ACETYLENE COMPLEXES OF NICKEL, PALLADIUM AND PLATINUM

DEDICATION

To my Grandparents, Mr. & Mrs. J.E. Greaves for their interest and encouragement throughout my studies.

SOME ACETYLENE COMPLEXES
OF
NICKEL, PALLADIUM AND PLATINUM

By

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SCOPE AND CONTENTS: The work describes the preparation of some acetylene complexes of nickel, palladium and platinum. The structure of and the bonding in these complexes is discussed in the light of their infrared and nuclear magnetic resonance spectra. Some reactions of the complexes are described.

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INTRODUCTION

INTRODUCTION

The first compound in which an unsaturated hydrocarbon ligand is bonded directly to a metal was prepared by Zeise, who in 1827 reported a compound which was later shown to be the ethylene complex $K[PtCl_3(C_2H_4)]H_2O$ (1). Since that time, and particularly during the last 15 years, a large number of metal-olefin complexes have been prepared.

The ease with which the metal-olefin bond is formed led to the investigation of acetylenes as ligands, and many metal-acetylene complexes are now known.

A discussion of metal-olefin complexes is particularly relevant in the context of metal-acetylene complexes, since the bonding scheme suggested for the former may be extended to metal-acetylene complexes, and also since the displacement of an olefin by an acetylene provides a useful synthetic route to some metal-acetylene complexes.

Metal-Olefin Complexes

Olefin complexes analogous to Zeise's salt (1) were prepared[1] for silver(I), palladium(II) and copper(I), but it was only recently that the structures of these complexes were elucidated. Also, it was originally thought that the olefin complexes were confined to the elements at the heavy end of the transition series, however, well characterized olefin complexes of the Group VI, VII and VIII metals are now known.[2-7]

Structure and Bonding

X-Ray studies have shown that in crystalline $K[PtCl_3(C_2H_4)]$[8] (1), $[PtCl_2 \cdot HN(CH_3)_2 \cdot (C_2H_4)]$[9] (2) (Fig I), and other platinum complexes[10] the olefin double bond is perpendicular to the co-ordination plane. (Fig. I)

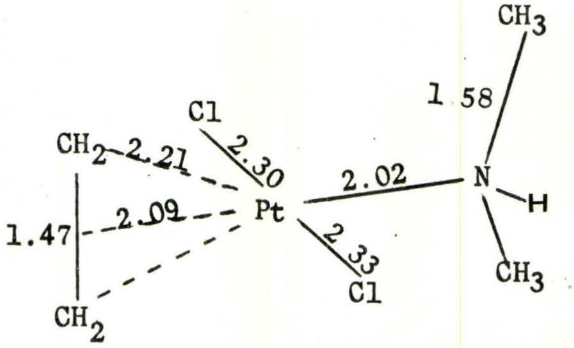
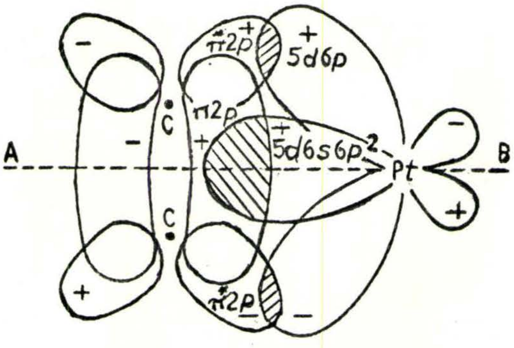


Fig. I

The first satisfactory bonding theory was the molecular orbital approach advanced by Dewar for the silver-olefin complexes[11], and later extended by Chatt and Duncanson to the platinum-olefin complexes[3]. (Fig. II).



▧ = bond of σ-symmetry ▨ = bond of π-symmetry

Fig. II A pictorial representation of the bonding in platinum-olefin complexes.

The bond by which olefins are co-ordinated to transition metals is seen as consisting of two parts: (a) A bond of σ-symmetry, corresponding to the classical co-ordination bond, formed by overlap of the filled π-orbitals of the olefin with a vacant metal orbital; this is often called a μ bond. (b) A bond of π-symmetry arising from overlap of the vacant π^* anti-bonding orbital of the olefin with a filled d-orbital of the metal. This effect, commonly termed back-donation, leaves the metal with less negative charge than if the olefin were acting purely as a two electron donor.

The geometry found in the platinum(II)[8,9,10] and palladium(II)[12] olefin complexes which have been examined by X-rays i.e., with the ethylene perpendicular to the co-ordination plane, (where the d_{xz} metal orbital is used for back-donation), has been generally assumed for the other platinum(II) and palladium(II) olefin complexes. However, Cramer[13] has pointed out that the d_{xy} metal orbital could also be used to bond to the metal atom; the olefin double bond would then lie in the co-ordination plane (Fig III).

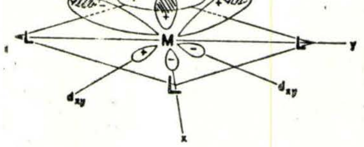


Fig III

For steric reasons this would not be a favourable conformation, but the structure could provide a low-energy pathway for rotation about the platinum-olefin axis. It was suggested[14] that the observed rotation of the olefin in a chloroform solution of $[PtCl_2(2,3,6\text{-trimethylpyridine})(PhCH = CH_2)]$ proceeded via structure III. Similar nuclear magnetic resonance studies on a chloroform solution of bis(ethylene)-π-cyclopentadienylrhodium[13] has shown the ethylene to rotate about the rhodium-ethylene axis, and the low energy barrier to rotation (6kcal.) was again taken as evidence that III provided the pathway.

Mono-nuclear metal-acetylene complexes

1. Historical and General

The first report of a stable acetylene complex was by Hel'man *et*.*al*.[15] who prepared the platinum(II) complex trans-$[PtCl_2(py)(ac)]$ (3), (py = pyridine, ac = $HOCMe_2C{\equiv}CCMe_2OH$). Subsequent attempts[3] to isolate the analogous dimethyl- and diphenyl-acetylene complexes were unsuccessful, but Chatt and Duncanson[16] were able to prepare a number of other alkyne complexes. It was shown that the stability of the complex is very dependant upon the nature of the substituents adjacent to the triple bond. Thus, complexes such as $Na[PtCl_3(ac)]$ (4), $[PtCl_2(ac)]_2$ (5) and trans-$[PtCl_2(\text{piperidine})(ac)]$ (6) (ac = acetylenic substance) can only be isolated when at least one tertiary carbon is adjacent to this bond. The simpler alkynes e.g., $Pr^iC{\equiv}CEt$, $RC{\equiv}CR$ (R = Me, Et, Pr^n or Bn^n), and alkynes conjugated to phenyl groups or another triple bond do not give stable complexes.

In 1957 Chatt *et*.*al*.,[17] reported a new and extensive series of platinum-acetylene complexes of the type $[(Ph_3P)_2Pt(ac)]$ (7), which were considerably more stable than those previously known. In both this series, and in complexes of the types (3) to (6) an acetylene monomer is bonded to one metal. Other such complexes have since been reported for vanadium,[18] chromium,[19] molybdenum,[20] tungsten,[20,21] manganese,[22,23] rhenium,[24] cobalt,[25] rhodium,[26,27,28] iridium,[27,28] nickel[5] and platinum.[15,16,17,29,30,31] Complexes in which one acetylene molecule is bonded to two or more metal atoms are also known (see page 8).

ii Structure and bonding

The probable structures of, and the nature of the bonding in platinum(II) complexes of the type $K[PtCl_3(ac)]$ and in complexes of the series $[(Ph_3P)_2Pt(ac)]$ were suggested [16,17,30] mainly on the basis of infrared spectral evidence.

The platinum(II) complexes (4), (5) and (6) all show weak absorptions at approximately 2,000 cm^{-1}, which could be attributed to the C≡C stretching frequency lowered by co-ordination of the acetylene to the platinum atom (The C≡C stretching frequency in disubstituted alkynes occurs between 2,190 and 2,260 cm^{-1})[32]. The low intensity of the bands was taken to indicate that the symmetry of the alkyne is little changed on co-ordination i.e. rehybridization of the acetylenic carbon atoms does not occur. The lowering in frequency (ca. 200cm^{-1}) was compared with a lowering of 140cm^{-1} in the C=C stretching frequency of olefins on complex formation with platinum(II)[3], and the lowering of 65cm^{-1} in the C=C stretching frequency of olefins on complex formation with silver(I)[33]. On the basis of these results it was suggested that the alkyne is symmetrically co-ordinated about the triple bond. and bound to the metal by the same type of bond as is ethylene in Zeise's salt (1) The multiple bond of the acetylene would then be expected to lie perpendicular to the co-ordination plane of the molecule. These predictions were recently shown to be correct by an X-ray study^{34} of [PtCl$_2$(Bu^{t}C≡CBu^t)(p-toluidine)] (8) (Fig IV).

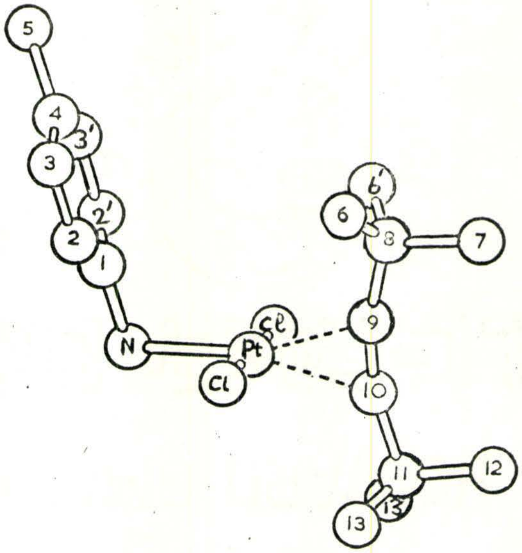
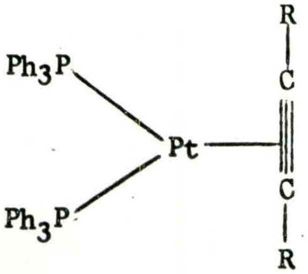


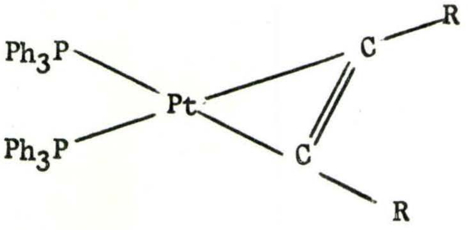
Fig. IV

The acetylene is symmetrically placed and perpendicular to the co-ordination plane of the platinum atom. The acetylenic carbon-carbon bond length of 1.27 ± 0.03°A is mid-way between the usual values for double and triple bonds.

Complexes of the type [(Ph$_3$P)$_2$Pt(ac)] (7) are found to show no infrared absorption in the region 2,200 – 1,800cm^{-1}. However bands in the region of 1,750cm^{-1} were attributed^{17} to the triple bond stretching frequency. The lowering of $\nu_{C\equiv C}$ by some 400cm.$^{-1}$ upon co-ordination of the acetylene to platinum was taken to indicate that the triple bond had been reduced almost to a double bond. Two possible structures were proposed, V and VI.



V



VI

For structure V, (- -) indicates a bond of the type suggested for olefin-platinum(II) complexes and acetylene-platinum(II) complexes such as (8). In such a structure the triple bond would be perpendicular to the platinum co-ordination plane, the acetylene should still be almost linear, and the reduction in the infrared stretching frequency of the triple bond would be approximately 200 cm.$^{-1}$ (by comparison with (8)).

The σ-bonded structure VI implies that rehybridization of the acetylenic carbons to sp^2 has occurred, the acetylene is no longer linear and the structure is planar.

On the basis of the lowering of the triple bond stretching frequency to approximately 1,750 cm.$^{-1}$ and the sensitivity of the dipole moments of the phenylacetylene complexes to polar substitution in the p-position[35], it was suggested that the principal structure is probably VI. This prediction was shown to be remarkably correct by a recent X-ray study of diphenylacetylenebis(triphenylphosphine)platinum.[36] (7, ac = PhC≡CPh)., Fig VII.

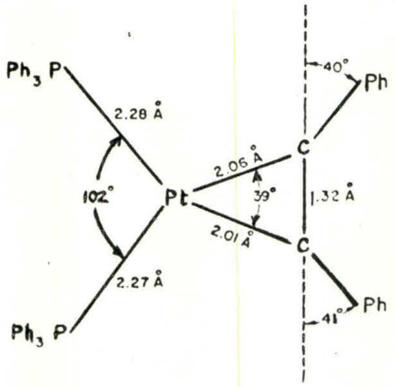


Fig. VII. X-ray structure of diphenylacetylenebis(triphenylphosphine)-platinum.

The structure in the crystal is found to lie between the two possibilities V and VI but is considerably closer to VI. Thus the platinum, two phosphorus and one of the acetylenic carbon atoms are found to lie in a plane, with a line through the two acetylenic carbons making an angle of approximately 14° with this plane. The carbon-carbon distance of 1.32±0.09 Å is typical of that for an olefinic double bond, and the platinum-acetylenic carbon distance of 2.06 Å is very similar to that found[37] for the platinum-carbon distance in σ-bonded complexes of platinum(II).

Polynuclear acetylene complexes

Acetylenes have two sets of mutually perpendicular π-orbitals, and the corresponding π^* antibonding orbitals, available for bonding to metal atoms. In the mono-nuclear acetylene complexes described above only one of these sets is used, but a number of complexes are known in which both sets are used. The acetylene may then act as a bridging ligand between two, three or even four metal atoms, and such polynuclear complexes have been reported for molybdenum,[38,39] iron,[40,41] cobalt[42-47] and nickel,[46,48] Several of these have been examined by X-rays e.g. diphenylacetylenedicobalthexacarbonyl[43] (9) (Fig VIII) formed by the reaction of dicobalt octacarbonyl (10) and diphenylacetylene.

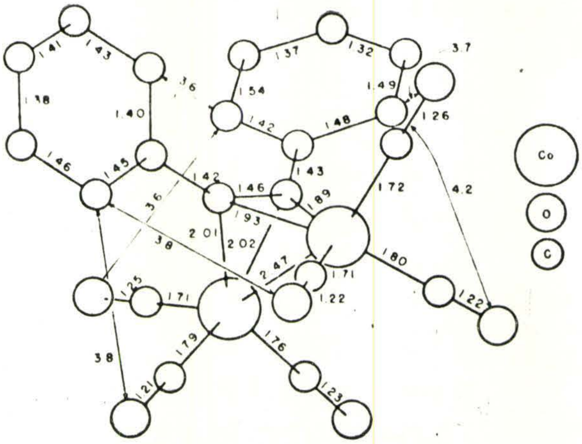


Fig. VIII

The Co-Co bond, 2.47 Å., is nearly normal (88°) to the C-C bond of the acetylene, and the planes of the benzene rings make an angle of 62° with each other.

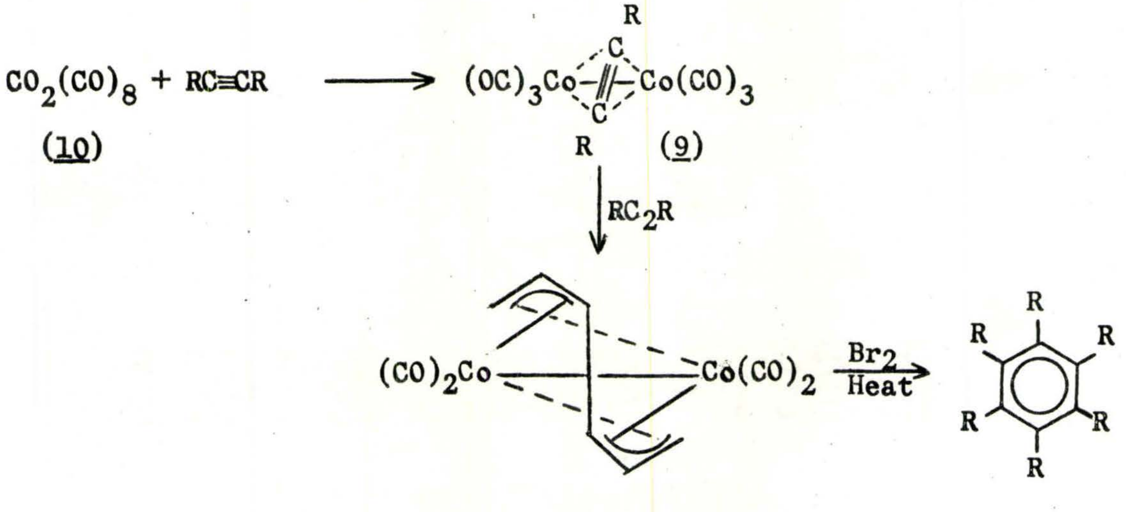
Preparation of acetylene complexes

1. Displacement of carbon monoxide from a metal carbonyl or substituted metal carbonyl.

By analogy with olefins, an acetylene bonded to one metal atom may be thought of as a two-electron donor; replacement reactions of other two-electron Lewis bases, e.g. carbon monoxide, are therefore possible. In practice, reactions of metal carbonyls with acetylenes often lead to complex products in which the acetylenes have been dimerized, sometimes with incorporation of carbon monoxide into the new organic ligand. However, many cases do exist where carbon monoxide is replaced by an acetylene e.g.[23]

$$(\pi\text{-}C_5H_5)\text{-}Mn(CO)_3 + CF_3C\equiv CCF_3 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)\text{-}Mn(CO)_2(CF_3C_2CF_3)$$

In the reactions where more complex products are obtained it is frequently postulated that the initial products are acetylene complexes of the mononuclear type, or of the type where the acetylene bridges two or more metals. In the case of the reaction of acetylenes with dicobalt octacarbonyl[45] (10) this sequence can be illustrated, as the intermediates are stable and have been fully characterized:



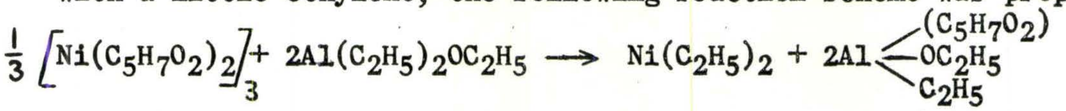
2. Displacement of other ligands

A number of other two-electron donor ligands may also be displaced by acetylenes to give acetylene complexes. Hel'man *et. al.*,[15] and later Chatt *et. al.*,[16] displaced chloride by an acetylene in platinum(II) complexes

$$[PtCl_4]^{=} + (ac) \xrightarrow[20^\circ C]{water} [PtCl_3(ac)]^{-} + Cl^{-}$$

(ac = $HOCMe_2C\equiv CCMe_2OH$, $Bu^tC\equiv CBu^t$ etc.)

