole) in liquid ammonia (30 ml.) at -76° . The mixture was stirred for $1\frac{1}{2}$ hrs. before ammonium chloride (0.85 g., 16 mmole) was added. The solvent was allowed to evaporate and the residue extracted with ether and water. The ether extracts were evaporated to leave an oil which was shown by ^1H n.m.r. spectroscopy to be a mixture of the starting phosphines in the ratio 80:20.

(ii) A 67:33 mixture [VII - 1(f)(i)] of cis- and trans-1,4-bis(dimethylphosphino)but-2-ene was condensed into an n.m.r. tube and was heated for 1 hr. at $100-110^\circ$. The ratio was shown to be 70:30. The mixture was heated for a further 1 hr. at $140-150^\circ$. Again the ratio was found to be 70:30. The tube was opened and a small amount of A.B.N. was added before heating for 1 hr. at $120-130^\circ$. The ratio changed slightly to 65:35.

(j) Reaction of Tetramethyldiphosphine with Cyclopentadiene. -

Tetramethyldiphosphine (2.01 g., 16.5 mmole) and cyclopentadiene (1.09 g., 16.5 mmole) were condensed into a glass flask which was fitted with a break-seal. The flask was sealed, heated at 110°

for 4 hr. , cooled and was opened on to the vacuum line.

Cyclopentadiene (0.09 g., 1.43 mmole) was recovered, together with a less volatile fraction (2.88 g.) of tetramethyldiphosphine and dicyclopentadiene. These reactants were condensed into a stainless steel bomb and were heated for 2 hr. at 145-180°. On reopening on to the line, cyclopentadiene (0.29 g., 4.04 mmole), tetramethyl-diphosphine and dicyclopentadiene, and a trace of an intractable product were obtained.

2. Preparation of Nickel(II) Complexes.

(a) trans-1,4-Bis(diphenylphosphino)but-2-ene and Nickel (II) Chloride. - (i) Nickel(II) chloride (1.18 g., 5 mmole) in ethanol (10 ml.) was added to a boiling solution of trans-1,4-bis-(diphenylphosphino)but-2-ene (2.13 g., 5 mmole) in ethanol (250 ml.). A little solid was formed, but this dissolved and a purple solid was precipitated. This was washed with ethanol, then benzene, and was dried to give a complex m.p. 206-210° (decomp.) (Found: C, 60.9; H, 4.7; Cl, 12.8. $C_{28}H_{26}Cl_2NiP_2$ requires C, 60.7; H, 4.7; Cl 12.8%). The complex, which was examined by i.r. spectroscopy (App. 2 - Tables 8, 9), did not readily dissolve in common organic solvents, but extraction with benzene or chloroform gave a deep red solution from which could be obtained the complex described in (ii) (i.r. evidence).

(ii) Nickel(II) chloride (0.59 g., 2.5 mmole) in ethanol (10 ml.) was added to trans-1,4-bis(diphenylphosphino)but-2-ene (1.06 g., 2.5 mmole) in benzene (100 ml.) at room temperature. The dark red solution which was formed was reduced to small bulk giving a red solid (1 g.), m.p. 146-149° (decomp.) (Found: C, 66.9; H, 5.3; Cl, 10.6. $C_{28}H_{26}Cl_2NiP_2 \cdot 2C_6H_6$ requires C, 66.85; H, 5.3; Cl, 9.9%). The complex was examined by i.r. spectroscopy (App. 2 - Tables 8,9).

(b) trans-1,4-Bis(diphenylphosphino)but-2-ene and Nickel(II)

Bromide. - (i) Nickel(II) bromide (2.73 g., 10 mmole) in ethanol (30 ml.) was added to a boiling solution of trans-1,4-bis(diphenylphosphino)but-2-ene (4.25 g., 10 mmole) in ethanol (500 ml.). A little solid was formed. This dissolved to give a brown solution from which a green solid was precipitated. The solid was washed with ethanol, chloroform and ether, and dried to give green crystals, m.p. 196-199° (Found: C, 52.8; H, 4.3; Br, 25.2. $C_{28}H_{26}Br_2NiP_2$ requires C, 52.3; H, 4.1; Br, 24.9%). The complex (i.r.: App. 2 - Tables 8, 9) was insoluble in common organic solvents. Extraction with chloroform for several hours gave a brown solution from which the same green complex was obtained by evaporation.

(ii) Nickel(II) bromide (0.68 g., 2.5 mmole) in ethanol (10 ml.) was added to a solution of trans-1,4-bis(diphenylphosphino)but-2-ene (1.06 g., 2.5 mmole) in benzene (100 ml.) at room temperature. The brown solution which was formed deposited on standing a green solid which was shown by comparison of its i.r. spectrum to be identical to the above complex.

(c) trans-1,4-Bis(diethylphosphino)but-2-ene and Nickel(II)

Chloride. - Nickel(II) chloride (1.55 g., 6.5 mmole) in ethanol (5 ml.) was added to trans-1,4-bis(diethylphosphino)but-2-ene (1.5 g., 6.5 mmole) in ethanol (10 ml.). The resulting dark red solution precipitated a pink solid. Recrystallisation by dissolving in chloroform and precipitating with ethanol gave a pink complex, m.p. 214-216° (decomp.) (Found: C, 40.8; H, 7.8; Cl, 19.5. $C_{12}H_{26}Cl_2NiP_2$ requires C, 39.8; H, 7.2; Cl, 19.6%). The i.r. spectrum of the complex is recorded in App. 2 - Table 11.

3. Preparation of Palladium(II) Chloride Complexes.

(a) trans-1,4-Bis(diphenylphosphino)but-2-ene. - The phosphine (2.32 g., 5.5 mmole) in benzene (100 ml.) was added to a boiling solution of bis(benzonitrile)palladium(II) chloride (2.12 g., 5.5 mmole) in benzene (200 ml.). After boiling for a further 1 hr., the solution was filtered, cooled, and evaporated, to small bulk. Yellow crystals (A), m.p. 242-245° (Found: C, 55.2; H, 4.7. $C_{28}H_{26}Cl_2P_2Pd$ requires C, 55.9; H, 4.3%) were obtained (i.r.: App. 2 - Tables 8, 9). These dissolved in benzene, from which the complex could be recovered, and chloroform. Precipitation from chloroform with ether gave the same complex, but on cooling a hot chloroform solution a complex with a different i.r. spectrum (App. 2 - Tables 8, 9) was obtained (B), m.p. 262-265° (decomp.) (Found: C, 55.9; H, 4.3. $C_{28}H_{26}Cl_2P_2Pd$ requires C, 55.9; H, 4.3%). A third isomer (C), m.p. 255-260° (decomp.) (Found: C, 55.6; H, 4.4; Cl, 12.4. $C_{28}H_{26}Cl_2P_2Pd$ requires C, 55.9; H, 4.3; Cl, 11.8%) was obtained from the chloroform solution on prolonged standing (i.r.: App. 2 - Tables 8, 9).

(b) trans-1,4-Bis(diethylphosphino)but-2-ene. - The phosphine (0.65 g., 2.8 mmole) in benzene (5 ml.) was added to a boiling solution of bis(benzonitrile) palladium(II) chloride (1.07 g., 2.8 mmole) in benzene (100 ml.). An orange precipitate was formed immediately, and redissolved to give a yellow solution. Evaporation to small bulk, followed by the addition of ether gave a yellow solid, which was recrystallised from chloroform by addition of ether. M.p. 212-216° (Found: C, 36.0; H, 6.8. $C_{12}H_{26}Cl_2P_2Pd$ requires C, 35.2; H, 6.4%). The i.r. spectrum of the complex is recorded in App.2-Table 11.

4. Preparation of Platinum(II) Chloride Complexes.

(a) trans-1,4-Bis(diphenylphosphino)but-2-ene. - The phosphine (1.06 g., 2.5 mmole) in benzene (100 ml.) was added to bis-(benzonitrile)platinum(II) chloride (1.18 g., 2.5 mmole) in benzene (100 ml.). A white solid was precipitated. Treatment of this solid with chloroform gave a white residue (D) (m.p. 299-303°, i.r.: App. 2 - Tables 8, 9) and a solution which deposited an oil. Treatment of the oil with ether gave a white solid (E), m.p. 219-222°, i.r.: App. 2 - Tables 8, 9. The mother liquor from the reaction was evaporated to dryness and the residue treated with ether. Recrystallisation from acetone gave a white residue, the i.r. spectrum of which was identical to that of the first complex, and a solution from which was precipitated a white compound, m.p. 216-225° (Found: C, 49.1; H, 3.9; Cl, 9.6. $C_{28}H_{26}Cl_2P_2Pt$ requires C, 48.7; H, 3.8; Cl, 10.3%), which had an identical i.r. spectrum to that of the second complex.

(b) trans-1,4-Bis(dimethylphosphino)but-2-ene. - The phosphine (1.25 g., 7.1 mmole) was added to a boiling solution of bis(benzonitrile)platinum(II) chloride (3.36 g., 7.1 mmole) in benzene (250 ml.). The precipitate, which was formed immediately, was washed well with benzene, ethanol, then ether, and was dried as a white powder, m.p. 173-178° (Found: C, 22.1; H, 4.5. $C_8H_{18}Cl_2P_2Pt$ requires C, 21.8; H, 4.1%). The i.r. spectrum of the complex is recorded in App. 2 - Table 13.

(c) cis- and trans-1,4-Bis(dimethylphosphino)but-2-ene. -

The mixture of phosphines (1.25 g., 7.1 mmole) from reaction VII - 1(g)(ii) was added to bis(benzonitrile)platinum(II) chloride (3.36 g., 7.1 mmole) in boiling benzene (300 ml.). Soxhlet extraction with chloroform of the white solid which was formed gave pure samples of the complexes from both cis- and trans- phosphines from the solution (using ether to precipitate the solid from the partially evaporates solution) and as the residue respectively. The complexes were identified by their i.r. spectra which are recorded in App. 2 - Table 13. cis- Phosphine complex: m.p. 319-324° (decomp.) (Found: C, 21.2; H, 4.0. $C_8H_{18}Cl_2P_2Pt$ requires C, 21.7; H, 4.1%). trans- Phosphine complex: m.p. 279-282° (decomp.) (Found: C, 22.1; H, 4.5. $C_8H_{18}Cl_2P_2Pt$ C, 21.7; H, 4.1%). Although the near i.r. spectra of the trans- isomer is identical to that from (b) above, the far i.r. has extra weak bands, and the m.p. is higher. These differences are probably due to variations in the polymer size.