Wilke and Hermann[5] found that acetylene-bis(triphenylphosphine)-nickel complexes were conveniently prepared by the displacement of ethylene from ethylenebis(triphenylphosphine)nickel (13). The ethylene complex (13) was prepared by the addition of diethylaluminum ethoxide to an ethylene-saturated benzene solution of bis(acetylacetonato)nickel(II) and triphenylphosphine (mole ratio 1:2). It was suggested that the product was formed by the co-ordination of two molecules of triphenylphosphine and one of ethylene to a "bare" nickel atom. To account for the gaseous reaction products, which were chiefly ethane and hydrogen, together with a little ethylene, the following reaction scheme was proposed:



$$\frac{1}{3}\left[Ni(C_5H_7O_2)_2\right]_3 + 2Al(C_2H_5)_2OC_2H_5 \longrightarrow Ni(C_2H_5)_2 + 2Al\begin{matrix}(C_5H_7O_2)\\ OC_2H_5\\ C_2H_5\end{matrix}$$

$$\begin{aligned}
Ni(C_2H_5)_2 &\longrightarrow NiH_2 + 2C_2H_4\\
NiH_2 &\longrightarrow Ni^{*} + H_2\\
Ni(C_2H_5)_2 &\longrightarrow Ni^{*} + 2\ \cdot C_2H_5\\
2\ \cdot C_2H_5 &\longrightarrow C_2H_4 + C_2H_6\\
Ni^{*} + 2Ph_3P + C_2H_4 &\longrightarrow (Ph_3P)_2Ni(C_2H_4),\ (\underline{13})
\end{aligned}$$

(Alternatively ethane may be formed by a hydrogenation reaction of ethylene.) The addition of diphenylacetylene or dimethylacetylene to a benzene solution of (13) resulted in rapid expulsion of ethylene and the formation of the corresponding acetylene complexes, in good yield. e.g.

$$\underset{(\underline{13})}{(Ph_3P)_2Ni(C_2H_4)} + PhC{\equiv}CPh \longrightarrow \underset{(\underline{14})}{(Ph_3P)_2Ni(PhC_2Ph)} + C_2H_4$$

Acetylenes bearing highly electronegative substituents will also displace other acetylenes from their complexes[17] e.g.

$$(Ph_3P)_2Pt(PhC_2H) + (p\text{-}NO_2\text{-}C_6H_4C{\equiv}CH) \longrightarrow (Ph_3P)_2Pt(p\text{-}NO_2\text{-}C_6H_4C_2H) + PhC{\equiv}CH$$

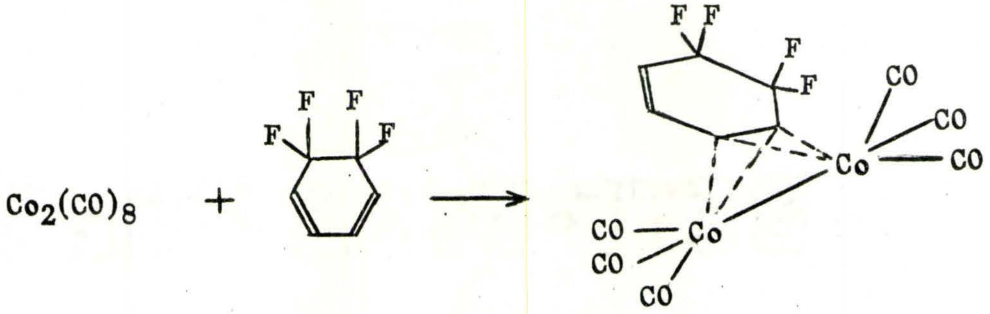
From an equilibrium study[31] on this and analogous reactions, it was proposed that an intermediate, $(Ph_3P)_2Pt$ (15) is formed which has a significant stability.

The ready displacement of one mole of triphenylphosphine from chlorotris(triphenylphosphine)rhodium (16) has been used to prepare rhodium-acetylene complexes[26]:

$$[(Ph_3P)_3RhCl] + CF_3C{\equiv}CCF_3 \longrightarrow [(Ph_3P)_2Rh(CF_3C_2CF_3)Cl] + Ph_3P.$$

3. Dehalogenation of fluoro-olefins

Dicobalt octacarbonyl (10) was found to dehalogenate octofluorocyclohexa-1,3-diene to give, (via the free acetylene), a perfluorocyclohex-1-yn-3-enedicobalt hexacarbonyl complex[47]:



4. Addition reactions

A number of metals in low oxidation states exhibit an "unsaturated" behaviour, and are capable of undergoing addition reactions with 2-electron donors, e.g.[49]

$$(Ph_3P)_2Ir(CO)Cl + HCl \longrightarrow (Ph_3P)_2Ir(CO)Cl_2H$$

Acetylenes will also react with these unsaturated complexes,[28] e.g.

$$\underset{(\underline{17})}{(Ph_3P)_2Ir(CO)Cl} + PhC{\equiv}CCOOEt \longrightarrow (Ph_3P)_2Ir(CO)Cl(PhC_2COOEt)$$

Similarly with rhodium[28]:

$$\underset{(\underline{18})}{[(Ph_3P)_2Rh(CO)Cl]} + HC{\equiv}CCOOH \longrightarrow [(Ph_3P)_2Rh(CO)Cl(HC_2COOH)]$$

Although this "unsaturation" is often associated with metals having a d^8 configuration, similar reactions are known for vanadium[18]:

$(\pi\text{-}C_5H_5)_2V + RC\equiv CR \longrightarrow (\pi\text{-}C_5H_5)_2V(RC_2R)$, $(R = CF_3,\ COOCH_3)$

The formation of the platinum-acetylene complexes (7) by the method of Chatt *et.al*. can also be thought of as arising in this way, since the addition of excess hydrazine to an alcoholic suspension of cis-dichlorobis(triphenylphosphine)platinum at 40 - 50° gives a mixture of the bis- and tris-triphenylphosphineplatinum(0) complexes[50]. These are known to undergo a wide variety of addition reactions,[51] e.g. with methyl iodide[71]:

$(Ph_3P)_3Pt + 2MeI \longrightarrow (Ph_3P)_2PtMeI + Ph_3MePI$

With oxygen[7]:

$(Ph_3P)_2Pt + O_2 \longrightarrow (Ph_3P)_2PtO_2$

The formation of the acetylene complex may thus be considered as:

$(Ph_3P)_2Pt + PhC\equiv CPh \longrightarrow (Ph_3P)_2Pt(PhC_2Ph)$.

Polymerization Reactions

As was mentioned above, acetylenes often undergo unexpected reactions in the presence of transition metal compounds. Thus linear or cyclic polymerization, with or without carbonyl insertion, may occur. It is these reactions which have attracted much of the attention currently focussed on transition metal - acetylene chemistry, since they represent possible routes to novel high polymers and other interesting organic molecules.

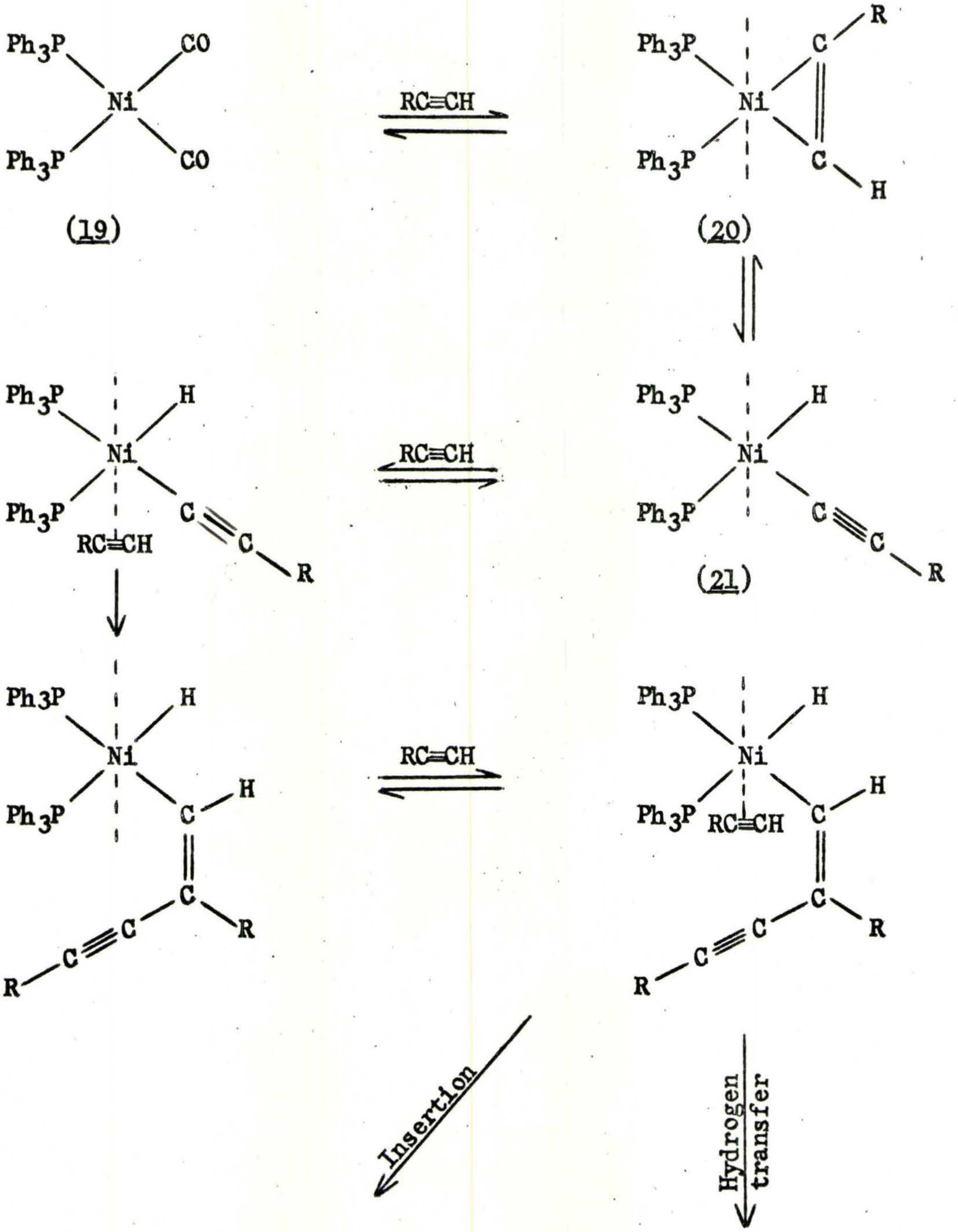
Prior to the second World War it was known that the thermal polymerization of acetylene over a copper catalyst gave benzene in low yield. Reppe and Schweckendiek[52], during the war years, discovered that dicarbonylbis(triphenylphosphine)nickel (19) brought about the selective cyclization of mono-substituted acetylenes. This represented a more convenient route to a number of benzene derivatives, e.g., trivinylbenzene, substituted styrenes etc. than conventional methods allowed.

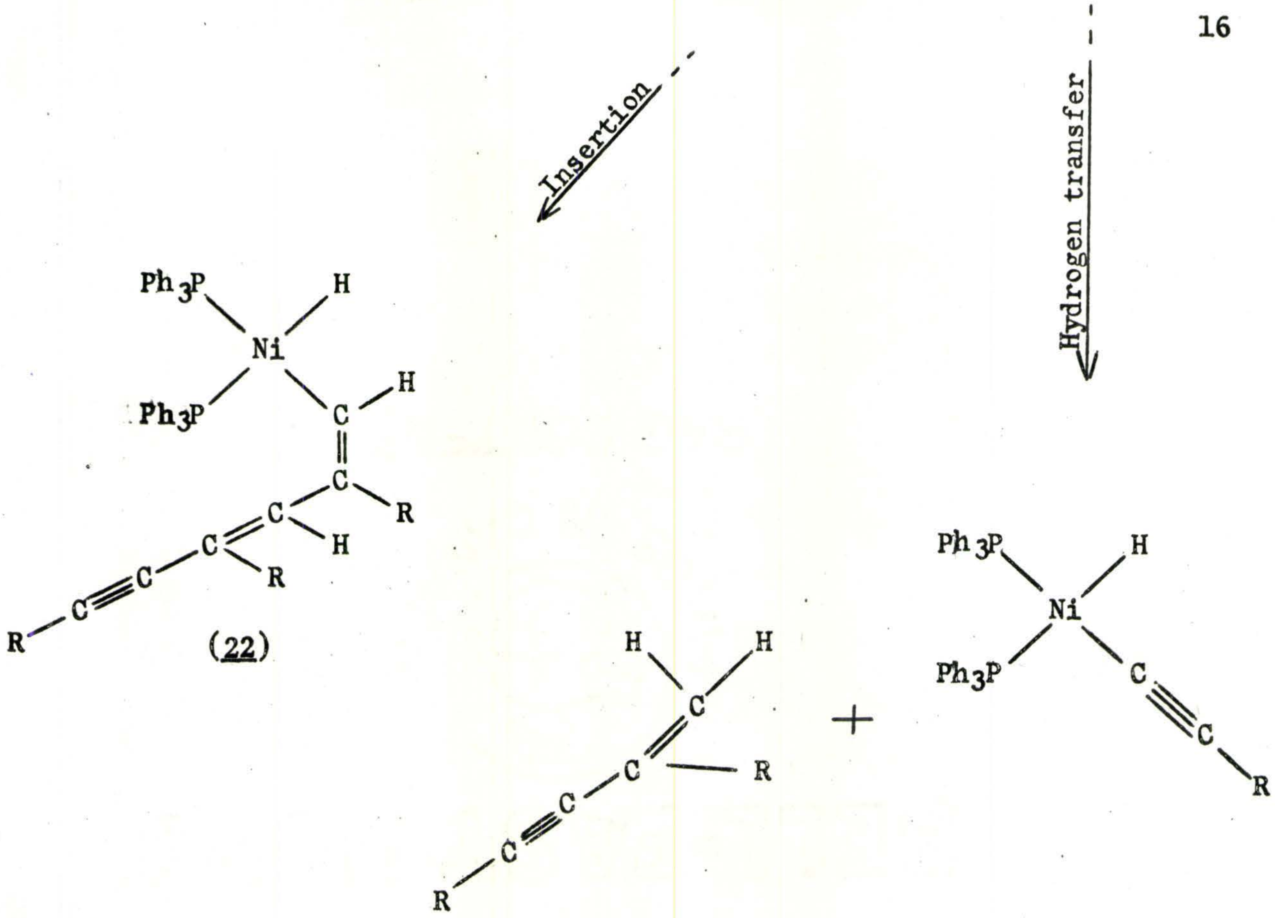
Meriwether et. al.[53] made a detailed study of the scope and products of this reaction. They found that the preferential formation of cyclic or linear products was mainly determined by the nature of the substituent at the triple bond. As the bulk of this substituent was increased the proportion of aromatic products decreased.