VIII Diphosphines - Acetylenic

1. Preparation of Phosphines

(a) Preparation of 1,6-Dichlorohex-3-yne. - (i) Ethylene oxide (55 g., 1.25 mole) was added to a stirred solution of sodium acetylide²¹⁵ (1 mole) in liquid ammonia (1 l.) at -40°. The mixture stirred overnight at -76°, then for 7 hr. at -40°, before ammonium chloride (53.5 g., 1 mole) was added. After the solvent had evaporated, the residue was extracted with water (500 ml.) and ether (300 + 5 x 100 ml.). The combined ether extracts were dried over anhydrous sodium sulphate and distilled to give but-3-yn-1-ol (17.1 g., 25% yield), b.p. 124-128° (lit.²¹³ b.p. 128-130°).

(ii) Concentrated hydrochloric acid (1.0 g.) was added to a stirred mixture of but-3-yn-1-ol (70 g., 1 mole) and dihydropyran (84 g., 1 mole) at 0°. The mixture was stirred for 22 hr. at room temperature, then distilled to give 4-(tetrahydro-2-pyranyloxy)but-1-yne²¹⁶ (117.6 g., 76.5% yield), b.p. 83-88°/13-14 mm. (lit.²¹⁶ b.p. 92-95°/18 mm.).

(iii) 4-(Tetrahydro-2-pyranyloxy)but-1-yne (105 g., 0.68 mole) in dry ether (50 ml.) was added dropwise to a suspension of lithamide (0.76 mole) in liquid ammonia (1 l.) at -76°. ¹⁶⁷ The mixture was stirred overnight and ethylene oxide (89 g., 2 mole) was added, all at once. The ammonia solvent was allowed to boil under reflux for 9 hr. , after which the mixture was decomposed by the addition of ammonia solution (24 ml.; d 0.88). The solvent was allowed to evaporate, and the residue was extracted with water (350 ml.) and ether (500 + 3 x 250 ml.). The ether extracts were washed with brine (250 ml.), were dried over anhydrous sodium sulphate, and were distilled to give 6-(tetrahydro-2-pyranyloxy)hex-3-yn-1-ol (119 g., 88% yield), b.p. 95-105°/0.1 mm. (lit.¹⁶⁷ b.p. 116°/0.4 mm.).

(iv) A mixture of 6-(tetrahydro-2-pyranyloxy)hex-3-yn-1-ol (47.5 g., 0.24 mole) and concentrated hydrochloric acid (40 ml.) in methanol (800 ml.) was stirred over a weekend. After neutralisation (p.H. paper) with aqueous methanolic caustic soda, the solution was evaporated to dryness. The white solid residue was extracted with boiling benzene (100 ml. portions) until an extract which did not precipitate solid on cooling was obtained. Evaporation of the benzene extracts to low bulk gave white crystals of hex-3-yn-1,6-diol (23.7 g., 87% yield), m.p. 82-83° (lit.¹⁶⁷ m.p. 80-80.5°).

(v) Thionyl chloride (7.75 g., 0.065 mole) in chloroform (25 ml.) was added dropwise to a stirred solution of hex-3-yn-1,6-diol (3.42 g., 0.03 mole) in chloroform (75 ml.) to which pyridine (0.1 ml.) had been added, at 0°. The mixture was stirred overnight at room temperature, boiled under reflux for 1 hr., then distilled. 1,6-Dichlorohex-3-yne (3.3 g., 73% yield); b.p. 42°/3 mm., was obtained. (Found: C, 47.4; H, 5.2; Cl, 46.9. $C_6H_8Cl_2$ requires C, 47.7; H, 5.3; Cl, 46.9%).

(b) Preparation of 1,6-Bis(diphenylphosphino)hex-3-yne. - 1,6-Dichlorohex-3-yne (3 g. 0.02 mole) in ether (5 ml.) was added to sodium diphenylphosphide (0.04 mole) in liquid ammonia (200 ml.) [III - 2(a)] at -76°. The solvent was allowed to evaporate, and the residue was washed with water. Recrystallisation from methanol gave 1,6-bis(diphenylphosphino)hex-3-yne (1.1 g., 12% yield), m.p. 84-87°. The 1H n.m.r. (App. 1 - Table 7), i.r. (App. 2 - Table 14), and mass (App. 3) spectra are consistent with this structure. The phosphine was characterised as its dimethiodide, m.p. 222-224° (Found: C, 52.3; H, 4.8; I, 33.7; P, 8.9. $C_{32}H_{34}I_2P_2$ requires C, 52.3; H, 4.7; I, 34.5; P, 8.5%).

(c) Attempted Preparation of 1,4-Bis(diphenylphosphino)

but-2-yne. - (i) 1,4-Dichlorobut-2-yne (6.15 g., 0.05 mole)

in ether (5 ml.) was added dropwise to sodium diphenylphosphide (0.1 mole) in liquid ammonia (300 ml.) [III - 2(a)] at -76°. Evaporation of the solvent, followed by treatment of the residue with water, gave a brown solid. This could not be recrystallised, nor could the colour be removed by washing.

(ii) 1,4-Dichlorobut-2-yne (6.15 g., 0.05 mole) in THF (20 ml.) was added dropwise to a solution of sodium diphenylphosphide

(0.1 mole) in THF (150 ml.), prepared from sodium (2.3 g., 0.1 mole) and diphenylphosphine (18.6 g., 0.1 mole), at -76° . The solvent was removed from the resulting brown solution, to yield a brown oil which would not crystallise. Hydrogen peroxide (11 ml.; 100 vol.) was added to an acetone solution of the oil. The reaction mixture was stirred overnight, and the resulting white solid was recrystallised from benzene-ethanol to give white crystals of 1,4-bis(diphenylphosphino)but-2-yne dioxide (5.8 g., 26% yield), m.p. $216-219^{\circ}$ (Found: C, 75.5; H, 5.5; P, 13.9. $C_{28}H_{24}O_2P_2$ requires C, 74.0; H, 5.3; P, 13.6%). The dioxide was identified by its 1H n.m.r. (App. 1 - Table 6), i.r. (App. 2 - Table 14) and mass (App. 3) spectra.

(iii) Trichlorosilane (3.4 g., 25 mmole) in benzene (10 ml.) was added to 1,4-bis(diphenylphosphino)but-2-yne dioxide (5.8 g., 12.5 mmole) in benzene (100 ml.) and chloroform (70 ml.).⁵³ The mixture was boiled under reflux for 2 hr. , and the solvent was reduced to half volume before aqueous caustic soda (20 ml.; 40%) was added. After separation, the ether layer was dried over anhydrous sodium sulphate and was evaporated to dryness. The residual yellow solid was washed with petroleum-ether (b.p. $60-80^{\circ}$), and was shown by its i.r. spectrum to be the starting dioxide.

IX Diphosphines - Saturated.

1. Preparation of Bis(dimethylphosphino)methane.

Dichloromethane (11.1 g., 0.134 mole) in dry THF (10 ml.) was added to a solution of lithium dimethylphosphide (0.268 mole) in THF (250 ml.) [III - 2(b)] at -40° . The colour was not completely discharged. The solvent was removed by distillation at atmospheric pressure, and the residue worked up in the usual way with ether and water. Distillation gave (a) tetramethyldiphosphine (4.5 g.,

28% yield), b.p. 45-50°/20 mm. (lit.³⁷ b.p. 138°), (b) a fraction b.p. 91-100°/20 mm. (2.15 g.) which may be the required product from its i.r. (App. 2 - Table 15) and ¹H n.m.r. (App. 1 - Table 8) spectra. More tetramethyldiphosphine was recovered from the distilled solvent as the methiodide (6.1 g., 18% yield), m.p. 124-128° (lit. m.p.³⁷ 128-130°) (Found: C, 22.2; H, 5.9. $C_5H_{15}IP_2$ requires C, 22.7; H, 5.7%).

2. Preparation of 1,2-Bis(dimethylphosphino)ethane.

1,2-Dichloroethane (20.1 g., 0.203 mole) in THF (20 ml.) was added dropwise to lithium dimethylphosphide (0.406 mole) in THF (250 ml.) [III - 2(b)] at -40°. The colour changed rapidly from green to orange, then turned slowly colourless as the chloride solution was added. The solvent was removed at atmospheric pressure, and the usual work-up of the residue gave 1,2-bis(dimethylphosphino)-ethane (17.1 g., 56% yield), b.p. 75-79°/22 mm. The product was identified by its ¹H n.m.r. (App. 1 - Table 8) and i.r. (App. 2 - Table 15) spectra, and was further characterised as its dimethiodide, m.p. 274° (decomp.) (Found: C, 21.9; H, 5.7. $C_8H_{22}I_2P_2$ requires C, 22.1; H, 5.1%).

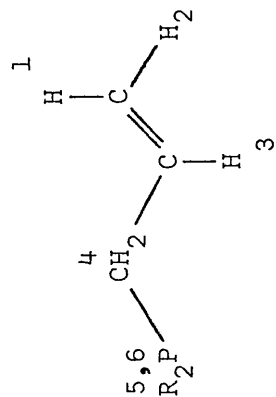
PART D - APPENDICES

Appendix 1

¹H n.m.r. Spectra

The ¹H n.m.r. spectra of compounds prepared in the course of this work are recorded in the following Tables. The spectra were measured in the solvent given at the head of each table, with tetramethylsilane as internal standard. The chemical shifts are given as τ -values, and the coupling constants in Hz. Unless stated otherwise, the protons are numbered according to the number of the carbon atom to which they are bonded from phosphorus.

Table 1 ¹H n.m.r. Spectra of Allyl Phosphines and Complexes in CDCl₃.



	Chemical Shifts						Coupling Constants					
	H-1	H-2	H-3	H-4	H-5	H-6	J _{1,3}	J _{2,3}	J _{3,4}	J _{P,3}	J _{5,6}	J _{P,6}
⁵ _R = -CH ₂ -CH ₃ ^a ligand	5.12	5.10	4.32	7.92	8.75	9.03	16.75	10.5	7.75	4.25	14.5	7.0
⁵ _R = -C ₆ H ₅ ligand	5.10	5.04	4.28	7.17	2.25-2.78	-	17.5	10.0	7.5	6.0	-	-
PdCl ₂ complex (<u>trans</u>)	5.20	5.12	4.18	6.67	2.3-2.75	-	17.5	10.0	-	-	-	-
PtCl ₂ complex (<u>cis</u>)	5.23	4.95	4.12	6.75	2.55-2.95	-	17.5	12.0	-	-	-	-

^aSpectrum in C₆D₆

Table 2

¹H n.m.r. Spectra of Acetylenic and Allenic Phosphines

in C₆D₆

	Ph	H-1	H-2'	H-3	Coupling Constants
Ph ₂ P.CH ₂ .C≡CH (6a)	2.4-2.8	7.28	-	8.16	J _{P,1} 1.7; J _{P,3} 4.2; J _{1,3} 2.8
Ph ₂ P.CH=C=CH ₂ (7a)	a	4.42	-	5.65	J _{P,1} 9.0; J _{P,3} 3.2; J _{1,3} 6.7
Ph ₂ P.C≡C.CH ₃ (8a)	2.1-3.0	-	-	8.45	J _{P,3} 1.8
$\begin{array}{c} \text{CH}_3 \\ \\ \text{Ph}_2\text{P} \cdot \text{CH} \cdot \text{C} \equiv \text{CH} \end{array}$ (6b)	2.3-2.95	6.92	8.78	8.05	J _{P,1} 1.5; J _{P,2} 14.2; J _{P,3} 2.6; J _{1,2} 7.5; J _{1,3} 2.6
$\begin{array}{c} \text{CH}_2 \\ \\ \text{Ph}_2\text{P} \cdot \text{C} = \text{C} = \text{CH}_2^b \end{array}$ (7b)	a	-	8.26	5.73	J _{P,2} 9.0; J _{P,3} 1.7; J _{2,3} 3.0
Ph ₂ P.CH ₂ .C≡C.CH ₃ (6c)	2.25-3.0	7.21	-	8.55 ^c	J _{P,1} 1.3; J _{P,4} 3.7; J _{1,4} 2.8

^aNot measurable as spectrum that of a mixture

^bCCl₄ solvent

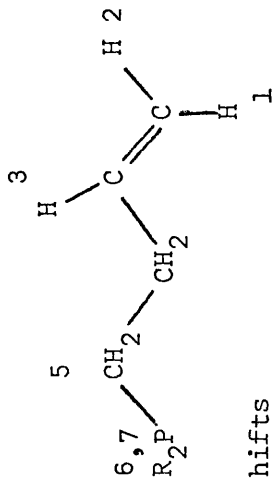
^cH-4

Table 3

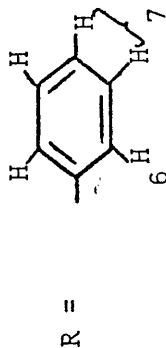
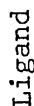
¹H n.m.r. Spectra of Platinum(II) Chloride Complexes of Ketonic Phosphines

Ph	<u>in CDCl₃.</u>		<u>Coupling Constants</u>	
	<u>Chemical Shifts</u>	<u>H-1</u>	<u>H-3</u>	<u>J_{P,1}</u>
$\begin{array}{c} \text{O} \\ \\ (\text{Ph}_2\text{PCH}_2\text{CCH}_3)_2\text{PtCl}_2 \end{array}$	2.40-2.93(10H)	6.22(2H)	7.72(3H)	10.5
$\begin{array}{c} \text{O} \\ \\ (\text{Ph}_2\text{PCD}_2\text{CCH}_3)_2\text{PtCl}_2 \end{array}$	2.30-2.90(10H)	-	7.76(3H)	-
$\begin{array}{c} \text{O} \\ \\ (\text{Ph}_2\text{PCD}_2\text{CCDH}_2)_2\text{PtCl}_2 \end{array}$	2.40-2.95(10H)	-	7.76(1H)	-

^1H n.m.r. Spectra of But-3-enyl-Phosphines and Complexes in C_6D_6



	6	7	H-1	H-2	H-3	H-4	H-5	H-6	H-7	J _{1,3}	J _{2,3}	J _{3,4}	J _{6,7}	J _{P,7}
R = CH ₂ -CH ₃			5.02	5.09	4.21	7.91	8.66	8.73	9.02	16.5	10	6.5	7	13.5



Ligand

PtCl ₂ complex	5.26	5.20	4.45	7.66	2.45 - 3.26
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Table 5

¹H n.m.r. of But-2-enyl-Diphosphines and Complexes in CDCl₃

	R	H-1	H-2
Ph ₂ P <chem>CCCC</chem> PPh ₃			
Ligand	2.60-2.79	7.25	4.60
PdCl ₂ complex (A)	2.16-2.80	6.72	4.10
PtCl ₂ complex (E)	2.46-3.0	6.85	4.60
Et ₂ P <chem>CCCC</chem> PEt ₂			
PdCl ₂ complex	8.18, 8.79	7.28	4.42
PtCl ₂ complex	8.08, 8.76	7.23	4.38
Me ₂ P <chem>CCCC</chem> PMe ₂			
Ligand	9.18	8.03	4.72
PtCl ₂ complex		Insoluble	
Me ₂ P <chem>CCC=C</chem> PMe ₂			
Ligand	9.16	7.98	4.57
PtCl ₂ complex		Insoluble	

Table 6

¹H n.m.r. Spectra of Diphosphine Dioxides in CDCl₃

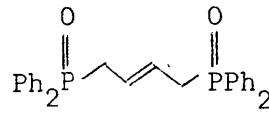
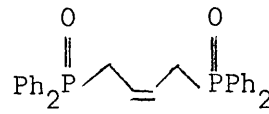
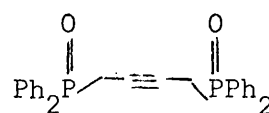
	Ph	H-1	H-2	<u>Coupling Constants</u>
	2.32-2.54	6.95	4.40	J _{P,1} 9.5
	2.29-2.08	6.95	4.43	J _{P,1} 10
	2.31-2.61	6.85	-	J _{P,1} 11

Table 7

¹H n.m.r. Spectrum of Acetylenic Diphosphines in C₆D₆

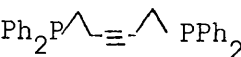

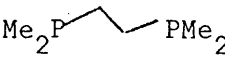
	R	H-1	H-2
	2.65-3.08	7.67-7.87	

Table 8

¹H n.m.r. Spectra of Saturated Diphosphines

	R	H-1
	8.98	8.55
	9.08	8.64

Appendix 2

Infrared and Raman Spectra

Details of the i.r. and Raman spectra of compounds prepared in this project are given in the Tables which follow. Where a detailed comparison is necessary full descriptions of the spectra are recorded, otherwise only the vibrations assigned to functional groups are given. The samples were examined in KBr discs or as neat liquids, and the data is given in cm^{-1} .

Table 1














Strong Absorptions in the I.r. Spectra of Bis(benzonitrile)metal(II)

Chlorides

<u>$(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$</u>	<u>$(\text{C}_6\text{H}_5\text{CN})_2\text{PtCl}_2$</u>
2230	2288
1600	1595
1490	1488
1448	1448
758	765
687	687

Table 2

$\nu(\text{C}=\text{C})$ Vibration in Olefin Monophosphines and Complexes

 PPh_2	1632 w
 PEt_2	1640 w
 PPh_2	1639 w
 PEt_2	1642 w
<u>cis</u> -( PPh_2) $_2\text{PtCl}_2$	1630 w
<u>trans</u> -( PPh_2) $_2\text{PtCl}_2$	1640 w
<u>trans</u> -( PPh_2) $_2\text{PdCl}_2$	1640 w
<u>cis</u> -( PEt_2) $_2\text{PtCl}_2$	1630 w
<u>trans</u> -( PEt_2) $_2\text{PdCl}_2$	1630 w
( PPh_2) PtCl_2 (9)	1503 w*
( PPh_2) PdCl_2 (9)	1525 w*
( PPh_2) $_2\text{PdCl}_2$ (10)	1640 w
( PEt_2) PdCl_2	1530 w*

*Tentative assignment - see refs. 1, 144.

Table 3

Acetylenic Vibrations in Monophosphines and Complexes

		<u>$\nu(\text{C}\equiv\text{C})$</u>	<u>$\nu(\text{C}\equiv\text{C}-\text{H})$</u>
$\text{---}\equiv\text{---PPh}_2$	(8a)	2183 s	-
$\equiv\text{---}\text{PPh}_2$	(6a)	2115 w	3290 m
$\equiv\text{---}\text{PPh}_2$	(6b)	2083 w	3247 m
$\text{---}\equiv\text{---}\text{PPh}_2$	(6c)	2273 w	-
<u>cis</u> -($\text{---}\equiv\text{---PPh}_2$) ₂ PtCl ₂	(14a)	2190 s	-
<u>cis</u> -($\text{---}\equiv\text{---PPh}_2$) ₂ PdCl ₂	(14b)	2203 s	-
($\text{---}\equiv\text{---PPh}_2$)HgCl ₂		2200 s	-
<u>cis</u> -($\equiv\text{---}\text{PPh}_2$) ₂ PtCl ₂	(13a)	2105 w	3226 w
<u>cis</u> -($\equiv\text{---}\text{PPh}_2$) ₂ PdCl ₂	(13a)	2205 w	3200 w
<u>cis</u> -($\equiv\text{---}\text{PPh}_2$) ₂ PtCl ₂	(13b)	2110 w	3280 w
<u>trans</u> -($\equiv\text{---}\text{PPh}_2$) ₂ PdCl ₂	(13b)	2110 w	3270 w
<u>cis</u> -($\text{---}\equiv\text{---}\text{PPh}_2$) ₂ PtCl ₂	(13c)	2092 w	-
<u>trans</u> -($\text{---}\equiv\text{---}\text{PPh}_2$) ₂ PdCl ₂	(13c)	2105 w	-

Table 4

Infrared Active Metal-Halogen Stretching Frequencies of Monophosphino Complexes

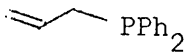
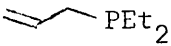
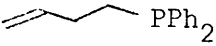
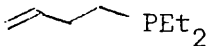
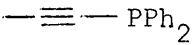
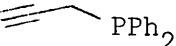
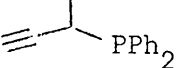
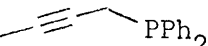
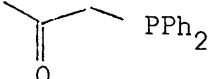
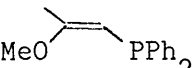
<u>Phosphine</u>	<u>Complex</u>	<u>Pt-Cl</u>	<u>Pd-Cl</u>
 <chem>CH2=CH-CH2-PPh2</chem>	<u>cis</u>	314, 291	-
	<u>trans</u>	355	352
 <chem>CH2=CH-CH2-PEt2</chem>	<u>cis</u>	304, 284	-
	<u>trans</u>	-	352
 <chem>CH2=CH-CH=CH-PPh2</chem>	1:1, <u>cis</u> (9)	329, 298	325, 298
	2:1, <u>trans</u> (10)	-	351
 <chem>CH2=CH-CH2-CH=CH-PEt2</chem>	<u>cis</u>	-	315, 289
 <chem>HC#C-PPh2</chem>	<u>cis</u> (14)	314, 294	319, 294
 <chem>HC#C-CH2-PPh2</chem>	<u>cis</u> (13a)	315, 294	309, 292
 <chem>(CH3)2C#C-CH3-PPh2</chem>	<u>cis</u> (13b)	315, 288	-
	<u>trans</u>	-	355
 <chem>CH3C#C-CH2-PPh2</chem>	<u>cis</u> (13c)	315, 292	-
	<u>trans</u>	-	356
 <chem>CH3CO-CH2-CH2-PPh2</chem>	<u>cis</u> (35)	312, 290	-
 <chem>MeO-CH2-CH=CH-CH2-PPh2</chem>	<u>cis</u> (39)	300, 278	-