In all cases an induction period of 10 to 30 minutes was required before the reaction started. Polymerization was found to be significantly slower if the catalyst solution was not agitated, or if it was saturated with carbon monoxide. It appeared therefore that an "active" catalyst was formed during the induction period by the loss of carbon monoxide. It was suggested that during this time both carbon monoxide molecules were lost from a given nickel atom, so that in a molecule of the "active" catalyst two of the four co-ordination positions were vacant and capable of being filled by an acetylene molecule. That the phosphines were still attached to the nickel atom in the "active" complex was shown by the great dependence of polymerization rate upon the nature of the phosphine.

With the exception of 2-butyne-1,4-diol, disubstituted acetylenes were not polymerized by this catalyst. This indicated that hydrogen transfer could be an important step in the reaction. It was found however, that pre-treatment of the catalyst (19) with a disubstituted acetylene greatly enhanced the rate of catalytic polymerization of those acetylenes which could normally be polymerized.

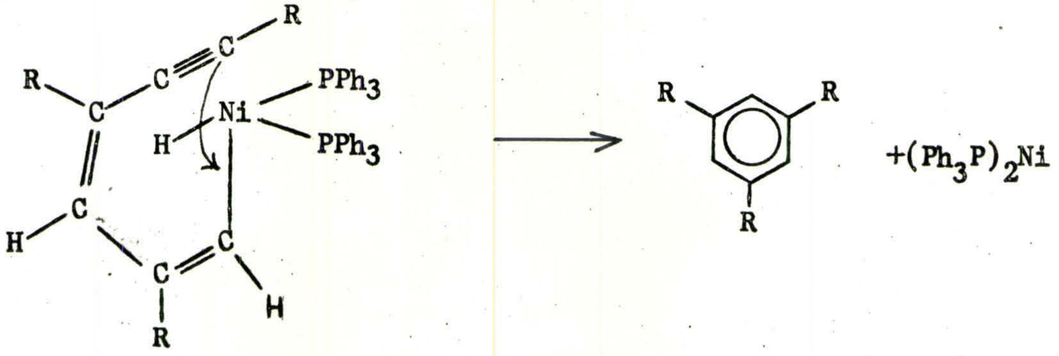
Meriwether et. al. proposed the "active" catalyst to consist of several nickel-phosphine-acetylene complexes in equilibrium with one another. It was suggested that complex (21) was actually responsible for both the linear and cyclic polymerization of acetylene itself and of monosubstituted acetylenes:





(22)

Aromatization can be readily incorporated into the above scheme by assuming that there is a favoured conformation of (<u>22</u>), in which the 1- and 6-carbon atoms of the butadienyl acetylenyl group can approach bonding distance. A concerted hydrogen transfer and ring closure would then give the aromatic product:



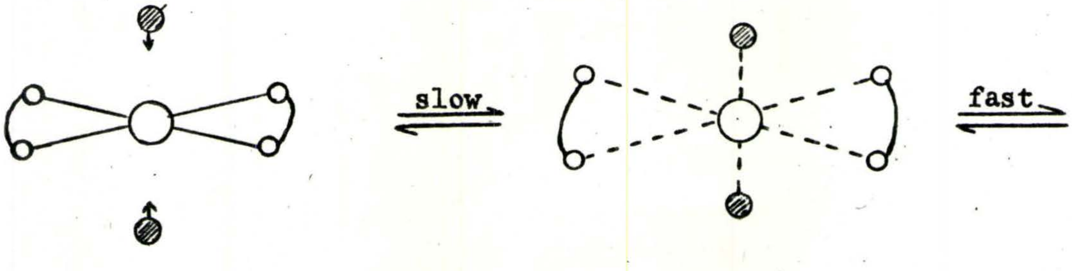
(22)

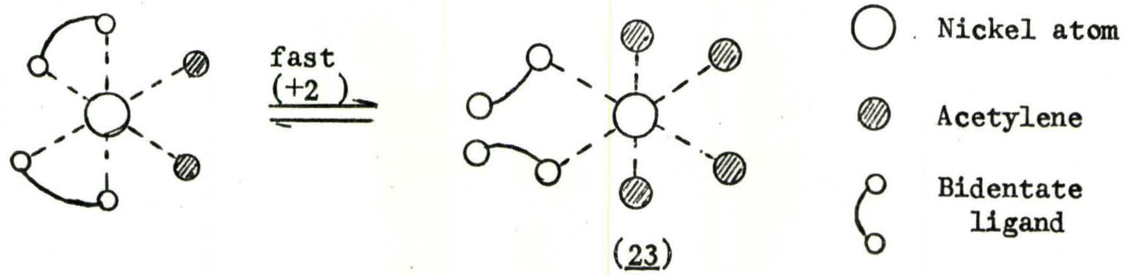
Reppe et. al.[54] discovered that on a different type of nickel catalyst, acetylene was tetramerized to cyclooctatetraene in 70% yield. The synthesis of this compound had previously been very laborious, and this new and highly selective synthetic route attracted much attention. Nickel(II) complexes, such as the acetylacetonate, cyanide and salicylaldehydate were originally used as catalysts, but it was later found[56] that a number of nickel(0) complexes were also active.

In contrast to Meriwether's stepwise polymerization process, Schrauzer[55] proposed that the tetramerization to form cyclooctatetraene (24) proceeds via an intermediate as show below (23).

It was noted that the only complexes which were catalytically active were those which underwent ligand exchange reactions fairly readily, and the highest yields of cyclooctatetraene were obtained with these complexes in moderately polar complexes such as dioxan; benzene gave poor yields, and solvents which co-ordinate strongly, such as pyridine, stopped the reaction completely.

It was concluded that the rate-determining factor in the reaction was the cleavage of the metal-ligand bonds, to make four vacant co-ordination sites available. These could then be occupied by acetylene molecules, which in the resulting approximately octahedral complex could assume a configuration which would favour the formation of cyclooctatetraene. The reaction scheme suggested by Schrauzer et. al., is shown below:

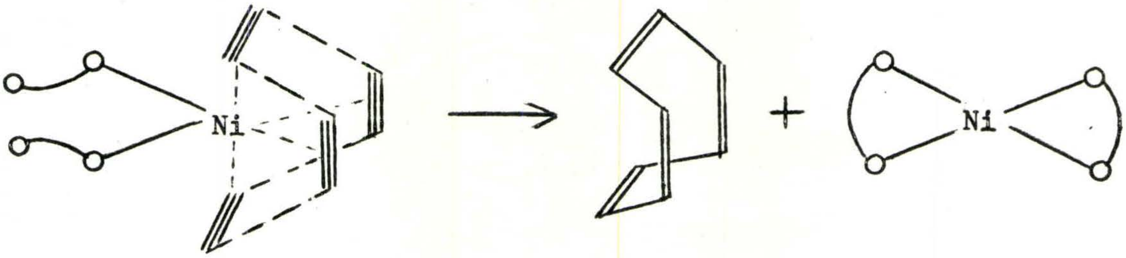




(23)

If the four acetylene molecules in (23) are oriented as shown, the formation of cyclooctatetraene can be readily visualized:

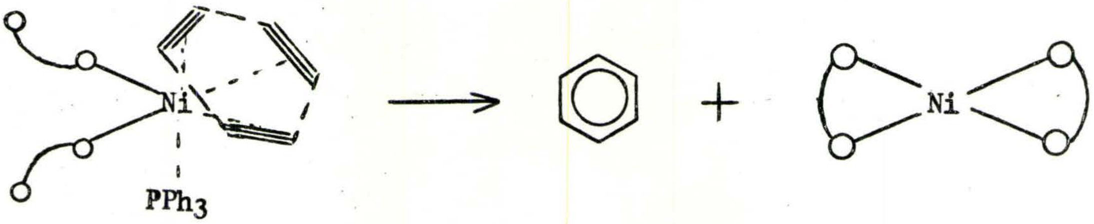
(23) (24)



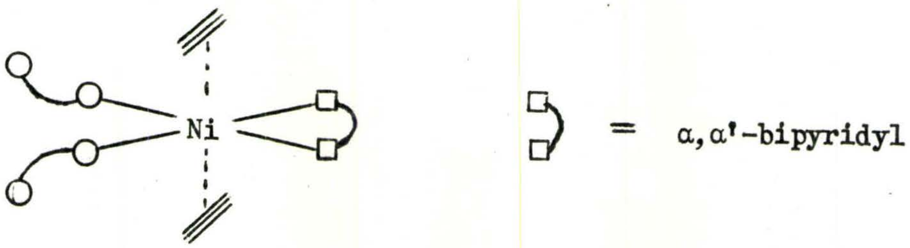
Since the rate of formation of cyclooctatetraene is controlled by a slow ligand-exchange process, no evidence regarding the nature of the transition state can be gained from kinetic measurements. However, the addition of one mole of triphenylphosphine to the catalyst completely inhibited the formation of cyclooctatetraene, only benzene was obtained.

It was suggested that only three co-ordination sites were then available, the fourth being occupied by triphenylphosphine:

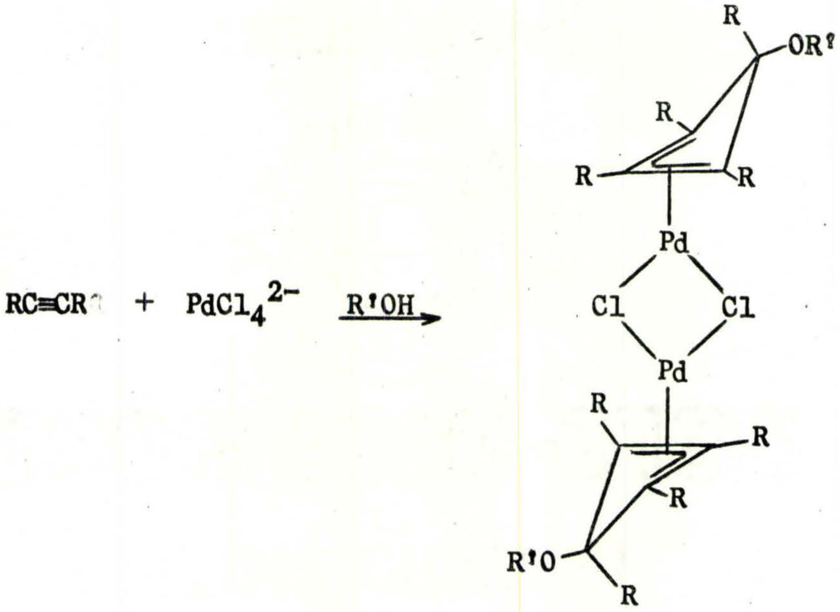
(25)



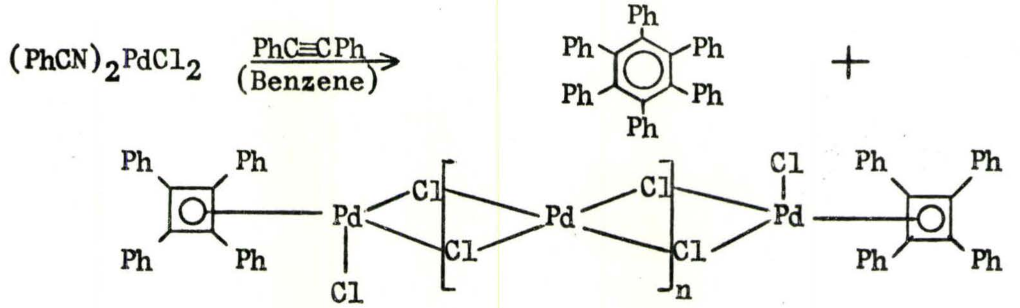
Further, it was found that strongly co-ordinating ligands which blocked two cis- positions e.g., $\alpha - \alpha' -$ bipyridyl, completely inhibited any reaction, and it was suggested that the situation as in (26) obtained:



A number of palladium compounds are also found to polymerise acetylenes e.g., Malatesta et. al.,[57] showed that in ethanol, diphenylacetylene is dimerized by palladium chloride, to give a dichloroethoxytetraphenylcyclobutenyl dimer (27).



Acetylenes may also be trimerized by palladium(II) complexes: Blomquist and Maitlis[58] found that in benzene diphenylacetylene was polymerized by dichlorobis(benzonitrile)palladium to hexaphenylbenzene. The catalyst was slowly deactivated by the formation of a tetraphenylcyclobutadienepalladium complex (28):



It was recently found that palladium(II) catalysts also dimerized olefins.[59]

Other catalysts for the polymerization of acetylenes have been reported (for a recent review see Reference 60), but in general little is known about the mechanisms of the reactions. Mechanistic study is often difficult since the reactions may give complex mixtures of products, or proceed very rapidly and exothermically, or they may have to be carried out under heterogeneous conditions. These considerations apply particularly to the palladium(II) catalysed polymerization of acetylenes to give cyclobutadiene complexes.

Purpose of current work

In the hope of shedding light on the mechanism of the palladium-catalysed polymerizations of acetylenes, it was decided that the preparation of palladium-acetylene complexes would be attempted, and their reactions studied. Complexes of the type $[(R_3P)_2M(ac)]$ had been reported for platinum and (without details) for nickel, and it seemed probable that their methods of preparation could be extended to the palladium analogues.

When this work was started, the platinum-acetylene complexes had not been examined by X-rays, and little physical data had been published on them. By the preparation and determination of such data for a series of analogous metal-acetylene complexes of the nickel sub-group it was hoped that further insight into bonding in the complexes could be obtained, as a prelude to more detailed examination of their chemistry.

RESULTS

RESULTS

1. Preparation of complexes

Acetylene-bis(triphenylphosphine)-nickel complexes were prepared by a modification of Wilke's method[5] (see page 11), substituting the more readily available triethylaluminum for diethylaluminum ethoxide. This was slowly added to an ethylene saturated ethereal solution of bis(acetylacetonato)nickel(II) and triphenylphosphine (mole ratio 1:2) at 0°C, and the mixture stirred for at least six hours. Care was taken to thoroughly wash the resulting ethylene complex with ether before adding an acetylene, otherwise polymerization, especially in the case of hexafluoro-2-butyne, was found to occur.

The complexes of diphenyl- and methylphenyl-acetylene were very air-sensitive and too unstable for elemental analysis. Attempts to prepare the dimethyl acetylenedicarboxylate complex gave an unidentified yellow compound. However, hexafluoro-2-butyne gave a more stable bright yellow crystalline complex. In the solid,this changed colour (to a pale green) only after exposure to air for several hours.

Attempts to prepare bis(trialkylphosphine)-nickel-acetylene complexes were all unsuccessful. The previously reported ethylenebis(tri-n-butylphosphine)nickel[5] is obtained as an air sensitive oil. With acetylenes this gave gums or oils which could not be crystallized or purified without decomposition. The relatively stable ethylenebis(tricyclohexylphosphine) nickel gave a gum with hexafluoro-2-butyne, and trimerized diphenylacetylene to hexaphenylbenzene.

Bis(triphenylphosphine)palladium-acetylene complexes could not be prepared by a method analogous to that used in the preparation of the nickel complexes; addition of small amounts of triethylaluminum to bis(acetylacetonato)palladium(II) and triphenylphosphine (mole ratio 1:2) gave tetrakis(triphenylphosphine)palladium. Further addition of triethylaluminum caused the deposition of metallic palladium.

Attempts to prepare the complexes by the hydrazine reduction of dichlorobis(triphenylphosphine)palladium, in the presence of the acetylene, led to the precipitation of palladium or the formation of gums. By analogy with the platinum complexes, a plausible intermediate in the reaction is $(Ph_3P)_2Pd$ (28); it is probable that this species is very unstable and decomposes under the reaction conditions required for its preparation. An attempt to prepare (28) under milder conditions (0°C, ether solvent) by hydrazine reduction of peroxybis(triphenylphosphine) palladium, $[(Ph_3P)_2PdO_2]$ was also unsuccessful.

Some acetylenes bearing electronegative substituents (e.g. $-CF_3$ or $-COOCH_3$) replaced two molecules of triphenylphosphine in tetrakis(triphenylphosphine)palladium to give the acetylene complexes. Other acetylenes (e.g. $PhC{\equiv}CPh$, $PhC{\equiv}CMe$ and $p\text{-}NO_2C_6H_4C{\equiv}CC_6H_4p\text{-}NO_2$) did not give isolable complexes.

The analogous bis(trialkylphosphine)-palladium-acetylene complexes were prepared in a similar manner, but without isolation of the intermediate $(R_3P)_4Pd$.

Platinum complexes of the type $[(Ph_3P)_2Pt(ac)]$ (7) were prepared by Chatt's method [17,31], by the hydrazine reduction of an ethanolic suspension of cis-dichlorobis(triphenylphosphine)platinum. Complexes of acetylenes bearing electronegative substituents were also prepared by the displacement of two molecules of triphenylphosphine from tetrakis(triphenylphosphine)platinum. Attempts to extend these preparations to the analogous bis(trialkylphosphine)platinum-acetylene complexes were unsuccessful; the hydrazine reduction of cis-dichlorobis(tri-n-butylphosphine)platinum at 30°C gave a water-soluble oil which was probably $[(Bu^n_3P)_2Pt(H_2NNH_2Cl]Cl$[61]. It was found, however, that potassium tetrachloroplatinate and tri-n-butylphosphine reacted smoothly in ethanolic potassium hydroxide, presumably to give $(Bu^n_3P)_4Pt$; subsequent addition of hexafluoro-2-butyne gave the acetylene complex. Bis(trialkylphosphine)-platinum-dimethyl acetylenedicarboxylate complexes could not be isolated.

2. Infrared spectra

The infrared spectra of all the complexes prepared in this work were recorded (Appendix I). Of particular interest are the triple bond stretching frequencies for the co-ordinated acetylenes, and these are listed in Table I. For comparison purposes the reported values of $\nu_{C\equiv C}$ for complexes of hexafluoro-2-butyne and dimethyl acetylenedicarboxylate are listed in Tables II and III respectively.

TABLE I

Triple bond stretching frequencies* for acetylene complexes of nickel, palladium and platinum.

Complex	$\nu_{C\equiv C}$ (cm.$^{-1}$)		
	Ni	Pd	Pt
$(Ph_3P)_2M(PHC_2Ph)$	1800^a	–	1768, 1740^b
$(Ph_3P)_2M(PhC_2Me)$	1795^a	–	1756^b
$(Ph_3P)_2M(CF_3C_2CF_3)$	1790^c	1838, 1811^b	1775^b
$(Ph_3P)_2M(CCOOCH_3)_2$	–	1845, 1830(sh)^b	1782, 1765(sh)^b
$(PhMe_2P)_2M(CF_3C_2CF_3)$	–	1837, 1800^b	1767^b
$(Bu^n{}_3P)_2M(CF_3C_2CF_3)$	–	1837, 1795^b	1758^b

Where a doublet was observed, the stronger band is underlined.

sh = shoulder

a = Nujol mull

b = solution

c = KBr. disc

* Recorded on a Perkin Elmer 521 Spectrophotometer.

TABLE II

Triple bond stretching frequencies in hexafluoro-2-butyne-M

Compound	$\nu_{C\equiv C}$ (cm.$^{-1}$)	Reference
$CF_3C{=}CCF_3$	2300(Raman)	62
$(\pi\text{-}C_5H_5)Mn(CO)_2C_4F_6$	1919(solution)	23
$(Ph_3P)_2RhCl\ C_4F_6$	1917(mull)	26
$(\pi\text{-}C_5H_5)_2VC_4F_6$	1800 -	18
$(Ph_3P)_2Ir(CO)ClC_4F_6$	1773(mull)	27
$(Ph_3P)_2PdC_4F_6$	1838,1811(solution)	-
$(Bu^n{}_3P)_2PdC_4F_6$	1837,1795(solution)	-
$(Ph_3P)_2NiC_4F_6$	1790(solution)	-
$(Ph_3P)_2PtC_4F_6$	1775(solution)	-
$(Bu^n{}_3P)_2PtC_4F_6$	1758(solution)	-

TABLE III

Triple bond stretching frequencies in dimethyl acetylenedicarboxylate complexes.

Compound	(cm.$^{-1}$)	Reference
$(Ph_3P)_2IrCl(CCOOCH_3)_2$	1855(KBr. pellet)	28
$(Ph_3P)_2Pd(CCOOCH_3)_2$	1845,1830(solution)	-
$(Ph_3P)_2Pt(CCOOCH_3)_2$	1782,1765(solution)	-
$(\pi\text{-}C_5H_5)_2V(CCOOCH_3)_2$	1821 - -	17
$(Ph_3P)_2Ir(CO)Cl(CCOOCH_3)_2$	1770(KBr. pellet)	28

3. Nuclear magnetic resonance (n.m.r.) spectra

The proton magnetic resonance spectrum of complexes of the type $[(Ph_3P)_2M(PhC_2Ph)]$ showed only a complex resonance at ca. 2.5τ due to phenyl protons. However the 60 mc. ^{1}H n.m.r. spectrum of methylphenylacetylenebis(triphenylphosphine)platinum (29) both in benzene and in chloroform solution, (Appendix III) showed a multiplet at 2.7τ (phenyl protons), and a doublet centred at 7.88τ due to methyl protons coupling with a phosphorus (J_{P-H}=6.2 cps.). Two pairs of satellite peaks due to coupling of the methyl protons with ^{195}Pt ($I = \frac{1}{2}$, 34% abundance) were also observed (J_{Pt-H}=41.5 cps.). The spectrum in chloroform solution was complicated by the appearance of an additional peak which was shown to be due to free methylphenylacetylene. The 100 mc. spectrum of (29) in chloroform - methylene chloride solution at 22.5°C (Appendix III) showed the same coupling constants, but in addition, the resonances noted above were further split into symmetrical doublets due to coupling with the second phosphorus ($J_{P'-H}$=ca. 1.2 cps.). Since it is generally agreed that trans-couplings in octahedral or square-planar complexes are larger than cis-couplings[63,64], the larger J_{P-H} couplings are assigned to coupling with the trans-phosphorus, and the smaller $J_{P'-H}$ to coupling with the cis-phosphorus.

A similar result was obtained with methylphenylacetylenebis(triphenylphosphine)nickel, the 60 mc. spectrum of which was examined in benzene at 34°C (Appendix III). The methyl protons are shown as a symmetrical doublet centred at 7.86τ (J_{P-H}=4.5 cps.), and again each resonance appears to be further split into a doublet ($J_{P'-H}$=ca. 1 cps.) due to coupling with the cis-phosphorus.

In order to determine if cis-coupling could also be observed in σ-alkylbis(triphenylphosphine)platinum complexes, the 60 mc. and 100 mc. ^{1}H n.m.r. spectrum of dimethylbis(triphenylphosphine)platinum was measured (Appendix IV). The methyl resonances occurred as a quartet at 9.63τ with two satellite quartets on either side due to coupling with ^{195}Pt (J_{Pt-H}=69 cps.). Thus, cis-coupling is observed, but the spectrum is not susceptible to first order analysis; it is an example of an $AA'MX_3X'_3$ system. Due to the limited solubility of the complex, and to the fact that further significant peaks may be hidden under the noise or under the satellite peaks, calculation of cis- and trans- P-H coupling constants was not attempted. However, they appeared to be of comparable magnitude to each other.

The 56.4 mc. ^{19}F n.m.r. spectra of $[(Ph_3P)_2M(CF_3C_2CF_3)]$ (30), (M = Ni, Pd and Pt) were also measured. The spectrum of hexafluoro-2-butynebis(triphenylphosphine)platinum (30,M=Pt) in benzene at 30°C showed a doublet centred at 10.4 ppm. on the low-field side of benzotrifluoride (internal standard) due to fluorine-phosphorus coupling (J_{P-F}=10.2 cps.). Two pairs of satellite peaks due to coupling of the fluorine with ^{195}Pt were also observed (J_{Pt-F}=64 cps.) The n.m.r. spectrum of (30,M=Pt) was also run in methylene chloride at 30°C. (J_{P-F}=10.3 cps., J_{Pt-F}=66 cps.). The coupling constants did not change on cooling the solution to -60°C, nor were the peaks further split.

The ^{19}F n.m.r. spectrum of hexafluoro-2-butynebis(tri-n-butylphosphine)platinum (31) (Appendix VI) similarly showed a doublet centred at 8.8 ppm. on the low-field side of benzotrifluoride (J_{P-F}=10.8 cps.), with two pairs of satellite peaks due to ^{195}Pt-F coupling (J_{Pt-F}= 67 cps.).

The spectrum of hexafluoro-2-butynebis(triphenylphosphine)nickel (30,M=Ni) in benzene at 30°C showed only a doublet centred at 10.6 ppm. on the low-field side of benzotrifluoride due to coupling with ^{31}P (J_{P-F}=6.1 cps.). Similarly the analogous palladium complex (30,M=Pd) showed a doublet centred at 10.7 ppm. from benzotrifluoride (J_{P-F}=11.2 cps.). In view of the magnitude of these P-F couplings they are assigned to coupling with the trans-phosphorus. Cis-P-F couplings could not be detected.

4. Reactions of methylphenylacetylenebis(triphenylphosphine)platinum (29)

(i) Oxygen

Oxygen was found to displace methylphenylacetylene from complex (29) in benzene solution, to give peroxybis(triphenylphosphine)platinum (32), identified by comparison of its i.r. specturm with that reported by Cook and Jauhal[7]. A dark red oil was also obtained from this reaction, the infrared spectrum of which suggested that it was a mixture of free methylphenylacetylene and unreacted complex (29). However, methylphenylacetylene could not be detected in the vapour phase chromatogram of the oil. The presence of carbonyl containing material could not be detected in the infrared spectrum of the oil.

(ii) Carbon monoxide

Carbon monoxide reacted rapidly with a benzene solution of (29) at 25°C, to give a dark red solution, from which was isolated dicarbonylbis(triphenylphosphine)platinum, identified by comparison of its i.r. spectrum with that reported by Cariati and Ugo[65]. The vapour phase chromatogram of the remaining solution showed only the presence of benzene and methylphenylacetylene.

Carbon monoxide was also found to displace diphenylacetylene from diphenylacetylenebis(triphenylphosphine)nickel, to give dicarbonylbis(triphenylphosphine)nickel (19).

(iii) Sulphur dioxide

In benzene solution at 25°C, sulphur dioxide was found to react readily with complex (29) to give the brown crystalline complex $[(Ph_3P)_2PtSO_2\cdot SO_2]$, identified by comparison of its i.r. spectrum with that reported in the literature[66]. When washed with methanol, one mole of sulphur dioxide was lost to give the bright green complex $[(Ph_3P)_2PtSO_2]$.[66]

Reaction of (29) with sulphur dioxide, in liquid sulphur dioxide solvent,[67] gave a brown solid. Chromatography of a chloroform solution of this solid gave the unreacted complex (29), and a yellow, unstable oil. The infrared spectrum of this oil showed bands at 1190 and 1040 $cm.^{-1}$, characteristic of co-ordinated sulphur dioxide.[66,68]

(iv) Hydrogen

Hydrogen was found to react fairly slowly with (29) in benzene at 25°C. Thus although the pale yellow colour of the solution had changed to a deep red after only ten minutes, the n.m.r. spectrum of the reaction mixture after 12 hours still showed the presence of appreciable quantities of the starting material (29).

(v) Chloroform

Chloroform was found to react with (29) in benzene solution at 25°C to give a 70% yield of chlorodichloromethylbis(triphenylphosphine)-platinum(II) (33). The presence of free methylphenylacetylene was shown by n.m.r. spectroscopy when the reaction was carried out in deuterochloroform.

DISCUSSION

DISCUSSION

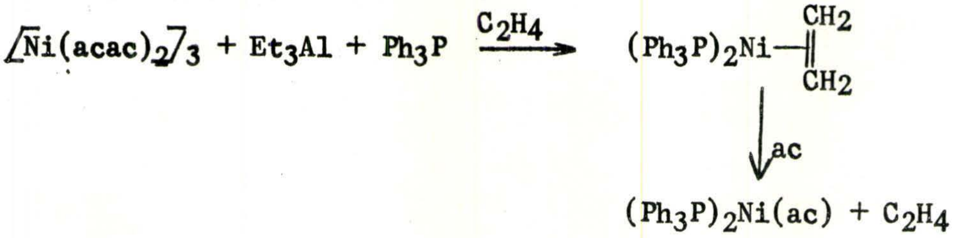
I. Preparation of Complexes

The bis(triphenylphosphine)platinum-acetylene complexes were prepared by the method of Chatt. However, attempts to prepare other bis(R_3P)-platinum-acetylene complexes (where $R_3P = Bu^n{}_3P$ or Me_2PhP) by this method were unsuccessful. Complexes of this type, and also the palladium complexes $[(R_3P)_2Pd(ac)]$ ($ac = CF_3C_2CF_3$, $R_3P = Ph_3P$, $Bu^n{}_3P$ and $PhMe_2P$; $ac = MeOOCC_2COOMe$, $R_3P = Ph_3P$) were prepared from $(R_3P)_4M$ by reaction with the appropriate acetylene:

$$(R_3P)_4M \ + \ ac \ \longrightarrow \ (R_3P)_2M.ac \ + \ 2R_3P.$$

It was found that only those acetylenes bearing strongly electron-withdrawing susbtituents (such as CF_3 or $COOCH_3$) replaced the phosphines in the complexes. The intermediate complexes $(R_3P)_4M$ were isolable as crystalline solids when R = Ph, M = Pd[69] and Pt[70]. In the cases where $R_3P = Bu^n{}_3P$ or Me_2PhP no attempts were made to isolate the tetrakis-complexes, and they were prepared and reacted with the acetylenes in situ. The complexes $(Bu^n{}_3P)_4Pt$ and $(Me_2PhP)_4Pt$ were prepared by the treatment of potassium tetrachloroplatinate with ethanolic potassium hydroxide in the presence of excess R_3P. $(Bu^n{}_3P)_4Pd$ and $(Me_2PhP)_4Pd$ were prepared by the hydrazine reduction of the appropriate $[(R_3P)_2PdCl_2]$ in the presence of excess R_3P. $(Ph_3P)_4Pd$ was most conveniently obtained by triethylaluminum reduction of bis(acetylecetonato)palladium(II) in the presence of excess triphenylphosphine. Only in the latter case was $(R_3P)_4Pd$ isolated before reaction with acetylenes.

The nickel complexes $[(Ph_3P)_2Ni(ac)]$ were prepared from π-ethylenebis(triphenylphosphine)nickel, which itself was obtained by the triethylaluminum reduction of bis(acetylacetonato)nickel(II) in the presence of triphenylphosphine and ethylene:



$$[\mathrm{Ni(acac)_2}]_3 + \mathrm{Et_3Al} + \mathrm{Ph_3P} \xrightarrow{C_2H_4} (\mathrm{Ph_3P})_2\mathrm{Ni}-\overset{\mathrm{CH_2}}{\underset{\mathrm{CH_2}}{\|}}$$

$$\big\downarrow \mathrm{ac}$$

$$(\mathrm{Ph_3P})_2\mathrm{Ni(ac)} + \mathrm{C_2H_4}$$

Methylphenyl-, diphenyl- and bis(trifluoromethyl)-acetylenes all gave the appropriate acetylene complexes when treated in this way. However the first two gave very unstable complexes which could not be analysed. Attempts to prepare the nickel-acetylene complexes $(R_3P)_2Ni(ac)$ where $R_3P = Bu^n{}_3P$, Me_2PhP and $(C_6H_{11})\cdot P$ were unsuccessful.

These restrictions on the scope of the preparative methods for acetylene complexes of nickel and palladium severely hindered our attempts to fill the gaps in Table I; only the series $[(Ph_3P)_2M(CF_3C_2CF_3)]$, (M = Ni, Pd and Pt) could be prepared. However the indications are that other members of the series would have the properties we would predict on the basis of our results with the series $[(Ph_3P)_2M(CF_3C_2CF_3)]$

II. Infrared Spectra

The infrared stretching frequency of the co-ordinated acetylenic bond has been used as a criterion for the assignment of structures to acetylene complexes. Two assumptions must be made in making such assignments:

(i) The simple harmonic group frequency approximation holds well.

(ii) The bond-order about the acetylenic carbon atoms remains constant (and equal to four). Then, any decrease in the order of the acetylenic bond is accompanied by an equivalent increase in the order of the metal-acetylene bond.

From Table I it can be seen that for a given acetylene and a given metal, a change from triphenylphosphine to dimethylphenylphosphine to tri-n-butylphosphine leads to a lowering in $\nu_{C\equiv C}$. On the above assumptions this is taken to indicate that the metal-acetylene bond is stronger in the tri-n-butylphosphine- than in the triphenylphosphine-complexes. This may be interpreted as follows: tri-n-butylphosphine is generally regarded as a better electron donor but a poorer electron acceptor than triphenylphosphine. The electron density at the metal atom is therefore greater in $(Bu^n_3P)_2M(ac)$ than in $(Ph_3P)_2M(ac)$. This in turn increases the degree of back-bonding from the filled metal d orbitals to the vacant π^* antibonding orbitals, and hence increases the strength of the metal-acetylene bond.

Upon the somewhat limited evidence available, (due to the preparative difficulties described above), Table I also shows that for a given phosphine and a given acetylene, the decrease in $\nu_{C\equiv C}$ is greater for complexes of platinum than for nickel than for palladium. This may be taken to indicate that the metal-acetylene bond strength is in the order $Pt > Ni > Pd$. This result is surprising in view of the well established[71] order of carbon-metal bond strengths for primarily σ-bonded complexes; $Pt > Pd > Ni$.