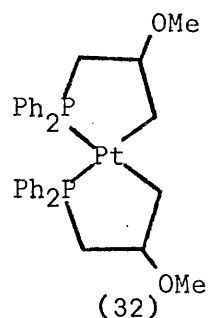
Table 5

Amine Vibrations in Phosphinoamines

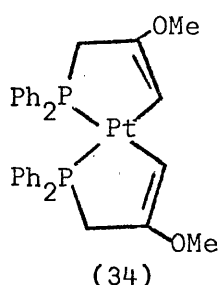
	<u>$\nu(\text{N-H})$</u>	<u>$\delta(\text{NH}_2)$</u>
Ph_2PNH_2	3390m	1577m
$(\text{Ph}_2\text{P})_2\text{NH}$	3226m	-

Table 6

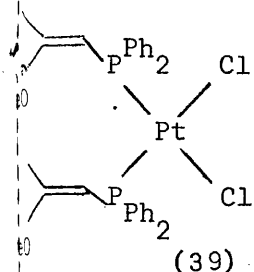
I.r. Spectra of Products from Methoxide Reactions



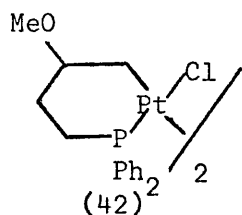
3030 w, 2941 w, 2900 m, 2841 m, 2780 m, 1587 w, 1473 m, 1449 w,
1429 s, 1387 w, 1376 w, 1335 m, 1316 w, 1299 w, 1282 w, 1224 m,
1205 m, 1170 w, 1152 w, 1111 w, 1099 s, 1085vs, 1072 s, 1020 m,
997 m, 948 s, 905 w, 899 m, 885 w, 844 m, 834 m,
813 w, 763 w, 744 s, 734 w, 704 m, 694 s.



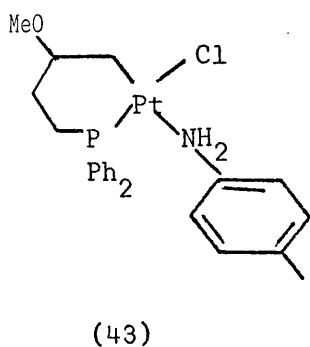
3049 w, 2950 m, 2924 m, 2857 w, 2817 w, 1667 s, 1613 w, 1567 w
1499 w, 1481 m, 1433 s, 1385 w, 1305 w, 1287 w, 1242 m, 1203 m
1160 w, 1115 w, 1098 s, 1083 s, 1036 s, 1026 m, 1016 w, 996 w
971 w, 921 s, 836 m, 826 m, 775 m, 738 s, 692 s, 556 w
532 m, 509 w, 481 m, 465 w.



3049 m, 2933 m, 2899 w, 2841 w, 1600 s, 1563 w, 1475 m, 1453 w,
1431 s, 1370 m, 1321 s, 1307 s, 1203 m, 1183 m, 1148 s, 1104 m,
1093 s, 1055 s, 1020 m, 997 w, 926 w, 858 m, 758 m, 750 s,
719 m, 694 s, 619 w, 597 w, 585 m, 578 s, 570 s, 521 w,
508vs, 497 m.



3049 w, 2959 w, 2907 m, 2882 w, 2809 w, 1600 w, 1497 m, 1477 w
1431 s, 1403 w, 1379 w, 1364 w, 1299 m, 1220 w, 1198 m, 1163 m.
1095vs, 1078 s, 1049 m, 1024 w, 997 w, 957 m, 926 m, 873 w,
838 m, 809 m, 745 s, 709 s, 690 s, 617 w, 562 w, 544 m,
526vs, 488 m



3419 m, 3106 w, 3049 w, 3012 w, 2924 w, 2915 m, 2817 m, 2793 w,
1600 w, 1506 m, 1471 w, 1449 w, 1431 s, 1410 m, 1404 m, 1300 w,
1266 w, 1205 m, 1171 m, 1159 m, 1136 m, 1099 s, 1075 m, 1020 m,
997 m, 961 w, 905 w, 862 s, 848 m, 826 s, 752 m, 744 s,
716 m, 702 s, 694 s, 690 s, 676 m, 671 m, 538 m, 521 s,
480 m.

Table 7

I.r. Spectra of Platinum(II) Chloride Complexes of Ketonic Phosphines,

	cis-PtCl_2	
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{PPh}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CD}_2 - \text{PPh}_2 \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CHD}_2 - \text{C} - \text{CD}_2 - \text{PPh}_2 \end{array}$
(35)	(38)	(37)
3058 w	3075 w	3075 w
3049 m	3055 m	3055 m
3003 w	3010 m	3020 w
3003 w	3010 m	3020 w
2959 w	-	3000 w
2915 w	2920 w	-
-	2215 w	2210 w
-	2130 w	2130 w
1704 s	1710 s	1703 s
1577 w	1588 w	1588 w
1567 w	1572 w	1573 w
1473 m	1482 m	1481 m
1429 s	1424 s	1433 s
-	1410 m	1399 w
1351 m	1355 s	1353 w
1309 w	1313 w	1312 m
-	-	1290 m
1280 m	1276 w	1275 m
1271 m	-	-
-	-	1260 s
1230 w	1228 s	1235 m
-	1200 m	-
1183 w	1190 w	1190 s
1156 w	1161 w	1162 m
1144 m	-	-
1099 s	1101 s	1100 s
-	1095 s	-
1068 w	1070 w	1072 w
1046 w	1041 w	-
1025 w	1028 m	1029 w

Table 7 (Cont.)

994 m	1004 s	1002 m
988 m	980 w	-
957 m	935 w	935 w
921 w	924 w	924 w
-	860 w	860 w
839 w	840 w	850 w
-	810 m	-
773 w	-	780 w
-	758 s	-
746 s	743 m	749 s
737 s	720 m	-
707 m	700 s	697 vs
694 s	-	-
-	668 m	660 w

Table 8

I.r. Spectra of Complexes of trans-1,4-Bis(diphenylphosphino)but-2-ene

<u>Ligand</u>	<u>PdCl₂</u>			<u>PtCl₂</u>		<u>NiCl₂</u>		<u>NiBr₂</u>
	A	B	C	D	E	(i)	(ii)	
1332 m	1330 w	1330 w	-					
1305 m	1311 m	1312 m	1316 m					
1279 w	1274 w	1277 m	1274 w					
1185 m	1188 m	1183 m	1189 m					
1166 w	-	-	-					
1156 w	1160 w	1160 m	1164 w					
1117 w	1124 m	1140 m	1130 m	1129 m	1115 w	1120 m	1119 m	1120 w
1099 m	1103 s	1099 s	1099 s					
1070 m	1072 w	1070 w	1075 m					
1057 m	-	1063 w	1052 w					
1030 m	1028 m	1024 m	1029 m					
1001 m	-	-	-					
999 m	999 m	997 m	1000 s	1000 m	995 m	1000 m	1000 m	1000 m
988 s	976 m	976 w	973 s	968 m	966 m	980 m	979 m	-
970 w	970 m	963 s	933 w	-	-	971 m	968 m	971 m
920 w	917 w	919 w	924 w					
909 w	-	-	-					
-	862 m	860 s	858 s	858 s	858 m	862 s	860 m	862 s
855 w	856 m	-	-	-	-	-	-	-
-	848 m	847 w	844 w	844 w	-	-	-	-
826 s	826 s	831 m	817 m	815 m	826 s	833 s	838 s	821 m
-	-	790 s	786 s	788 s	-	803 m	803 m	797 s
753 m	751 m	755 s	751 s					
741 s	738 vs	745 s	740 s					
720 s	725 m	735 s	-					
-	706 m	706 m	712 m					
-	-	699 s	-					
694 vs	692 vs	692 s	692 s					
684 w	685 s	-	-					

Table 8 (Cont.)

-	676 m	671 w	668 m
-	621 w	621 w	621 w
-	-	575 m	578 w
-	544 w	-	-

Table 9

Metal-Halogen Stretching Frequencies of Complexes of trans-1,4-Bis(diphenylphosphino)but-2-ene

<u>Complex</u>		<u>I.R.</u>		<u>Raman</u>	
NiCl ₂	[CVII-2(a)(i)]	333	296		
	[CVII-2(a)(ii)]	338	314		
NiBr ₂		263	233		
PdCl ₂	A	354		306	
	B	354 (317)		304	
	C	313	287	315	298
PtCl ₂	D	314	289		
	E	316	290		

Table 10

I.r. spectra of cis- and trans-1,4-Bis(diphenylphosphino)but-2-ene Dioxides

<u>trans-</u>	<u>cis-</u>	<u>Additional bands in cis-</u> <u>dioxide containing H₂O₂.</u>
3020 m	3030 m	3497 m
-	2976 m	3390 m
2907 w	2907 w	
2882 w	2857 w	
-	1623 w	
1587 w	1587 w	
1481 m	1479 m	
1433 s	1430 s	
1404 m	1397 m	1379 m
1330 w	1326 w	
1312 w	1307 w	
1217 m	1215 w	1205 s
-	1198 m	
1186 s	1183 s	
1163 m	1163 m	
1129 m	1130 m	1136 m
1120 s	1119 s	
1104 s	1101 m	
1068 m	1067 m	
1059 m	-	1044 m
1029 w	1026 w	
999 w	1010 m	
986 m	986 m	
957 w	952 w	
924 w	917 w	
862 w	858 w	877 s
-	846 w	
844 s	836 s	
831 m	826 m	
-	803 m	
764 m	770 m	759 s
746 s	746 s	
719 s	719 s	
694 s	694 s	
658 w	-	

Table 11

I.r. Spectra of Complexes of trans-1,4-Bis(diethylphosphino)but-2-ene

<u>Ligand</u>	<u>NiCl₂</u>	<u>PdCl₂</u>	<u>PtCl₂</u>
2915 s	2933 s	2941 s	2899 s
2857 s	2874 s	2899 s	2857 s
2778 m	2849 m	2849 m	2817 m
1449 s	1443 s	1449 m	1435 m
1404 m	1429 s	1389 s	1387 s
1370 m	1366 m	1366 m	1359 m
-	1304 w	1307 w	1300 w
1235 w	1230 s	1230 m	1225 m
1163 m	1199 m	1205 m	1200 w
-	1114 m	1121 w	1112 w
1060 m	1055 m	1053 m	1053 m
1042 s	1033 s	1036 s	1033 s
1010 m	1002 vs	1005 vs	1003 vs
964 m	975 s	978 s	973 s
-	837 s	835 m	833 m
763 s	770 vs	769 vs	769 vs
751 s	749 s	749 vs	758 vs
730 m	694 m	690 w	692 w