A possible explanation of the observed order in the acetylene complexes is that the bonding arises from two superimposed types. One type of bonding, described classically by a three-membered σ-bonded "metallo-cyclopropene" ring would give the bond strength order $Pt > Pd > Ni$. The second type of bonding, described by a π-bonded structure, would depend on the ability of the metal to back-bond. Since nickel appears to be better able to back-bond than palladium or platinum (viz. the non-existence of the tetracarbonyls $Pd(CO)_4$ and $Pt(CO)_4$ in contrast to the well known $Ni(CO)_4$), this might well account for the observed inversion of stability of nickel and palladium. However, a similar stability sequence has also been observed in $\nu_{c=c}$[76] for complexes of the type [olefin $M(CO)_4$], where M=W>Cr>Mo, and so these results may reflect the existence of a general trend throughout the transition series.

Unfortunately conclusions regarding the order of bond strengths in the acetylene complexes cannot be readily checked by experiment. The platinum complexes are the least susceptible to aerobic decomposition both in the solid and in solution, but this could reflect kinetic rather than thermodynamic stability. A more reliable conclusion would be provided by a measure of the metal-acetylene bond strengths, for example by measurement of the appearance potential of the non-acetylenic fragment in the mass spectra of the complexes.

III. Nuclear Magnetic Resonance Spectra

The observation of both cis- and trans- coupling in the nickel and platinum complexes of methylphenylacetylene implies that the rate of rotation of the acetylene about the metal-acetylene axis is slow on the n.m.r. time scale (less than approx. 1.2 sec^{-1})[72], that this process therefore has a fairly high activation energy and that the molecule is constrained to an approximately planar geometry even in solution.

In contrast the ^{19}F n.m.r. spectra of the hexafluoro-2-butyne complexes $[(R_3P)_2M(CF_3C_2CF_3)]$ all showed a symmetrical doublet with (J_{P-F} ca. 10 cps.) This is not compatible with free rotation of the acetylene about the metal-acetylene axis (which should give rise to a triplet due to coupling of the fluorines with two equivalent phosphorus atoms). It is possible that the observed coupling is J_{P-F}-trans and that cis-P-F coupling is small and not observable.

Another explanation is that these are further examples of "deceptively simple spectra", and that the additional fine-structure to be expected of A_2X_6 or A_2MX_6 systems may be hidden under the noise. However, it is clear that, in solution, the complexes $[(R_3P)_2MCF_3C_2CF_3]$ must have a planar (or nearly planar) arrangement of the two phosphorus, the metal and the acetylenic carbon atoms.

IV. Nature of the Material Obtained from Reaction of $(Ph_3P)_2Ni(CO)_2$,(19) and RC≡CR.

An attempt was made to obtain some evidence for Meriwether's postulate that pretreatment of dicarbonybis(triphenylphosphine)nickel (19) with disubstituted acetylenes led to the formation of a complex $[(Ph_3P)_2Ni(ac)]$. Thus, complex (19) was reluxed in benzene with diphenylacetylene for 12 hours. Extensive decomposition occurred and the experiment was inconclusive.

Complex (19) was also reacted with hexafluoro-2-butyne in benzene at 25°C. The infrared spectrum of the reaction mixture was recorded during the course of the reaction; the bands at 1975-1995 cm.$^{-1}$, associated with (19) gradually decreased in intensity, while new bands appeared at 2055 cm.$^{-1}$ and 1855 cm.$^{-1}$.

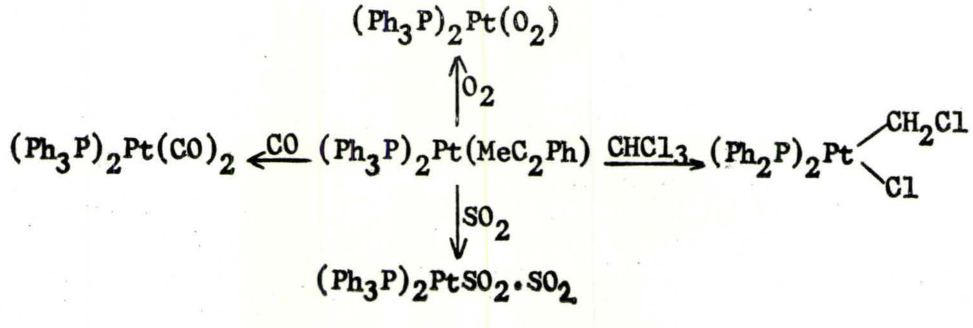
Assignment of the bands is open to question. A likely interpretation is that the band at 2055 cm.$^{-1}$ is best assigned to a metal carbonyl stretching frequency, and that at 1855 cm.$^{-1}$ (which is much weaker) is

best assigned to $\nu_{C\equiv C}$ of co-ordinated hexafluoro-2-butyne.
(c.f. $(Ph_3P)_2Ni(CF_3C_2CF_3)$; $\nu_{C\equiv C} = 1790$ cm.$^{-1}$)

It seems, therefore, that one mole of carbon monoxide per mole of (<u>19</u>), rather than two, is replaced by one mole of hexafluoro-2-butyne. However work-up of the reaction mixture gave no carbonyl-containing material. The isolation of hexakis(trifluoromethyl)benzene was contrary to the findings of earlier workers[73] and was surprising in view of the general inertness of disubstituted acetylenes to catalytic polymerization by (<u>19</u>).

V. <u>Reactions</u>

Oxygen, carbon monoxide, sulphur dioxide and chloroform were found to readily displace methylphenylacetylene from methylphenylacetylene-bis(triphenylphosphine)platinum in benzene solution. The complexes which were isolated from the reactions viz. $[(Ph_3P)_2PtO_2]$, $[(Ph_3P)_2Pt(CO)_2]$, $[(Ph_3P)_2PtSO_2 \cdot SO_2]$ and $[(Ph_3P)_2PtCl \cdot CHCl_2]$ were the same as those isolated from the reaction of these reagents and $[(Ph_3P)_2Pt]$. It seems probable therefore, that the first step in the reaction is dissociation of the co-ordinated acetylene to give $[(Ph_3P)_2Pt]$. The reactions are summarised below:



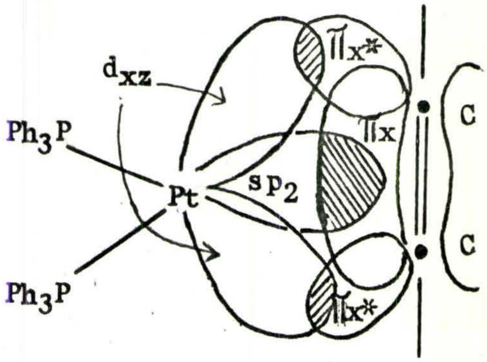
$$\begin{tikzcd}
 & (Ph_3P)_2Pt(O_2) & \\
(Ph_3P)_2Pt(CO)_2 & (Ph_3P)_2Pt(MeC_2Ph) \arrow[l, "CO"'] \arrow[u, "O_2"'] \arrow[r, "CHCl_3"] \arrow[d, "SO_2"] & (Ph_2P)_2Pt(CH_2Cl)(Cl) \\
 & (Ph_3P)_2PtSO_2 \cdot SO_2 &
\end{tikzcd}$$

Evidence for reaction between the displacing ligand and methylphenylacetylene could not be obtained, although only in the case of the reactions with chloroform and carbon monoxide could the displaced acetylene be detected by either vapour phase chromatography or proton magnetic resonance spectroscopy. The reaction with hydrogen was inconclusive and requires further study.

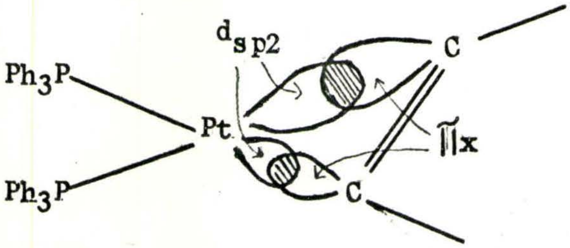
CONCLUSION

CONCLUSIONS

As discussed in the introduction, Chatt suggested that there were two possible ways of describing the structure of, and bonding in complexes of the type $[(R_3P)_2M(ac)]$, which may be represented by (A) and (B).



(A)



(B)

Tables II and III show that considerable variation exists in the co-ordinated triple bond stretching frequencies for a given acetylene; e.g., for hexafluoro-2-butyne values cover the range 1919-1758 cm.$^{-1}$. The Chatt picture of the bonding in metal-acetylene complexes would suggest that this is due to a gradual change in bond type from (A) to (B), with no clear demarcation between the two.

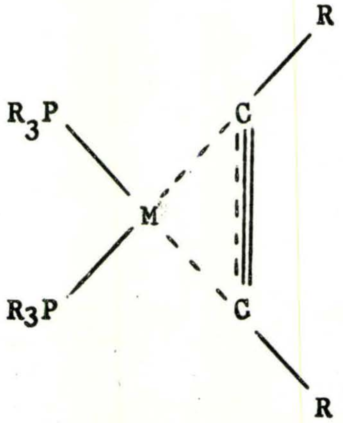
A third possibility is that the bonding in all the acetylene complexes is best described as consisting of a bond of σ-symmetry (involving the acetylenic π-orbital and a vacant metal orbital) and one of π-symmetry (involving the vacant acetylenic π^* orbital and a filled metal orbital). The differences in the orientation of the acetylene which are observed in the crystal structures could be due to the geometries of the molecule concerned. Thus, only those acetylenes bearing very bulky substituents form complexes of the type $[PtCl_3(ac)]$, and it is possible that the acetylene is sterically constrained to be perpendicular to the plane of the molecule. The latter model has the advantage that only one type of bonding need be invoked to describe all the mononuclear acetylene complexes. It can account for the spectrum of $\nu_{C\equiv C}$ observed for different complexes solely in terms of the extent of the "donation" and "back-donation" interactions between the acetylene and the metal. The crystal structure of the complex $[(Ph_3P)_2Pt(PhC_2Ph)]$ (7, R =Ph) would not be in conflict with this. Although the platinum-carbon distances of 2.06Å and 2.01Å are similar to those found for Pt-C in σ-bonded complexes, they are still only a little shorter than the Pt-C bonds in olefin-platinum(II) complexes, while the non-linearity of the acetylene can be attributed to the population of the π^* orbitals, which has the effect of bending the carbon-phenyl bonds away from the metal.

The lability of the acetylenes in the complexes (7), is illustrated by the equilibrium studies on the reaction:

$$(Ph_3P)_2Pt(ac) + (ac)' \rightleftharpoons (Ph_3P)_2Pt(ac)' + (ac)$$

This lability would appear to support a system in which the acetylene is π-bonded, rather than σ-bonded, to the metal atom. On the other hand, if the acetylene were π-bonded to the metal it should exert a large trans effect, manifest by an increased P-Pt bond length. The observed lengths in (7, R =Ph) of 2.27 and 2.28Å are, however, typical of those found in several platinum complexes where a trans effect is inoperative e.g. $[(Ph_3P)_3Pt]$,[77] (2.25-2.28Å) and trans-$[(Et_3P)_2PtHBr]$,[78] 2.26Å.

In view of the difficulty in devising an experiment to decide between these possibilities perhaps the best representation for the complexes would be:



EXPERIMENTAL

EXPERIMENTAL

Experimental Procedures

Melting points

These were determined using a Thomas Hoover capillary melting-point apparatus and are uncorrected. Melting-points of all organometallic compounds were measured in sealed capillaries evacuated to about 1 mm.Hg. pressure.

Molecular weight measurements

These were made on a vapour pressure osmometer (Mechrolab Inc.).

Infrared spectra

Air-stable compounds were made up as potassium bromide discs, while air-sensitive compounds were made up as Nujoll mulls in a nitrogen atmosphere and placed between potassium bromide plates. Spectra were recorded on a Beckmann IR 5 spectrophotometer.

A number of benzene and chloroform solution spectra were also recorded on a Perkin Elmer 521 grating infrared spectrophotometer.

Nuclear magnetic resonance spectra

Solutions of air-sensitive compounds for n.m.r. spectrometry were made up and sealed in vacuo.

Proton magnetic resonance spectra were run on a Varian A60 60mc. spectrometer (unless otherwise stated). Internal standards (tetramethylsilane, benzene or methylene chloride) were used in all cases.

Fluorine magnetic resonance spectra were run on a Varian HR60 56.4mc. spectrometer. Internal standards (trifluorotoluene or trichlorofluoromethane) were used in all cases.

Analyses were by A. Bernhardt, Max Planck Institute, Germany.

Reagents

Reagent grade benzene, hexane, toluene and diethyl-ether were all sodium-dried and saturated with nitrogen before use. Matheson ethylene (C.P. Grade) was used without further purification. Nitrogen (Purified Grade) was deoxygenated by passage through a vanadium(II) solution and then dried by concentrated sulphuric acid and anhydrous silica gel. Triethylaluminum was purchased from Texas Alkyls Inc., as a 10% solution in n-hexane, and was used as received.

Products were dried at 25°C/0.2mm.Hg.

Experimental Techniques

Reactions involving air-sensitive compounds were carried out in heavy-walled centrifuge tubes of 30ml. or 40ml. capacity, sealed with butyl-rubber cap liners and crimped bottle caps. The cap liners were softened by soaking them in benzene for 12 hours prior to use, and the bottle caps had two 1/8" diameter holes drilled in them to accommodate syringe needles. Liquids were introduced and removed by a "Luer-Lok" hypodermic syringe, stopcock and Gauge 20 6" needle assembly. Gases were introduced and removed by Gauge 20 needles fitted with rubber-hose connectors. Solutions were stirred magnetically using 15 mm. "micro" Teflon-coated stirring bars, and solids were separated by centrifuging the tubes in a hand-driven centrifuge. Solids were isolated by removing the liquor with a syringe.

Preparation of ethylene complexes of nickel

Particular care was taken to exclude air from all solvents and apparatus used in the preparation of these complexes. Bis(acetylacetonato)-nickel(II) was prepared by the method described in the literature,[74] and then dried for 24 hours at 110°C/0.1mm.Hg.

1. Ethylenebis(triphenylphosphine)nickel (13)

Bis(acetylacetonato)nickel(II) (1.0g.,0.00386 moles) and triphenylphosphine (2.0g.,0.076 moles) were dissolved in ether (10 ml.) and the green solution saturated with ethylene at 0°C. To this stirred solution was then added an excess of triethylaluminum (7 ml. of 10% hexane solution) over a period of 30 minutes; a vigorous effervescence occurred, the solution became brown, then yellow, and after 1 hour yellow crystals began to form. Stirring was continued at o°C for 24 hours, and the yellow crystalline material was then separated from the red liquor, washed three times with ethylene-saturated ether and finally dried under a rapid stream of ethylene to give the yellow product (2.02g.,85%). The i.r. spectrum was recorded (Appendix I).

2. Ethylenebis(tri-n-butylphosphine)nickel

This was prepared in a manner analogous to the above, but substituting tri-n-butylphosphine (1.6g.,0.0079 moles) for triphenylphosphine. After stirring the reaction mixture for 24 hours at 0°C, n-hexane (10 ml.) was added, and the solution cooled to -78°C, to give a yellow air-sensitive oil which could not be obtained in a pure state.

3. Ethylenebis(tricyclohexylphosphine)nickel

A slow stream of ethylene was passed through a solution of bis(acetylacetonato)nickel(II) (1.0g.,0.00386 moles) and tricyclohexyphosphine (2.2g., 0.0078 moles) in toluene (25 ml.) at 25°C. Triethylaluminum solution (7 ml.) was then added, and the solution stirred for 12 hours. A yellow crystalline material formed; this was separated, washed with n-hexane, then ether, and finally dried in a fast stream of ethylene.

Preparation of acetylenic complexes of nickel

Diphenylacetylenebis(triphenylphosphine)nickel (14)

To a benzene solution (15 ml.) of ethylenebis(triphenylphosphine) nickel (13), (2.0g.,0.0033 moles) was added a solution of diphenylacetylene (0.90g.,0.005 moles) in benzene (5 ml.). A steady evolution of gas occurred. After stirring at 25°C for 30 minutes, n-hexane (15 ml.) was added, the solution cooled to 10°C, and a yellow crystalline material isolated (80% yield). The product was moderately stable at room temperature under nitrogen, but was immediately decolourised upon contact with air. It was too unstable for an analysis to be made. However the close similarity of the i.r. spectrum of (13) (Appendix I) to that of diphenylacetylenebis-(triphenylphosphine)platinum, (Appendix I) suggested that the product was diphenylacetylenebis(triphenylphosphine)nickel.

Methylphenylacetylenebis(triphenylphosphine)nickel

This was prepared in a manner analogous to the above, but substituting methylphenylacetylene (0.70g.,0.006 moles) for dipheynl-acetylene. A yellow crystalline product was obtained (80% yield) which was moderately stable at 25°C under nitrogen, but which was rapidly decolourised by air. The compound was too unstable for an analysis to be made, but the close similarity of its i.r. and n.m.r. spectra (Appendix III) to those of methylphenylacetylenebis(triphenylphosphine)platinum (Appendix III) suggested that the product was methylphenylacetylenebis(triphenylphosphine)nickel.

Hexafluoro-2-butynebis(triphenylphosphine)nickel. (30, M=Ni)

Hexafluoro-2-butyne (ca.4g.) was condensed from the cylinder into a trap at -78°C. The liquid was allowed to warm up and the gas then passed into a vigorously stirred solution of ethylenebis(triphenylphosphine)nickel

(13), (2.2g.,0.0036 moles), in benzene (20 ml.) at 25°C. A rapid evolution of gas occurred, and yellow crystals began to form after 10 minutes. Crystallization was completed by the addition of n-hexane (15 ml.) and cooling to 10°C. The crystals were separated from the liquor and recrystallized from methylene chloride - methanol to give yellow hexafluoro-2-butynebis(triphenylphosphine)nickel (30,M=Ni), (13.g.,48%). M.Pt. 221-222°C(dec.). Anal. Calcd. for $C_{40}H_{30}F_6NiP_2$: C, 64.46; H, 4.06; F, 15.30; P, 8.31%. M. Wt., 745.
Found: C, 64.56; H, 4.07; F, 15.36; P, 8.24%. M.Wt.; sample decomposed too rapidly in both benzene and chloroform for a measurement to be made.

Attempted preparation of dimethyl acetylene-dicarboxylatebis(triphenylphosphine)nickel.

The above procedure was repeated but substituting dimethyl acetylenedicarboxylate for hexafluoro-2-butyne. A yellow non-crystalline material was obtained which showed a broad infrared absorption band in the region of 1700 cm.$^{-1}$. There was no absorption in the region of 1750 cm.$^{-1}$ and the material was not examined further.

Attempted preparation of diphenylacetylenebis(tri-n-butylphosphine)nickel

To a benzene solution of ethylenebis(tri-n-butylphosphine)nickel (0.50g.,0.001 moles) was added a benzene solution (5 ml.) of diphenylacetylene (0.90g.,0.005 moles). After stirring for 12 hours, the solvent was evaporated to leave a red oil which could not be characterized due to its instability.

Attempted preparation of hexafluoro-2-butynebis(tri-n-butylphosphine)nickel

A benzene solution (15 ml.) of ethylenebis(tri-n-butylphosphine)-nickel (0.50g.,0.001 moles) and hexafluoro-2-butyne (ca.4g.) was stirred for 4 hours at 25°c under a -78°C reflux condenser. n-Hexane (10 ml.) was then added, and evaporation of the solvent in a stream of nitrogen left a brown gum which could not be crystallized.

Reactions of complexes of nickel

Reaction of diphenylacetylenebis(triphenylphosphine)nickel (14) with carbon monoxide

Carbon monoxide was passed through a stirred suspension of (14), (2.0g.,0.0015 moles) in n-hexane (20 ml.) at 25°C. Rapid absorption of the gas occurred, and the colour of the suspension changed from yellow to grey. After 1 hour the mixture was cooled to -78°C and the solid filtered off. Recrystallization from chloroform gave cream coloured crystals of dicarbonylbis(triphenylphosphine)nickel (19) (Yield, 1.1g.) M.Pt. 112-115°C(dec.) (Lit. 110-115°C).

Reaction of dicarbonylbis(triphenylphosphine)nickel with diphenylacetylene

A benzene solution (15 ml.) of dicarbonylbis(triphenylphosphine) nickel (19)[75](0.64g.,0.001 moles) and diphenylacetylene (0.71g.,0.004 moles) was stirred under nitrogen for 12 hours at 25°C. The i.r. spectrum of the solution did not change during this time.

The solution was then refluxed for 12 hours. An intense yellow colour quickly developed; this began to fade after about 3 hours and a quantity of metallic nickel was deposited. The solution was extremely air-sensitive, and identifiable products, apart from unreacted starting materials, could not be isolated.

The i.r. spectrum of the solution was recorded in the range 2300-1650 cm.$^{-1}$ after 2 and 12 hours (Appendix II).

Reaction of dicarbonylbis(triphenylphosphine)nickel (19) with hexafluoro-2-butyne.

This was carried out in a similar manner to the above, except that hexafluoro-2-butyne (ca.4g.) was substituted for diphenylacetylene, and the reaction was carried out for 12 hours at 25°C. The almost colourless solution quickly became deep yellow, and the infrared spectrum of the reaction mixture was periodically recorded, in the range 2300-1600 cm.$^{-1}$ (Appendix II).

After 12 hours the solvent was removed on a rotary evaporator and the residue recrystallized from methylene chloride - methanol to give the white crystalline hexakis(trifluoromethyl)benzene (0.090g.) M.Pt., 209-212°C. (Lit. 210-215°C).

Preparation of palladium complexes

The preparation and recrystallization of all palladium complexes was carried out in an atmosphere of nitrogen. Complexes of the type trans-$(Ph_3P)_2PdCl_2$ were prepared by the methods described in Gmelin"Handbuch Der Anorganischen Chemie".

Tetrakis(triphenylphosphine)palladium (34)

Method (a): To a stirred ethanolic suspension (30 ml.) of trans-dichlorobis(triphenylphosphine)palladium (0.7g.,0.001 moles) and triphenylphosphine (0.52g.,0.002 moles) at 40°C, was added anhydrous hydrazine (2 ml.). The pale cream suspension slowly became light green in colour, and after stirring for 45 minutes, the mixture was cooled and the product isolated under nitrogen, (0 9g.,80%) M.Pt., 190-195°C(dec.).

Method (b): A solution of bis(acetylecetonato)palladium(II)[74] (0.92g.,0.003 moles) and triphenylphosphine (3.2g.,0.012 moles) in ether (15 ml.) was cooled to 0°C. Triethylaluminum solution (7 ml.) was added, and the mixture stirred for 3 hours. The yellow solid was then separated and washed three times with ether to give the pale yellow crystalline product (3.1g.,90%). M.Pt., 194-196°C(dec.). This method was generally used for the preparation of (34).

Attempted preparation of diphenylacetylenebis(triphenylphosphine)palladium

Method (a): A solution of hydrazine (1 ml.) in ethanol was slowly added to a stirred suspension of trans-dichlorobis(triphenylphosphine)palladium (0.70g.,0.001 moles) in ethanol (20 ml.) at 50°C. The white suspension darkened in colour, and after 30 minutes the mixture was filtered under nitrogen. The filtrate was discarded and the residue washed with methylene chloride to leave black metallic palladium and a yellow solution.

To this solution was added an ethanolic solution (10 ml.) of diphenylacetylene (0.72g.,0.004 moles) and the mixture allowed to stand overnight. Addition of aqueous methanol gave a green crystalline precipitate of tetrakis(triphenylphosphine)palladium (0.2g.).

Method (b): The above procedure was repeated except that the diphenylacetylene (0.9g.,0.005 moles) was added before the hydrazine. Removal of the solvent in a stream of nitrogen gave a semi-crystalline solid, which was found to be a mixture of diphenylacetylene and a brown gum which could not be crystallized.

Method (c): A solution of tetrakis(triphenylphosphine)palladium (34) (1.15g.,0.001 moles) and diphenylacetylene (0.89g.,0.005 moles) in benzene (20 ml.) was stirred for 2 hours. Concentration of the solution in a stream of nitrogen, and the addition of petroleum-ether (B.Pt. range 30-60°C) precipitated a brown oil, the i.r. spectrum of which was identical to that of tetrakis(triphenylphosphine)palladium.

Method (d): An ethanolic solution of peroxybis(triphenylphosphine)-palladium (0.66g.,0.001 moles) and diphenylacetylene (0.9g.,0.005 moles) was cooled to 0°C. A solution of hydrazine (2 ml.) in ethanol (5 ml.) was then slowly added, with stirring. An intense yellow colour appeared almost immediately; after 20 seconds this darkened to give a brown suspension, from which metallic palladium and an intractable brown gum were obtained.

Hexafluoro-2-butynebis(triphenylphosphine)palladium (30, M=Pd)

A methylene chloride solution (20 ml.) of tetrakis(triphenylphosphine)palladium (34) (1.05g.,0.001 moles) and hexafluoro-2-butyne (ca.5g.) was stirred for 30 minutes at 25°C, under a -78°C reflux condenser. Methanol (15 ml.) was then added to the pale yellow solution, and the methylene chloride removed on a rotary evaporator to give a grey precipitate. This was recrystallized from methylene chloride - methanol and washed with a little ether to give white crystals of hexafluoro-2-butynebis(triphenylphosphine)palladium. (0.4g.,50%). M.Pt. 194-195°C(dec.) Anal. calcd. for $C_{40}H_{30}F_6P_2Pd$: C, 60.59; H, 3.82; F, 14.37; P, 7.81% M.Wt., 793. Found: C,60.29; H, 3.76; F, 14.88; P, 7.82%. M.Wt.,(Chloroform) 770. The i.r. and n.m.r. spectra were recorded (Appendix I and VI).

Dimethyl acetylenedicarboxylatebis(triphenylphosphine)palladium.(35)

This was prepared in a manner analogous to the above, but substituting dimethyl acetylenedicarboxylate (0.84g.,0.006 moles) for hexafluoro-2-butyne. Recrystallization from methylene chloride - methanol gave the white crystalline product (0.45g.,58%). M.Pt.,195-195°C(dec.). Anal. calcd. for $C_{40}H_{36}O_4P_2Pd$: C, 65.25; H, 4.69; P, 8.01%. M.Wt., 773. Found: C, 64.71; H, 4.87; P, 8.62%. M.Wt. (Chloroform), 763. The infrared and n.m.r. spectra were recorded (Appendix I and V). In the solid, the product slowly turned yellow on exposure to air; more rapid decomposition occurred in solution.

Attempted preparation of p-p'-dinitrodiphenylacetylenebis(trephenylphosphine)palladium.

The above procedure was repeated, but p-p'-dinitrodiphenylacetylene was substituted for dimethyl acetylenedicarboxylate. The solution was stirred for 3 hours, and then concentrated to give unreacted p-p'-dinitrodiphenylacetylene (0.41g.), together with an unstable red oil which could not be identified.

Attempted preparation of diphenylacetylenebis(tri-n-butylphosphine) palladium.

The preparation of this compound was attempted by methods (a), (b) and (c) used in the attempted preparation of diphenylacetylenebis-(triphenylphosphine)palladium. In each case a red air-sensitive oil was obtained, which could not be crystallized, and which did not show absorption maxima in the $\nu_{C\equiv C}$ region (2300-1700 cm.$^{-1}$) of the infrared spectrum.

Hexafluoro-2-butynebis(tri-n-butylphosphine)palladium(36)

To a solution of trans-dichlorobis(tri-n-butylphosphine) palladium (0.59g.,0.001 moles) in ethanol (20 ml.) at 40°C was added an ethanolic solution (5 ml.) of hydrazine (2 ml.). A gas was evolved and the yellow colour of the solution became less intense. The solution was allowed to cool to 25°C, hexafluoro-2-butyne (ca.5g.) passed into it, and stirring continued under a -78°C reflux condenser for 1 hour. Water (15 ml.) was then added, and after the solution had stood at 0°C for 24 hours, the product was obtained as white crystals, (0.37g.,55%) M.Pt., 34-36°C(dec.) Anal. calcd. for $C_{28}H_{54}F_6P_2Pd$: C, 49.96; H, 8.09; F, 16.94%. Found: C, 49.83; H, 8.04; F, 17.05%. The infrared and n.m.r. spectra were recorded (Appendix I and VI).

Attempted preparation of dimethyl acetylenedicarboxylatebis(tri-n-butylphosphine)palladium

The preparation of this complex was attempted by a reaction analogous to the above, but substituting dimethyl acetylenedicarboxylate (0.43g.,0.003 moles) for hexafluoro-2-butyne. A yellow unstable oil was obtained which could not be characterized.

Hexafluoro-2-butynebis(dimethylphenylphosphine)palladium (37)

This was prepared in a manner analogous to the above, but substituting trans-dichlorobis(dimethylphenylphosphine)palladium (0.45g.,0.001 moles) for trans-dichlorobis(tri-n-butylphosphine)-palladium and dimethylphenylphosphine (0.28g.,0.002 moles) for triphenylphosphine. The crude product was crystallized, with difficulty, from aqueous methanol to give white crystals (0.090g.,16%). M.Pt. 118-119°C(dec.) Anal. calcd. for $C_{20}H_{22}F_6P_2Pd$: C, 44.10; H, 4.07; F, 20.92; P, 11.37%. Found: C, 43.97; H, 4.08; F, 21.11; P, 11.31%. The infrared spectrum was recorded (Appendix I).

Attempted preparation of hexafluoro-2-butynebis(tricyclohexylphosphine) palladium.

To a stirred suspension of trans-dichlorobis(tricyclohexylphosphine)palladium (0.37g.,0.0005 moles) and tricyclohexylphophine (0.28g.,0.001 moles) in ethanol (15 ml.) at 50°C was added an ethanolic suspension (5 ml.) of hydrazine (2 ml.). After 30 minutes hexafluoro-2-butyne (ca.5g.) was added, and the mixture stirred under a -78°C reflux condenser for 2 hours. The solution was then concentrated on a rotary evaporator, and the grey solid filtered off. This was found to be a mixture of trans-dichlorobis(tricyclohexylphosphine)palladium and tricyclohexylphosphine.

Preparation of platinum complexes

All complexes were prepared under nitrogen, the subsequent work up being performed in open vessels. Complexes of the type $[(R_3P)_2PtCl_2]$ were prepared by the methods described in Gmelin "Handbuch Der Anorganischen Chemie".

Diphenylacetylenebis(triphenylphosphine)platinum (7, ac = PhC_2Ph)

To a stirred ethanolic suspension (15 ml.) of cis-dichlorobis-(triphenylphosphine)platinum (0.79g.,0.001 moles) at 45°C was added an ethanolic solution (5 ml.) of hydrazine (2 ml.). A gas was evolved, and the suspension dissolved to give an intense yellow solution, from which yellow crystals rapidly separated. After stirring for 30 mins, an ethanolic solution of diphenylacetylene (0.72g.,0.004 moles) was added A further evolution of gas occurred, and the yellow suspension dissolved to give a pale yellow solution. Water (50 ml.) was added, and the solution allowed to stand for 12 hours at 0°C. The white crystals which had formed were filtered off, washed with a little aqueous ethanol and recrystallized from 95% ethanol to give the white crystalline product (0.52g.,58%). M.Pt., 161-164°C(dec.) identical to that of an authentic sample provided by Dr. C.D. Cook, University of Toronto. The infrared spectrum was recorded (Appendix I).

Methylphenylacetylenebis(triphenylphosphine)platinum (29).

This was prepared in a manner analogous to the above but substituting methylphenylacetylene (0.70g.,0.006 moles) for diphenylacetylene. Recrystallization from methylene chloride - methanol under nitrogen, gave the cream coloured crystalline product (0.70g., 84%). M.Pt. 176-178°C(dec.), with a colour change from cream to red at

153-155°C. Anal.calcd. for $C_{45}H_{38}P_2Pt$: C, 64.73; H, 4.59; P, 7.42% Found: C, 64.68; H, 4.74; P, 7.61%. The infrared and 60mc. and 100mc. n.m.r. spectra were recorded (Appendix I and III respectively).

Hexafluoro-2-butynebis(triphenylphosphine)platinum (30, M = Pt)

Method (a): To a stirred ethanolic suspension (15 ml.) of cis-dichlorobis(triphenylphosphine)platinum (0.79g.,0.001 moles) at 45°C was added a solution of hydrazine (2 ml.) in ethanol (5 ml.). After 30 minutes, the solution was cooled to 25°C and the yellow crystals which had formed were isolated and dissolved in benzene (20 ml.) under nitrogen. Hexafluoro-2-butyne (ca.5g.) was added and the solution stirred at 25°C under a -78°C reflux condenser for 4 hours. n-Hexane (10 ml.) was added and the white solid filtered off. Recrystallization from methylene chloride - methanol gave the white crystalline product (0.48g.,54%). M.Pt., 212-214°C. (Lit.,[23] 215-216°C). The infrared and n.m.r. spectra were recorded (Appendix I and VI).

Method (b): Hexafluoro-2-butynebis(triphenylphosphine)platinum (0.50g.,60%) was also prepared in a manner analogous to that used to prepare hexafluoro-2-butynebis(triphenylphosphine)palladium, but substituting tetrakis(triphenylphosphine)platinum[70] for tetrakis(triphenylphosphine)palladium.

Dimethyl acetylenedicarboxylatebis(triphenylphosphine)platinum. (38)

This was prepared in a manner analogous to method (b) above, but substituting dimethyl acetylenedicarboxylate (0.57g.,0.004 moles) for hexafluoro-2-butyne. The grey solid obtained from the reaction was recrystallized from methylene chloride - methanol to give the white crystalline product (0.50g.,58%) M.Pt. 188-190°C(dec.). Anal. calcd.

for $C_{40}H_{36}O_4P_2Pt$: C, 57.41; H, 4.33; P, 7.39%.
Found: C, 58.00; H, 4.19; P, 7.71%
The infrared and n.m.r. spectra were recorded (Appendix I and V).