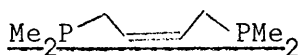
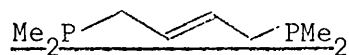
Table 12

I.r. and Raman Spectra of cis- and trans-1,4-Bis(dimethylphosphino)but-2-enes

<u>trans-</u>			<u>Addition bands in cis: trans mixture</u>	
<u>i.r.</u>	<u>Raman</u>	<u>Assignment</u>	<u>i.r.</u>	<u>Assignment</u>
3008 m		=C-H str.	3065 w	=C-H str.
2959 s		CH ₃ asym.str.		
2933 m		CH ₂ in-phase str.		
2890 s		CH ₃ sym.str.		
2809 m		CH ₂ out-of-phase str.		
	1655 s	C=C str.	1640 w	C=C str.
	1611 m			
1587 w	1594 w			
	1507 w			
1481 w		CH ₂ def.		
1418 s	1416 m	CH ₃ asym.def.		
	1306 wm	=C-H def.		
1282 m	1285 m	CH ₃ sym. def.		
1269 m				
1198 w				
	1185 s			
	1120 vw			
1105 w				
1060 m			1041 m	
	1032 w			
1020 w				
	1003 s			
961 s	968 w	H-C=C-H out-of phase def.		
935 s	939 w	CH ₃ asym. rock		
909 s				
897 s				
877 m	880 w	CH ₃ sym. rock		
	842 w	CH ₃ sym. rock		
816 w				
781 w	782 w			
704 s	707 ms	PC ₂ asym.str.	716 m	H-C=C-H out-of-plane def.
682 wm	684 m			
662 wm	662s	PC ₂ sym. str.	625 m	

Table 13

I.r. Spectra of Dichloroplatinum Complexes of cis- and trans-1,4-
Bis(dimethylphosphino)but-2-ene.



	1640 w
1409 m	1409 m
1365 m	1365 m
1310 m	
1284 s	1285 m
	1279 s
	1234 w
	1222 wm
1212 m	1217 m
	1183 w
	1131 m
1122 m	
1058 m	
1000 w	
980 m	
	957 vs
947 vs	
	934 vs
900 vs	
	876 wm
	863 wm
850 m	852 m
	830 w
	800 w
788 w	
	781 s
752 m	
	746 s
740 m	
	730 w
719 w	719 w
	701 m
687 w	688 s
	647 s

Table 13 (Cont.)

	598 w
456 w	
433 w	
382 w	
	374 w
	365 m
303 s	302 s
283 s	
274 s	278 s
	267 m

Table 14

I.r. Spectra of Acetylenic Diphosphines and Oxides

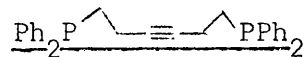
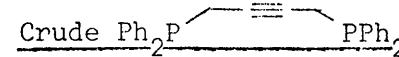
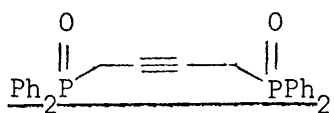
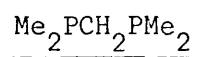
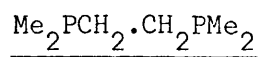
		
3030 w	3040 w	-
2985 w	3021 w	3021 w
2865 w	-	2857 w
1587 w	1587 w	1587 w
1453 m	1477 m	1481 w
1429 s	1431 s	1431 s
1427 w	1403 m	1397 m
1321 m	1323 w	1332 w
1299 m	1299 w	1311 w
1285 w	1266 w	1241 w
1190 w	1205 w	1195 s
-	1182 w	-
1153 w	1157 w	1159 s
1136 w	1135 w	1121 s
1096 m	1095 m	1103 s
1085 w	-	-
1065 m	1066 m	1066 m
1022 m	1027 m	1027 w
998 m	1000 m	999 m
987 m	-	-
935 s	-	-
-	909 w	910 m
-	-	858 w
-	825 m	832 w
-	-	820 s
-	812 m	807 w
755 m	-	761 w
751 s	752 s	749 m
743 s	738 s	735 s
730 s	-	-
722 w	714 s	719 s
699 s	699 s	-
-	694 s	694 s

Table 15

I.r. Spectra of Saturated Diphosphines



2940 s

2941 s

2865 s

2860 s

2778 w

2780 w

1425 s

1420 s

1284 m

1284 m

1271 m

1270 w

1250 w

1242 w

1190 w

-

1170 m

1179 m

1085 w

-

935 s

939 s

893 m

890 m

862 m

865 w

813 w

-

758 s

760 m

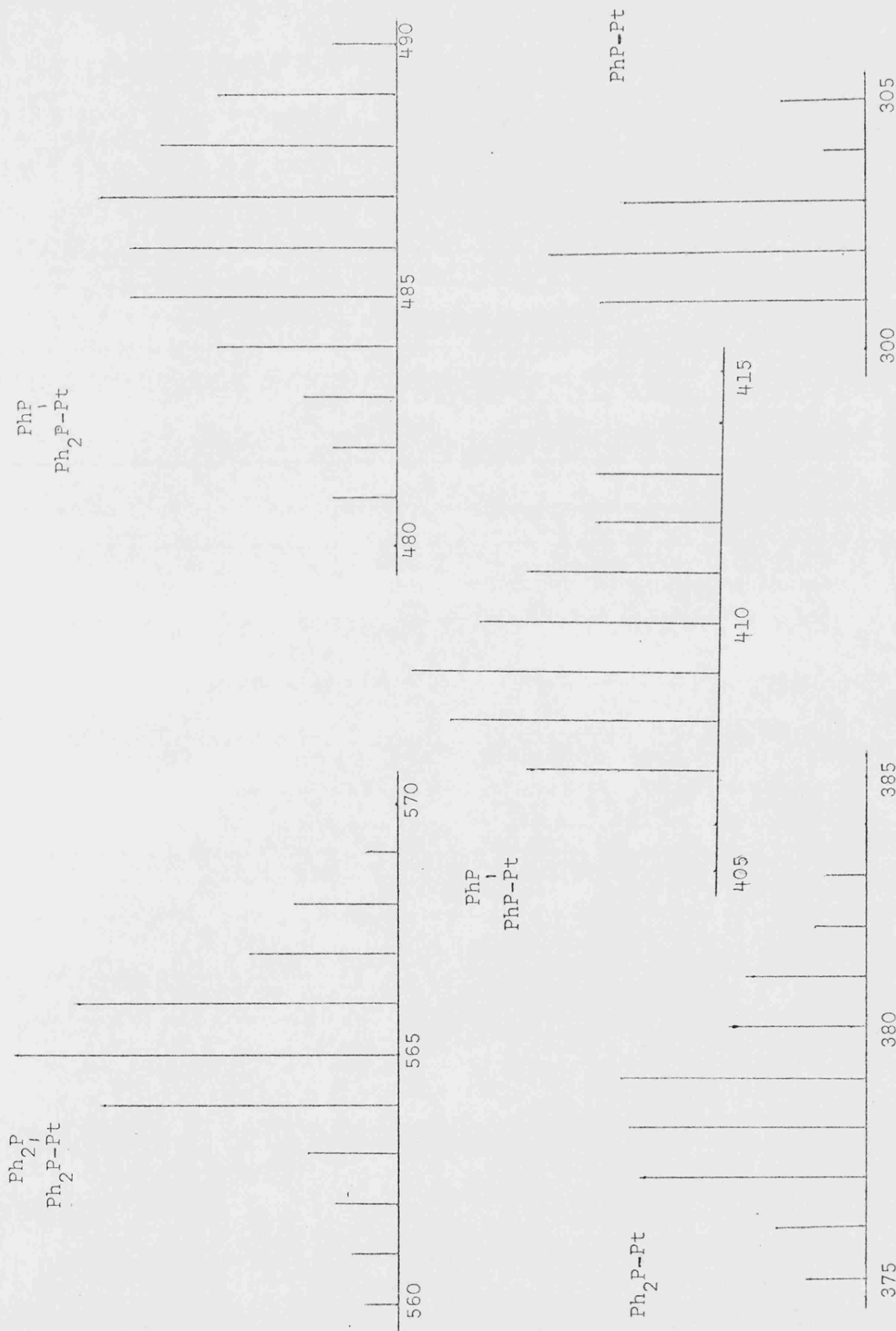
Appendix 3

Mass Spectra

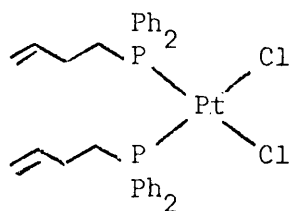
The mass spectra of some of the phosphines and complexes prepared during the course of this work are recorded below.

<u>Compound</u>	<u>m/e</u>
	424(M ⁺), 370 (M-C ₄ H ₆), 347 (M-Ph), 315 (M-PhPH), 294 (M-130), 293, 262 (Ph ₃ P), 239 (M-Ph ₂ P), 186 (Ph ₂ PH), 185 (Ph ₂ P), 183, 154 (Ph ₂), 108 (PhP), 77 (Ph).
	456 (M ⁺), 402 (M-C ₄ H ₆), 379 (M-Ph), 332 (M-PhPO), 325, 315, 262 (Ph ₃ P), 255 (M-Ph ₂ PO), 239 (M-Ph ₂ PO ₂), 201 (Ph ₂ PO), 183, 77 (Ph).
	456 (M ⁺), 401 (M-C ₄ H ₇), 380 (M-PhH), 378 (M-C ₆ H ₄), 332 (M-PhPO), 325, 315, 262 (Ph ₃ P), 255 (M-Ph ₂ PO), 239 (M-Ph ₂ PO ₂), 229 (M-Ph ₂ P(O)C ₂ H ₂), 227 (M-Ph ₂ P(O)C ₂ H ₄), 183, 77 (Ph).
	454 (M ⁺), 401 (M-C ₄ H ₅), 377 (M-Ph), 330 (M-PhPO), 325, 313, 262 (Ph ₃ P), 253 (M-Ph ₂ PO), 237 (M-Ph ₂ PO ₂), 201 (Ph ₂ PO), 185 (Ph ₂ P), 183, 77 (Ph).
	450 (M ⁺), 422 (M-C ₂ H ₄), 421 (M-C ₂ H ₅), 373 (M-Ph), 359 (M-91), 341 (M-PhPH), 298, 296 (M-Ph ₂), 265 (M-Ph ₂ P), 251 (M-Ph ₂ PCH ₂), 236 (M-Ph ₂ PC ₂ H), 233 (M-Ph ₂ PC ₂ H ₄) 153 (M-PhC ₆ H ₄), 134 (PhPC ₂ H ₄), 121 (PhPCH), 108 (PhP) 91, 77 (Ph).
Me ₂ PCH ₂ CH:CHCH ₂ PMe ₂	176 (M ⁺), 161 (M-Me), 122 (M-C ₄ H ₆), 115 (M-Me ₂ P), 107 (M-99), 99, 61 (Me ₂ P).
Ph ₂ PNH ₂	385 (M ⁺), 262 (Ph ₃ P), 200 (M-Ph ₂ P), 185 (Ph ₂ P), 183, 152, 122 (PhPN), 107 (PC ₄ H ₄), 77 (Ph).