Hexafluoro-2-butynebis(tri-n-butylphosphine)platinum. (39)

An attempt was made to prepare this compound by a method analogous to that used to prepare diphenylacetylenebis(triphenylphosphine) platinum. viz., by the hydrazine reduction of an ethanolic solution of dichlorobis(tri-n-butylphosphine) with subsequent addition of hexafluoro-2-butyne. However, a red oil was obtained which could not be crystallized.

The complex was successfully prepared by the addition of an aqueous solution (5 ml.) of potassium tetrachloroplatinate (0.42g., 0.001 moles) to an alcoholic solution (5 ml.) of potassium hydroxide (0.112g.,0.002 moles) and tri-n-butylphosphine (1.01g.,0.005 moles). After stirring for 30 minutes at 25°C, a small quantity of metallic platinum was filtered off under nitrogen, the solution was transferred to a flask fitted with a -78°C reflux condenser, and hexafluoro-2-butyne (ca.5g.) was passed into it. After stirring for 4 hours, water (10 ml.) was added to give a fine white crystalline precipitate. Recrystallization from aqueous methanol gave white crystals of hexafluoro-2-butynebis(tri-n-butylphosphine)platinum (0.23g.,30%) M.Pt., 53-54°C(dec.) Anal. calcd. for $C_{28}H_{54}F_6P_2Pt$: C, 44.3; H, 7.14; F, 14.95; P, 8.13%. M.Wt., 762. Found: C, 44.06; H, 7.17; F, 15.31; P, 8.31%. M.Wt., 764.

The infrared and ^{19}F n.m.r. spectra were recorded (Appendix I and VI).

Reactions of methylphenylacetylenebis(triphenylphosphine)platinum (29)

1. Oxygen

Oxygen was passed into a benzene solution (15 ml.) of (29), (0.42g.,0.0005 moles) at 25°C. A cream coloured precipitate formed after 20 minutes, and after 2 hours n-hexane (15 ml.) was added. The crystalline solid (0.30g.) was filtered off and its infrared spectrum recorded. This showed a strong absorption maximum at 820 $cm.^{-1}$, similar to that reported for $[(Ph_3P)_2Pt(O_2)]$ (32), (818,824(sh.),$cm.^{-1}$).

The filtrate was concentrated on a rotary-evaporator to give a red oil. The infrared spectrum (liquid film) of this oil suggested that it was a mixture of unreacted complex (29) and free methylphenylacetylene. However the free methylphenylacetylene could not be detected by vapour phase chromatography.

2. Carbon monoxide

Complex (29), (0.42g.,0.0005 moles) was dissolved in benzene at 25°C, under nitrogen. A steady stream of carbon monoxide was passed into the stirred solution, the pale yellow colour rapidly changed to a deep red, and stirring was continued for 12 hours. n-Hexane (10 ml.) was then added, and the precipitated solid filtered off to give a cream coloured crystalline compound (0.23g.). The infrared spectrum (Nujoll mull) of this compound showed strong absorptions in the metal-carbonyl region, at 1985 $cm.^{-1}$ and 1955 $cm.^{-1}$. Absorptions at 1982 and 1950 $cm.^{-1}$ are reported for dicarbonylbis(triphenylphosphine)platinum.[65] The filtrate was concentrated on a rotary evaporator to give a dark red oil, the vapour phase chromatogram of a benzene solution of which indicated the presence of free methylphenylacetylene. The infrared spectrum of the oil (KBr plates) showed no absorption in the carbonyl region.

3. Sulphur dioxide

(a) Complex (29) (0.42g.,0.0005 moles) was dissolved in benzene under nitrogen, and the solution stirred at 25°C whilst sulphur dioxide was passed into it. The gas was rapidly absorbed and the pale yellow solution became dark red in colour. After 30 minutes n-hexane was added to precipitate a red-brown crystalline material (0.25g.). The infrared spectrum of the product showed strong absorption maxima at cm.$^{-1}$, identical to those reported in the literature for $[(Ph_3P)_2PtSo_2 \cdot SO_2]$. Upon washing with a little methanol, the colour rapidly changed to a bright green. The infrared spectrum of this material showed strong absorption maxima at 1190 and 1040 cm.$^{-1}$, identical to those reported for $[(Ph_3P)_2PtSO_2]$.

(b) Complex (29) (0.84g.,0.001 moles) was placed, together with a stirring bar, in a nitrogen-filled tube and cooled to about -30°C. Sufficient sulphur dioxide was then condensed into the tube to dissolve the solid. The solution was stirred for 1 hour at -30°C, the coolant was removed, and the sulphur dioxide allowed to evaporate. The red-brown solid which was left was dissolved in chloroform (8 ml.) and chromatographed on an alumina column. Elution with chloroform gave two bands:

Band 1 - Colourless, eluting to give a yellow solution. Concentration of the solution and addition of n-hexane gave the starting material (29).

Band 2 - Yellow, eluting to give a yellow solution. Concentration of the solution gave a very small quantity of a yellow oil which could not be crystallized. The infrared spectrum of this showed bands characteristic of co-ordinated sulphur dioxide, but the oil was not obtained in sufficient quantity to enable its full characterization.

4. Hydrogen

Hydrogen was passed into a benzene solution (10 ml.) of (29) (0.84g.,0.001 moles) at 25°C. After 10 minutes the pale yellow colour had changed to a deep red. Passage of hydrogen was continued for a total of 12 hours. The solution was then concentrated to a volume of 3 ml. in a rapid stream of hydrogen and the vapour phase chromatogram and n.m.r. spectrum of this solution was determined.

5. Chloroform

A benzene solution of (29) (0.42g.,0.0005 moles) and chloroform (1.5g.,0.008 moles) was stirred for 48 hours under nitrogen at 25°C. The precipitate which had formed was then filtered off to give pale yellow crystals of chloro-dichloromethylbis(triphenylphosphine)platinum(II), (33) (0.28g.). M.Pt., 248-266°C. Anal calcd. for $C_{37}H_{31}CL_3P_2Pt$: C, 53.00; H, 3.72; Cl 12.68; P, 7.38%.

Found: C, 53.48; H, 3.74; Cl, 12.40; P, 7.45%.

Preparation of alkyl-platinum(II) complexes.

Dimethylbis(triphenylphosphine)platinum (39)[71]

To a fine suspension of cis-dichlorobis(triphenylphosphine)platinum (0.79g.,0.002 moles) in dry benzene (10 ml.) at 25°C was added a 10% excess of ethereal methyl lithium, (1.0 ml. of 1.88M solution). The suspended solid quickly dissolved to give a pale yellow solution. This solution was stirred for 2 hours and then water (10 ml.) was added. The organic layer was separated, dried with anhydrous sodium sulphate and concentrated on a rotary evaporator to give a grey solid. Recrystallization from benzene - n-hexane solution gave the white crystalline product (1.26g.,85%). M.Pt., 234-237°C. (Lit., 235-237°C). The infrared spectrum and the 60mc. and 100 mc. n.m.r. spectra were recorded, (Appendix I and IV).

Attempted preparation of diethylbis(triphenylphosphine)platinum.

This reaction was carried out in a manner analogous to the above, but substituting an ethereal solution of ethyl lithium (10% excess) for methyl lithium. A grey, air sensitive, material was obtained in low yield (ca. 0.03g.), which decomposed during recrystallization.

APPENDIX

APPENDIX I

Infrared Spectra

Unless otherwise stated, infrared spectra were recorded on a Beckmann I.R.5 spectrophotometer with the sample made up as a potassium bromide disc.

/$(Ph_3P)_2Ni(MeC_2Ph)$/ - (29)

(Nujoll mull - Perkin Elmer 521).

Principal absorption maxima in the range 2,000 - 650 cm.$^{-1}$: 1785(m), 1590(w), 1476(m), 1426(s), 1300(w), 1178(w), 1087(s), 1025(w), 732(s), 686 (s).

/$(Ph_3P)_2Pt(CCOOCH_3)_2$/ - (38)

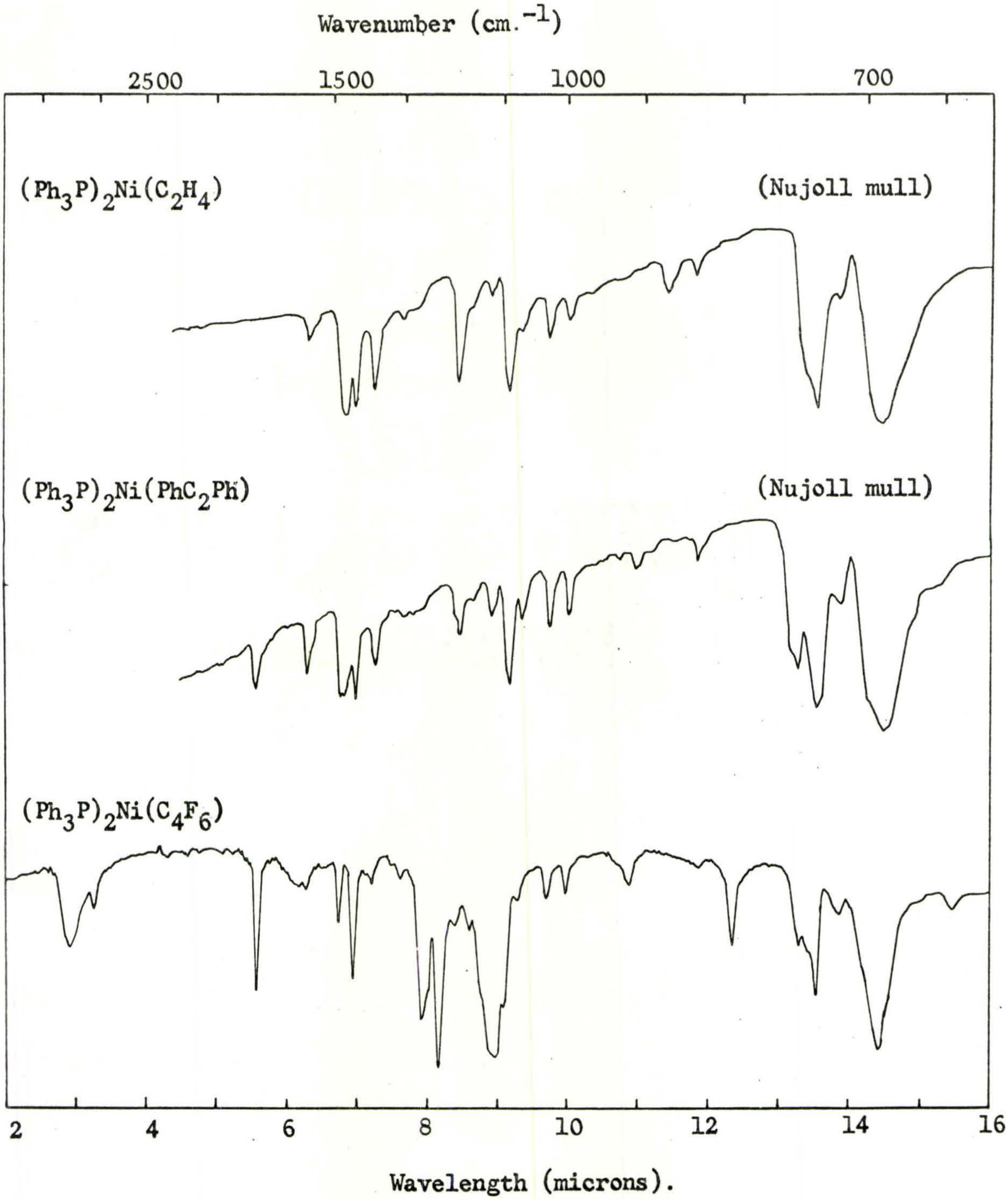
(Perkin Elmer - 521).

Pri Principal absorption maxima in the range 2,000 - 650 cm.$^{-1}$: 1765(m), 1700(sh), 1680(s), 1477(m), 1432(s), 1220-1190(s), 1091(m), 1035(w), 740(s), 690(s).

(s = strong, m = medium, w = weak, sh = shoulder).