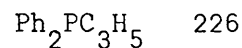
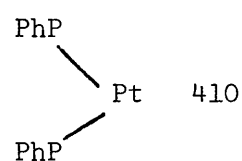
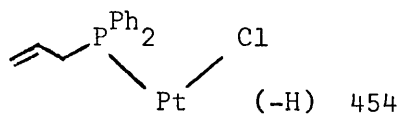
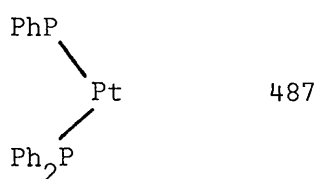
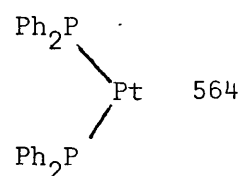
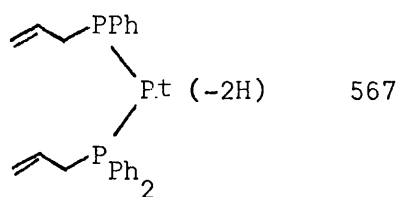
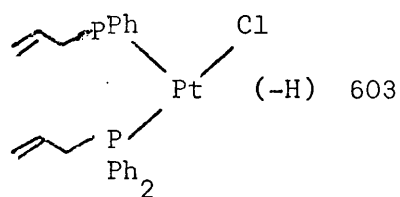
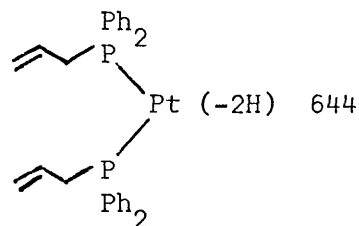
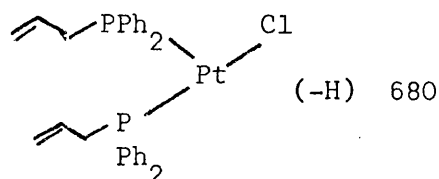
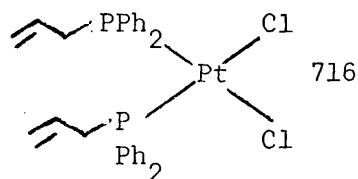
Characteristic Patterns of P-Pt Fragments.



Mass Spectrum of

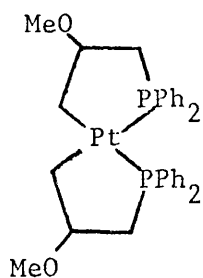


Patterns due to the following fragments were identified.

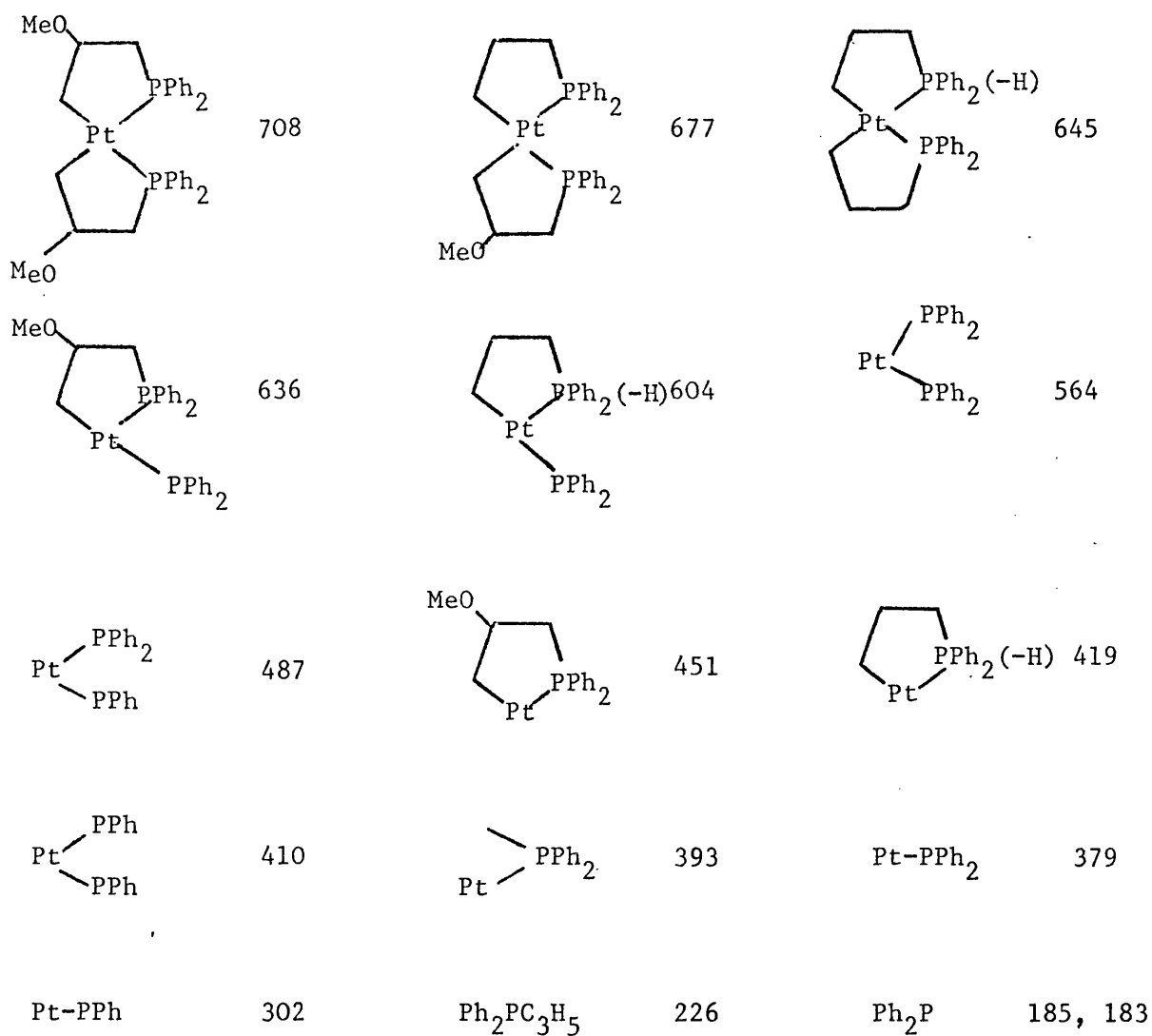


Fragments were also observed at m/e 459, 363, 339, 313, 199, 91 and 77.

Mass Spectrum of

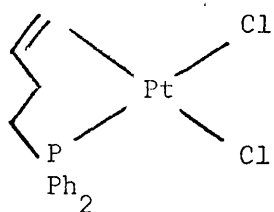


Patterns due to the following fragments were identified:

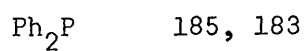
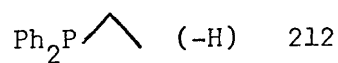
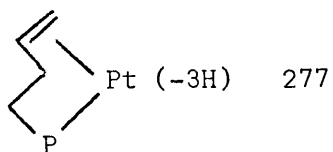
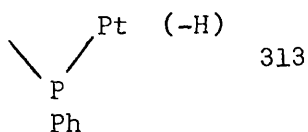
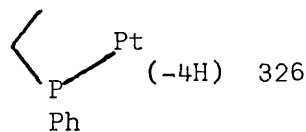
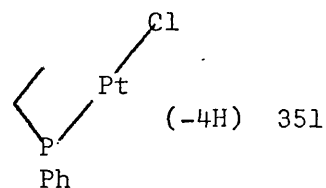
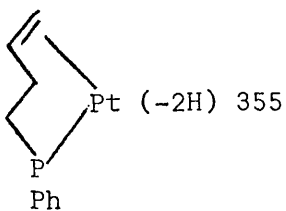
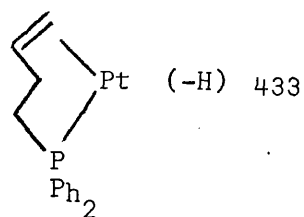
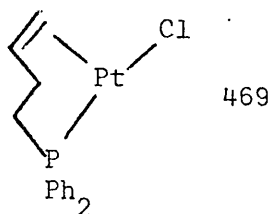
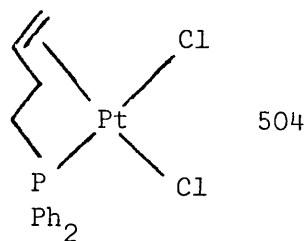


Fragments were also observed at m/e 154, 152, 121, 108, 91 and 77.