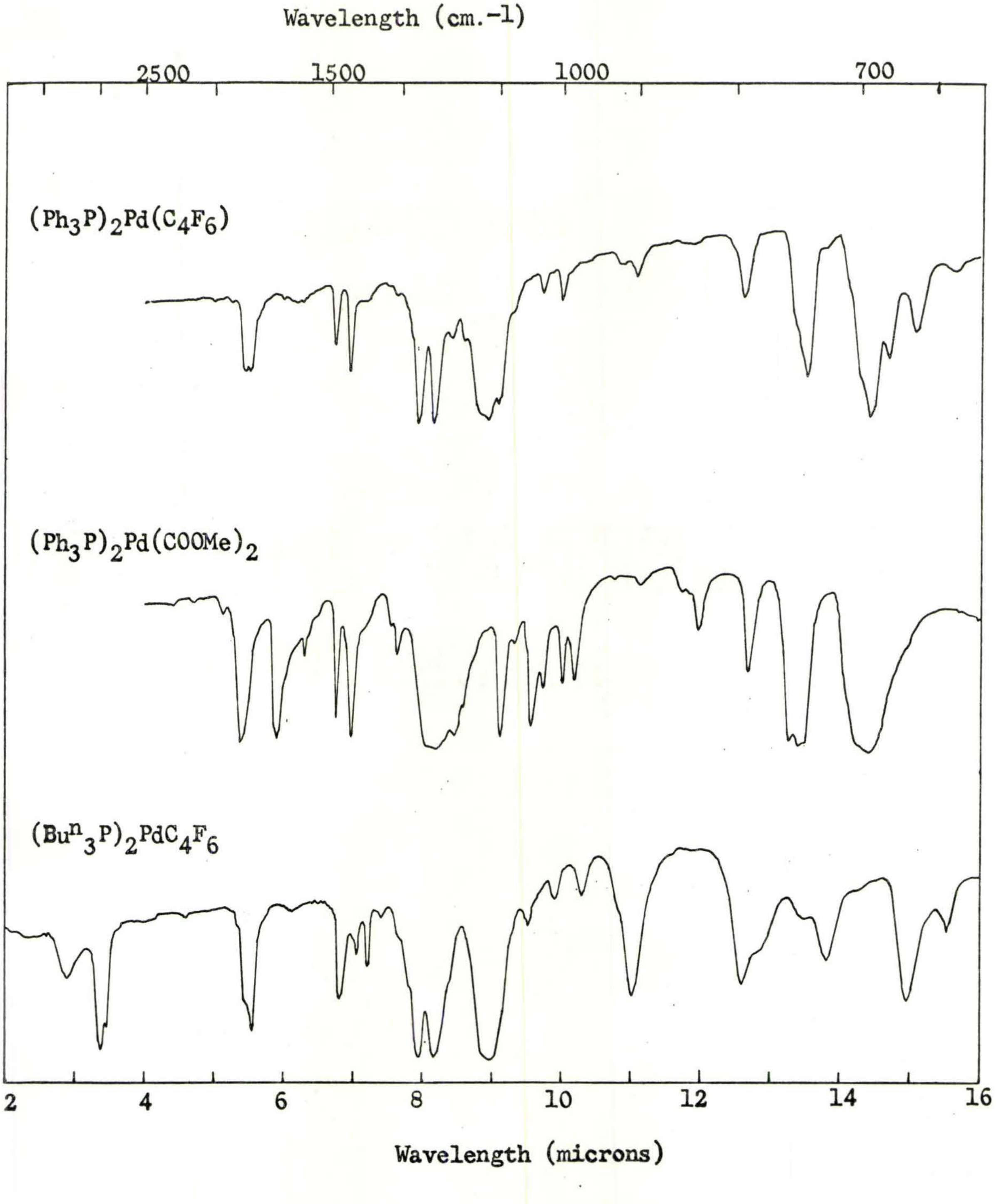
APPENDIX I

Infrared Spectra



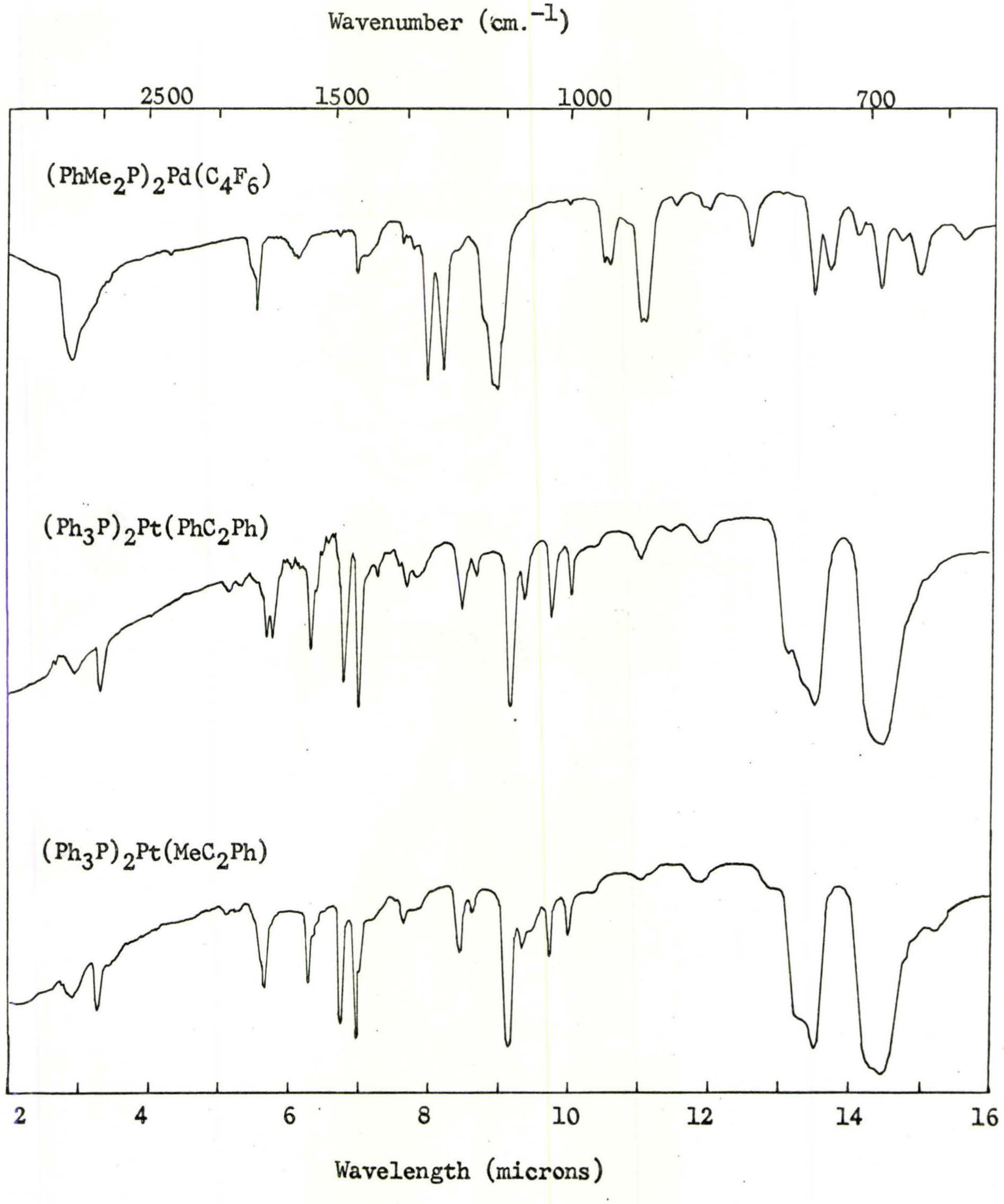
APPENDIX I

Infrared Spectra



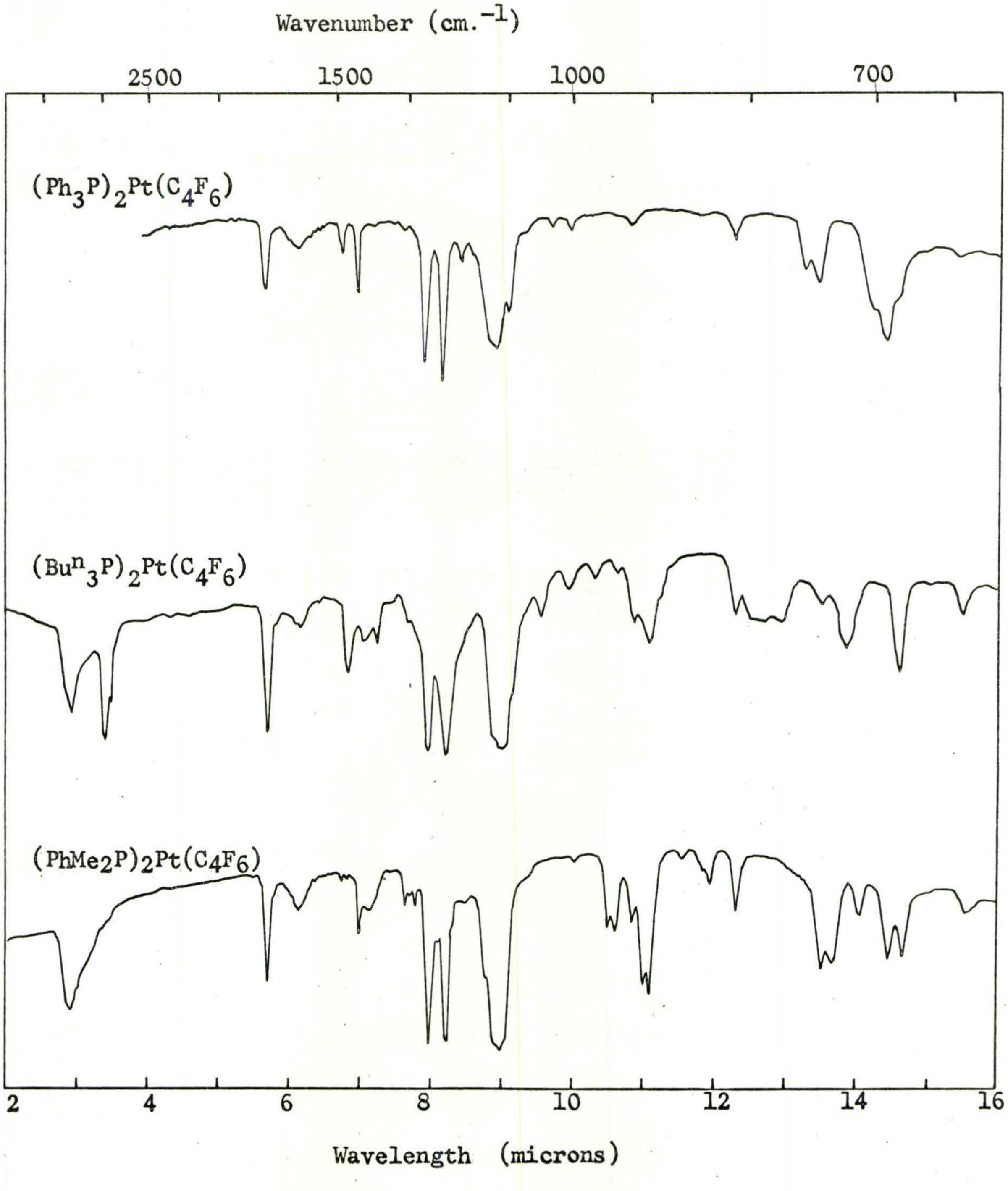
APPENDIX I

Infrared Spectra



APPENDIX I

Infrared Spectra



APPENDIX II

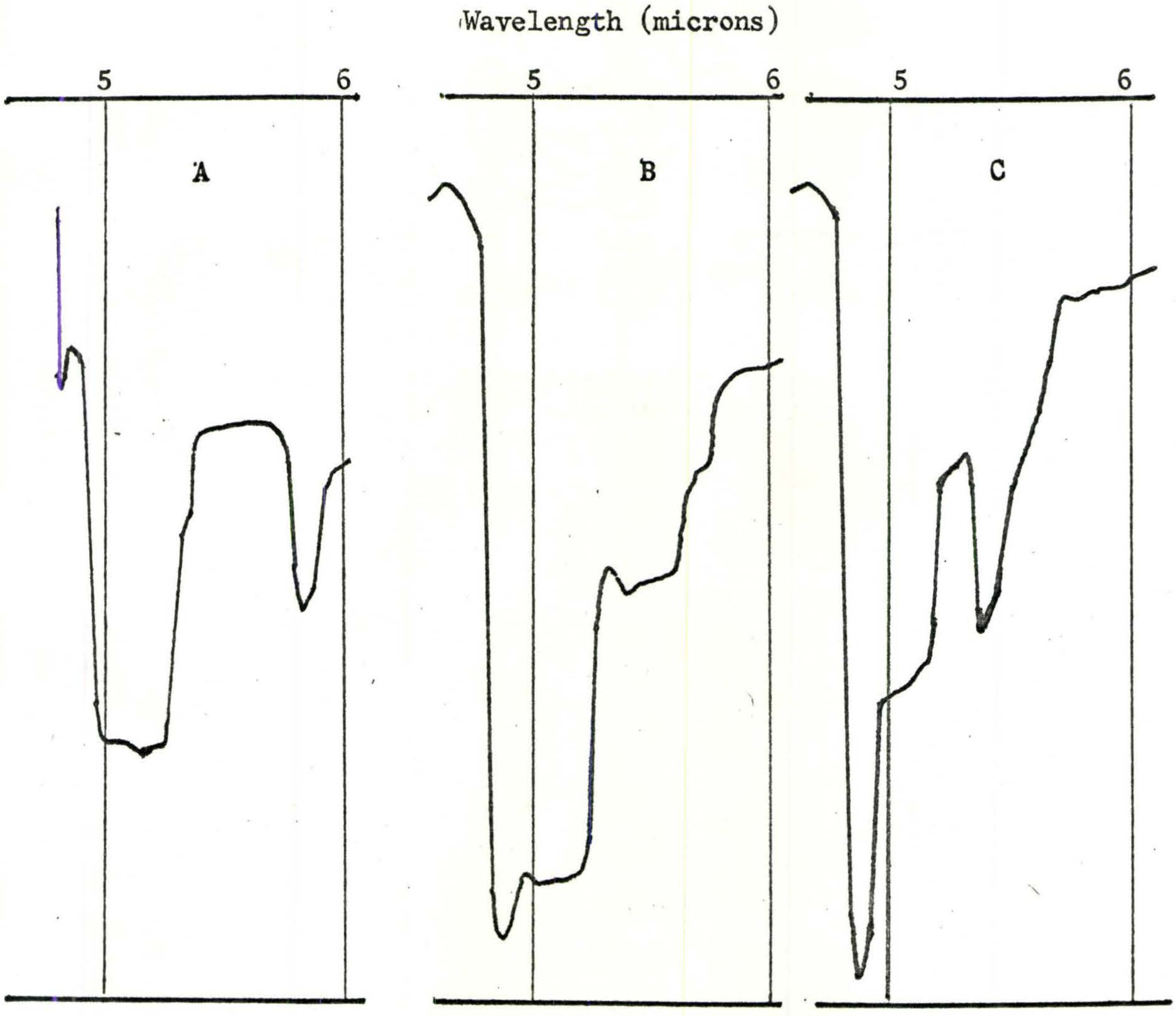
Infrared Spectra

Reaction of $[(Ph_3P)_2Ni(CO)_2]$ (19) and $CF_3C\equiv CCF_3$

A. Solution of (19) in benzene.

B. Reaction mixture after 20 minutes.

C. Reaction mixture after 120 minutes.



APPENDIX II

Infrared Spectra

Reaction of $[(Ph_3P)_2Ni(CO)_2]$ (19) and $PhC{\equiv}CPh$:

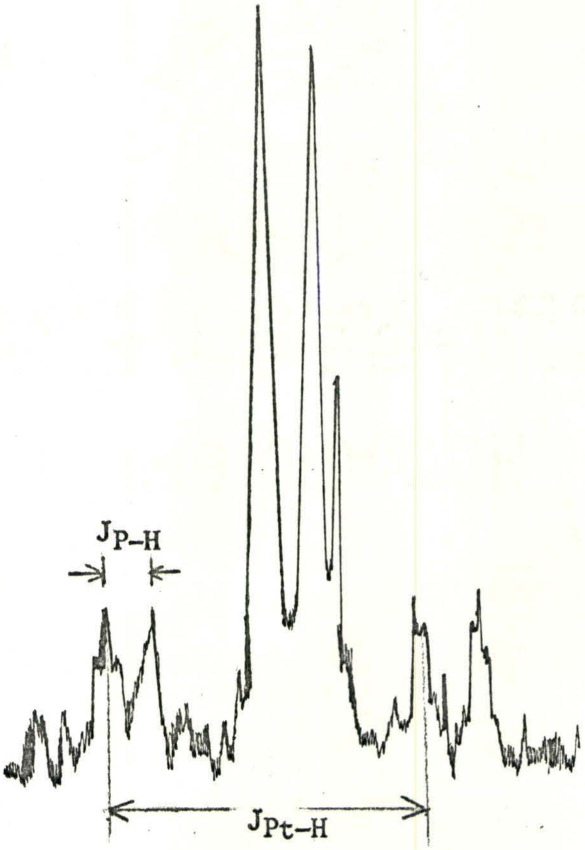
Absorption maxima in the range	2,200 – 1700 $cm.^{-1}$
Initial (benzene) solution	1990(s), 1900(s).
30 minutes reflux	1995(m), 1900(s), 1800(w).
3 hours reflux	2000(m), 1900(s), 1870(sh), 1800(w).

APPENDIX III

Nuclear Magnetic Resonance Spectrum

$[(Ph_3P)_2Pt(MeC_2Ph)]$(29) in Chloroform solution.

(i) 60mc. spectrum : methyl resonance at 7.88τ



J_{P-H} = 6.2 cps.

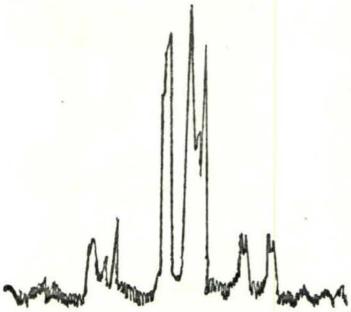
J_{Pt-H} = 41.5 cps.

APPENDIX III

Nuclear Magnetic Resonance Spectrum

$[(Ph_3P)_2Pt(MeC_2Ph)]$ (29) in Chloroform solution

(ii) 100mc. spectrum : methyl resonance at 7.88τ



J_{P-H} = 6.2 cps $J_{P'-H}$ = 1.2 cps. J_{Pt-H} = 41.5 cps.

Nuclear Magnetic Resonance Spectrum (60mc.)

Of $[(Ph_3P)_2Ni(MeC_2Ph)]$ in benzene at 34°C

Methyl resonance at 7.86τ (doublet) :

J_{P-H} = 4.5 cps.

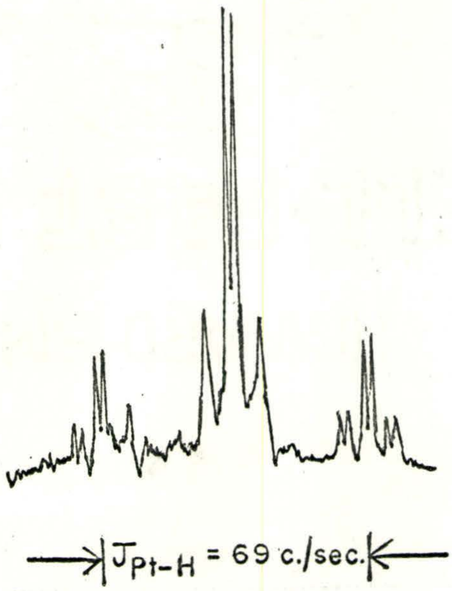
$J_{P'-H}$ = ca. 1 cps.

APPENDIX IV

Nuclear Magnetic Resonance Spectrum

Of cis-$(Ph_3P)_2PtMe_2$ (39) in Chloroform - methylene chloride solution at 22.5°C.

100mc. spectrum : methyl resonance at 9.63τ



APPENDIX V

Proton Magnetic Resonance Spectra (60mc.)

Of complexes of dimethyl acetylenedicarboxylate in deuterochloroform at 25°C.

	Phenyl protons	Methyl protons
$(Ph_3P)_2Pt(CCOOCH_3)_2$	2.9τ (multiplet)	6.75τ (singlet)
$(Ph_3P)_2Pd(CCOOCH_3)_2$	2.9τ (multiplet)	6.8 τ (singlet)

APPENDIX VI

^{19}F Nuclear Magnetic Resonance Spectra (56.4mc.)

Of complexes of hexafluoro-2-butyne in benzene at ca.30°C.

Complex	J_{P-F}(cps.)	J_{M-F}(cps.)	δ.(ppm.)*
$(Ph_3P)_2Ni(C_4F_6)$	6.1	-	10.6
$(Ph_3P)_2Pd(C_4F_6)$	11.2	-	10.7
$(Ph_3P)_2Pt(C_4F_6)$	10.2	64	10.4
$(Bu^n{}_3P)_2Pt(C_4F_6)$	10.8	67	8.8

* Chemical shifts are quoted with reference to benzotrifluoride (internal standard) and are all to the low-field side of the standard.

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