Mass spectrum of

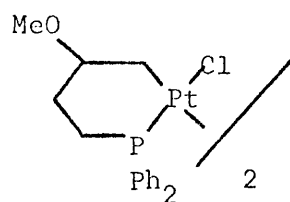


Patterns due to the following fragments were identified:

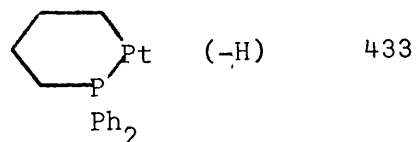
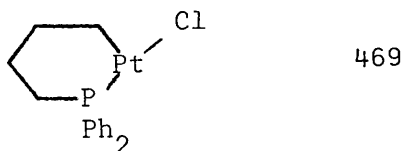
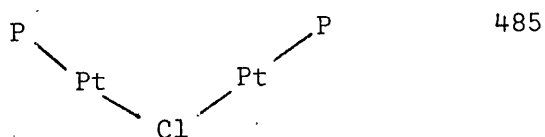
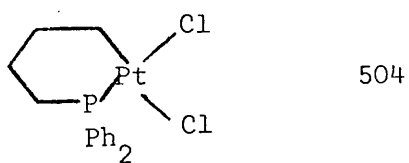
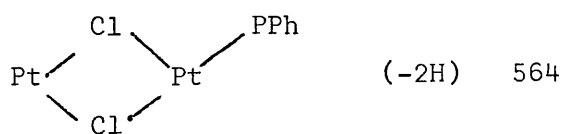
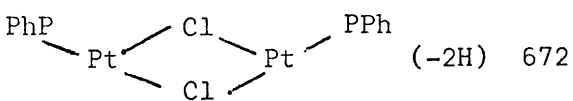
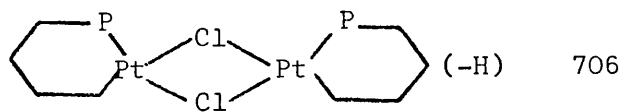
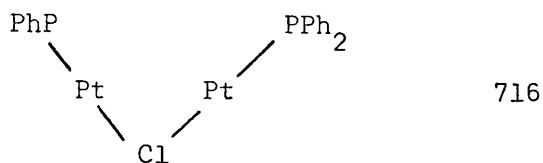
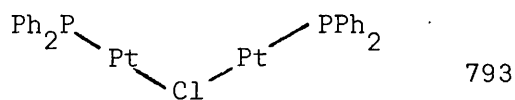
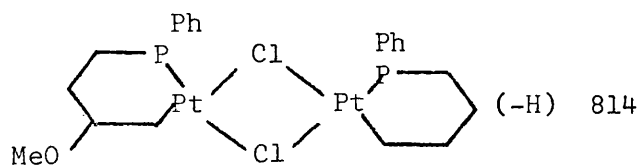
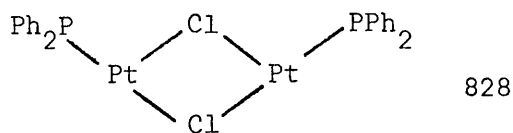
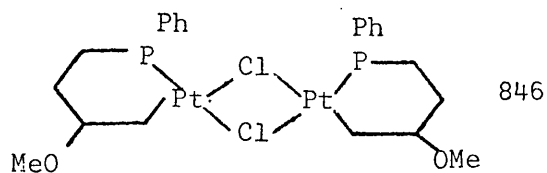


Other fragments were observed at m/e 154 and 78.

Mass Spectrum of

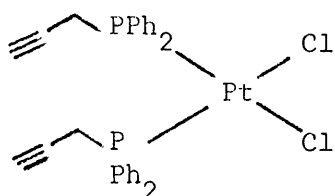


Patterns due to the following fragments were observed:

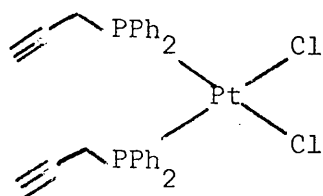


Fragments were also observed at m/e 770, 738, 702, 654, 239, 129 and 78.

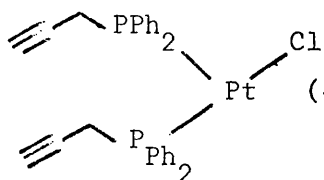
Mass Spectrum of



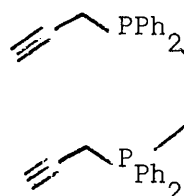
Patterns due to the following fragments were identified:



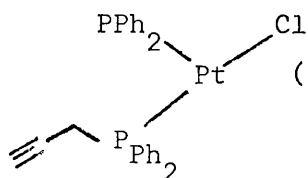
712



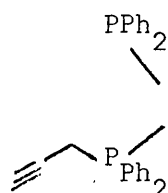
(-H) 676



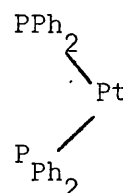
(-2H) 640



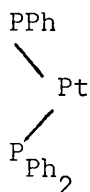
(-2H) 636



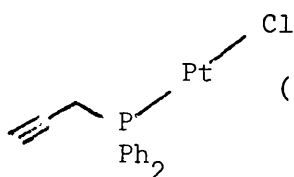
(-3H) 600



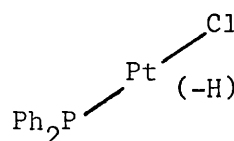
564



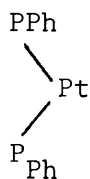
487



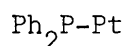
(-2H) 451



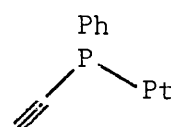
(-H) 413



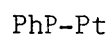
410



379



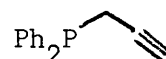
338



302



262



224



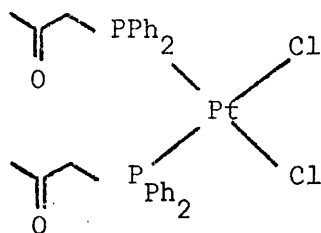
185, 183



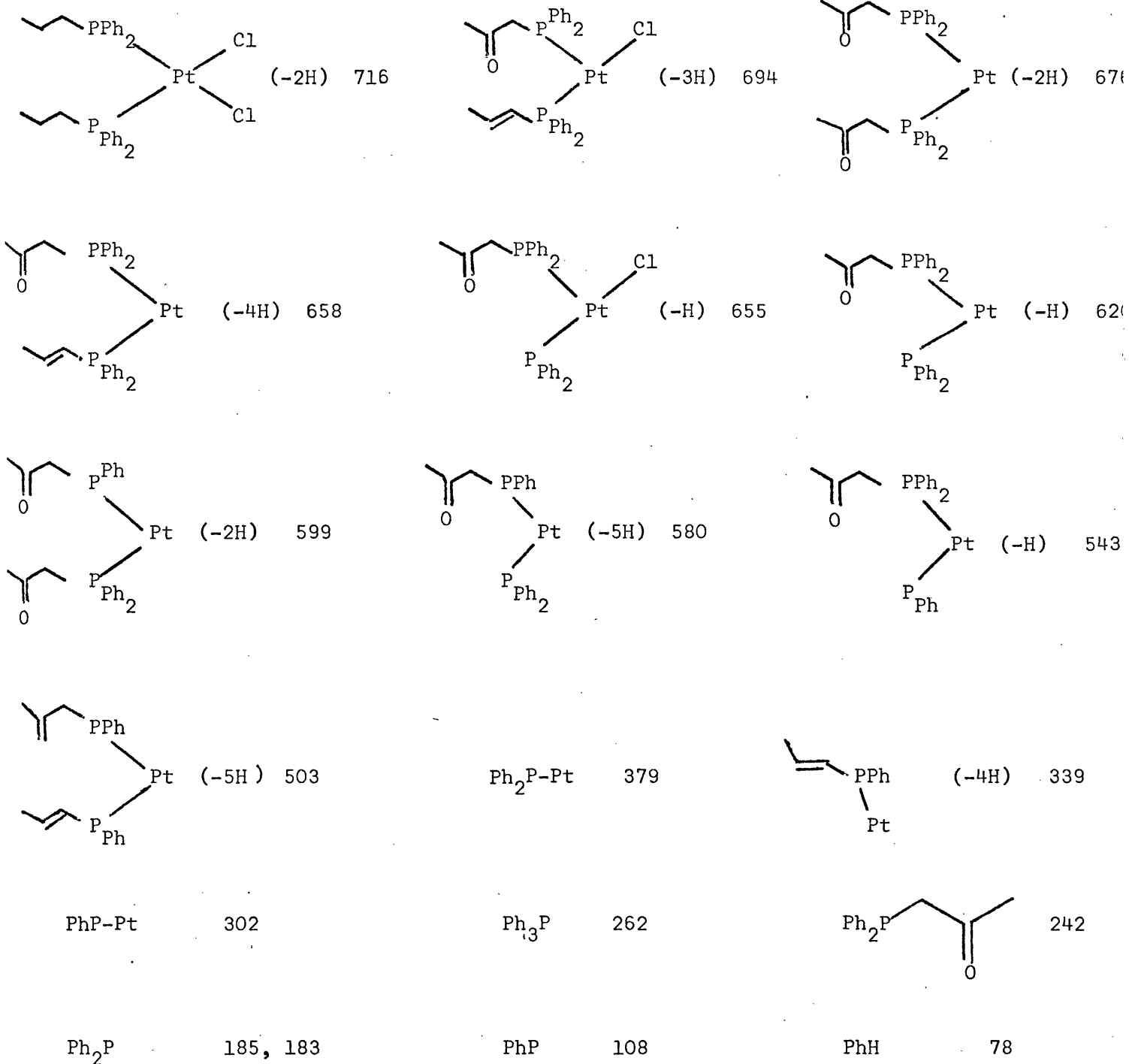
78

Other fragments were observed at m/e 533, 491, 455.

Mass Spectrum of

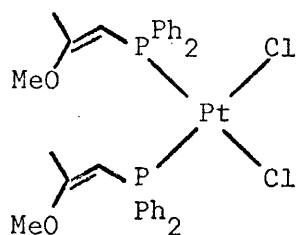


Patterns due to the following fragments were identified:

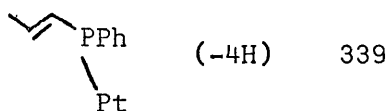
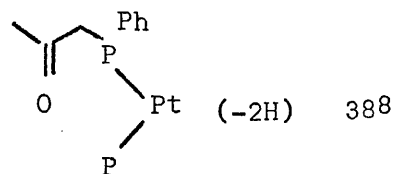
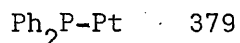
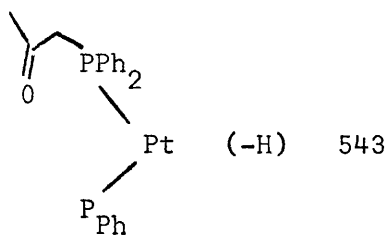
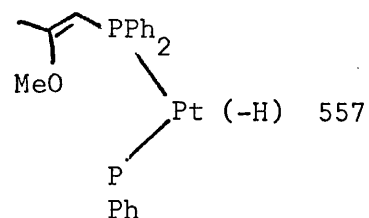
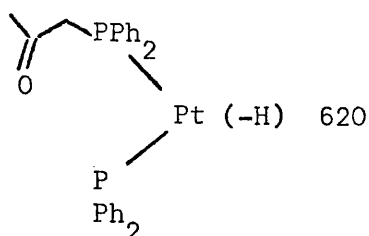
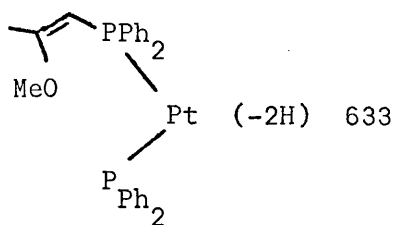
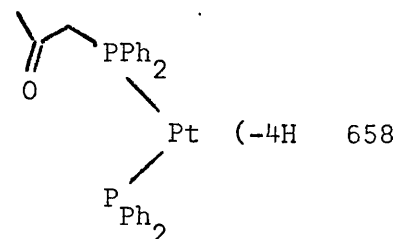
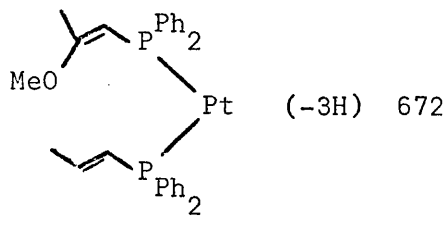
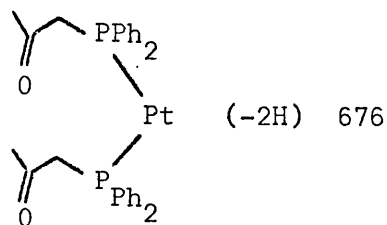
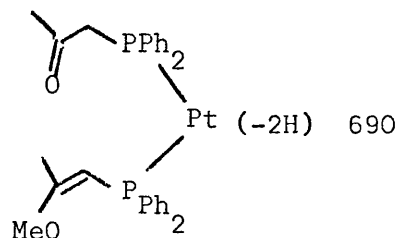
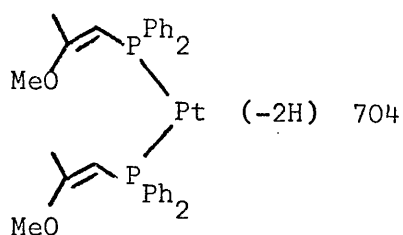
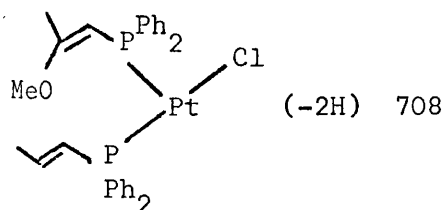


Other fragments were observed at m/e 704, 690, 559, 455, 394, 387, 351 and 327.

Mass Spectrum of

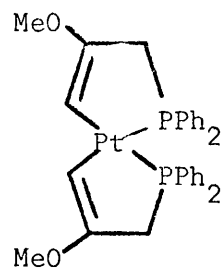


Patterns due to the following fragments were identified:

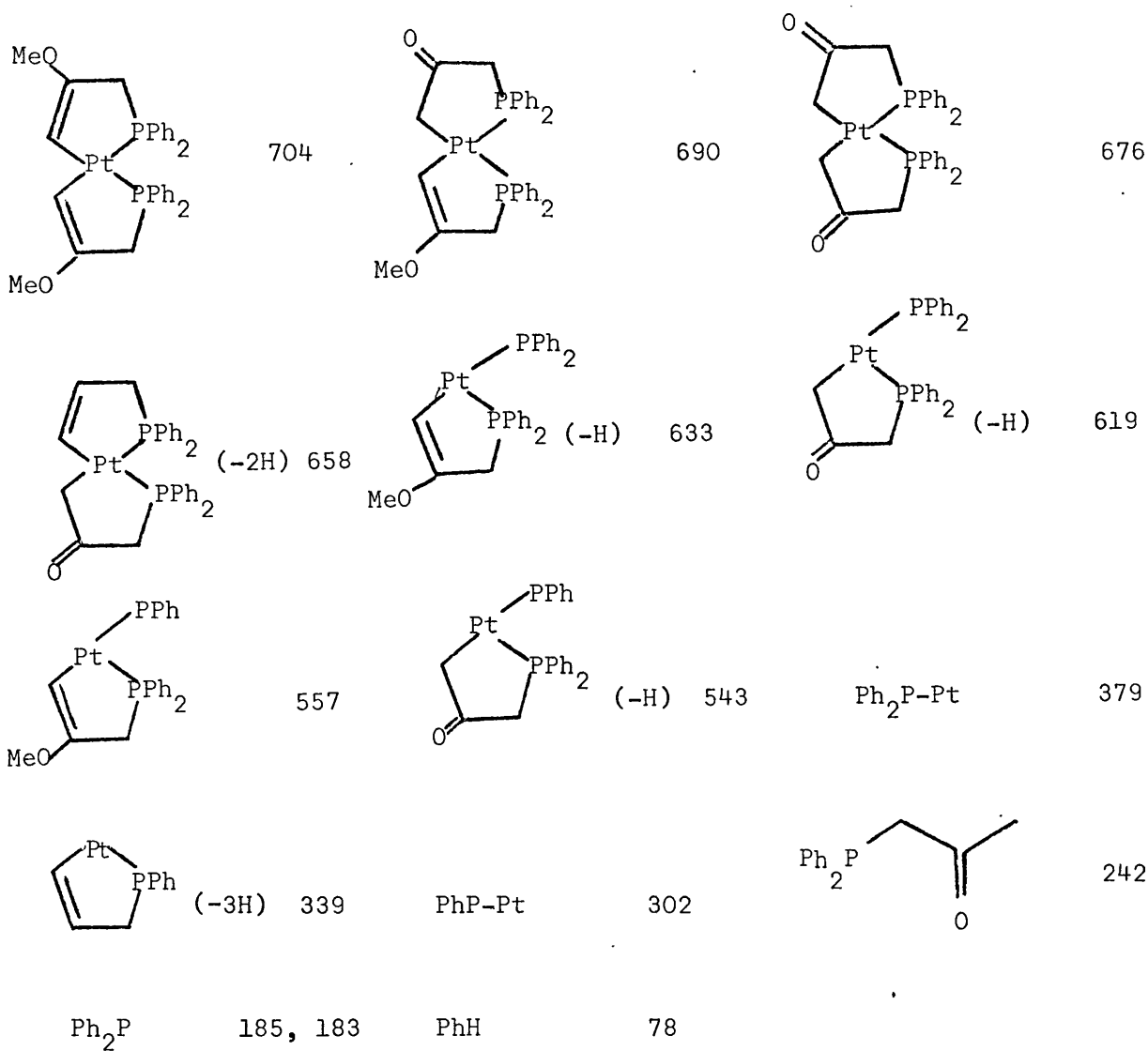


Other fragments were observed at m/e 647, 503, 454, 388 and 201.

Mass Spectrum of



Patterns due to the following fragments were identified:



Other fragments were observed at m/e 647, 503, 454, and 388.

Appendix 4

Apparatus

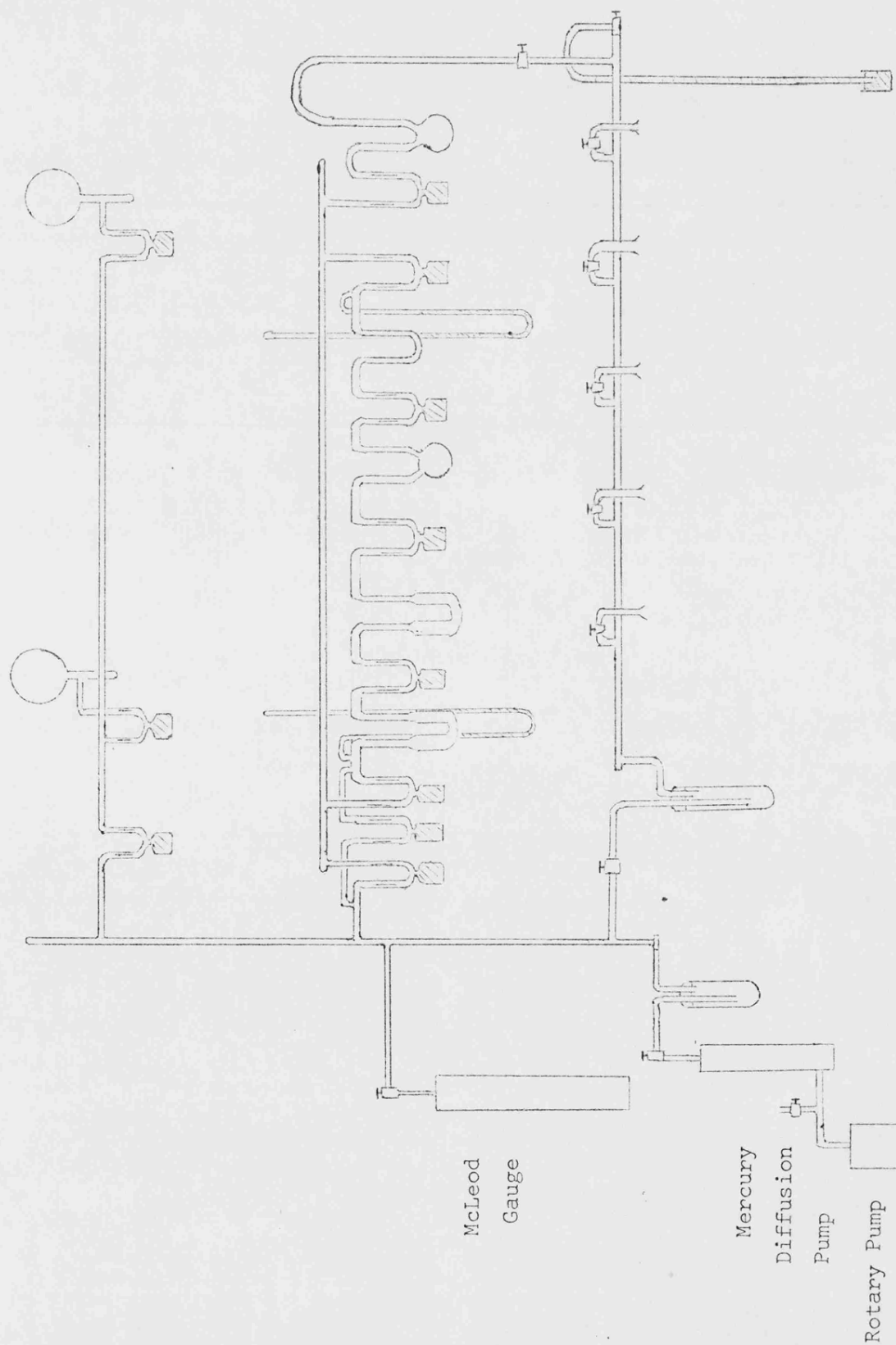


Figure 1: Vacuum Line

Appendix 5

Publications

1. Preparation of Tertiary Phosphines, British Patent Application 57393/69.
2. Nucleophilic Attack by the Diphenylphosphide Ion on Alk-2-aryl Halides, Chem. Comm., 1970, 119.
3. Formation of Platinum-Carbon σ -Bonded Complexes from Co-ordinated and Unco-ordinated Olefins and Acetylenes, Chem. Comm., 1970, 428.
4. The Synthesis and Rearrangement of Alk-2-aryl Phosphines. J. Chem. Soc. (c), in the press.
5. The Reaction of Tetramethyldiphosphine with Butadiene. J. Chem. Soc. (c), in the press.

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