THE CHEMISTRY OF THE DIETL COMPLEX

Never measure the height of a mountain, until you have reached the top. Then you will see how low it was.

Dag Hammarskjöld

THE CHEMISTRY
OF
THE DIETL COMPLEX, $[Cl(MeC_2Me)_3PdCl]_2$

By

JAMES HENDERSON MOFFAT, B.Sc.

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AUTHOR: James Henderson Moffat, B.Sc. (Mount Allison University)

SUPERVISOR: Dr. P. M. Maitlis

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SCOPE AND CONTENTS:

In benzene solution at 10°, 2-butyne and bis-(benzonitrile)palladium chloride reacted together to give the Dietl complex $[(Me_2C_2)_3PdCl_2]_2$. Reaction of this complex with Ph_3E (E = P, As, Sb) gave hexamethylbenzene, 1-vinyl-1,2,3,4,5-pentamethylcyclopentadiene, and 1-(1-chlorovinyl)-1,2,3,4,5-pentamethylcyclopentadiene. The complex was decomposed by hydrazine to the vinylpentamethylcyclopentadiene; with halogen hexamethylbenzene was formed; while lithium aluminum hydride gave largely 1-ethyl-1,2,3,4,5-pentamethylcyclopentadiene. In the presence of o-phenanthroline a new complex was formed, identified as 1-(chloro-(o-phenanthroline)-palladium)-vinyl-1,2,3,4,5-pentamethylcyclopentadiene. Similar complexes were obtained with bipyridyl and pyridine. A structure for the Dietl complex is proposed and the mechanisms of some of its reactions are discussed.

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INTRODUCTION

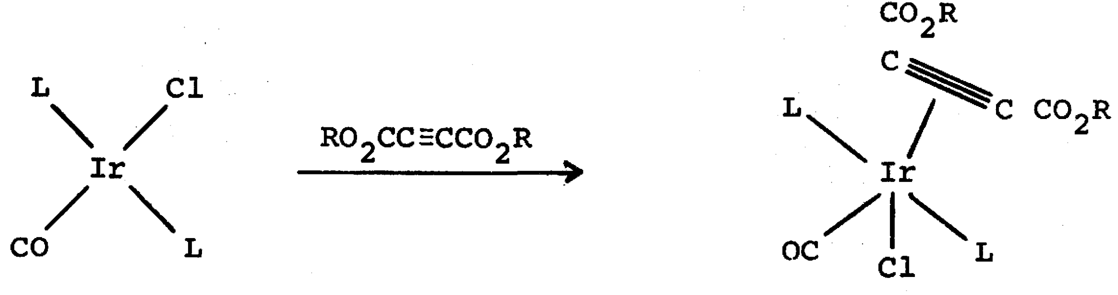
INTRODUCTION

Zeise prepared the first ethylene complex $KPt(C_2H_4)Cl_3$ in 1827, but until 1950 few complexes containing an unsaturated hydrocarbon ligand bonded to a metal had been made. During the past 20 years a number of metal-acetylene complexes have also been reported and the discussion of the mode of bonding in these complexes has attracted considerable attention. Such complexes are of interest as they are considered to be intermediates in metal-catalysed cyclooligomerisations[1,2] and polymerisations[2,3] of acetylenes.

The acetylenic bond has two perpendicular sets of π and π^* orbitals which are capable of complexing with metals via synergic donor and acceptor bonds. Although such compounds are known, acetylenes frequently react to give new ligands or organic products formed by the polymerisation of the acetylene molecules.

Complexes in which the acetylene is bonded, unchanged, to the metal.

Mononuclear acetylene complexes of a number of transition metals have been prepared. Vaska's compound[4] $L_2Ir(CO)Cl$ is characterised by its ability to add an extra ligand, e.g. CO, C_2H_4. It also gives 1:1 adducts with many acetylenes.[5]



L = PPh_3, PPh_2Me

R = H, Me, Et

Palladium[6] and platinum[6,7,8] form a fairly large number of mono-acetylene complexes. In 1961, Chatt[7] reported the preparation of stable acetylene-platinum complexes of the type $[(RC_2R')PtCl_3]^-$ (1) and $(RC_2R')_2Pt_2Cl_4$ (2). The simple alkynes did not form complexes of this type. Stable complexes were isolable only when the acetylene had at least one bulky electron-releasing substituent adjacent to the C≡C bond. In addition, some α-hydroxy acetylenes also readily formed complexes of this type.[8]

Acetylenes also form a series of stable complexes of the type $(Ph_3P)_2M(RC_2R')$, (M=Ni, Pd, and Pt), (3).[9,10] These have been conveniently prepared by the reaction of the acetylene with ethylenebis(triphenylphosphine)nickel, tetrakis(triphenylphosphine)palladium, or the hydrazine reduction product of cis-dichlorobis(triphenylphosphine)-platinum. Complexes with substituents R=R'=Ph, CF_3, COOMe and R=Ph, R'=Me are known.

Structure and bonding.

The structures of mononuclear acetylene complexes have been suggested mainly on the basis of infrared spectral evidence, owing to the lack of extensive X-ray determinations.

Two conceivable extremes by which a single alkyne molecule may be bonded to a single metal are illustrated by Figures I and II. In I, the bonding is similar to that found in olefin complexes[11] and the mutual charge transfer between metal and ligand results in only small perturbations of the triple bond. In II, the triple bond has been effectively reduced to a double bond through a reorganisation of electron density on the carbon atoms.

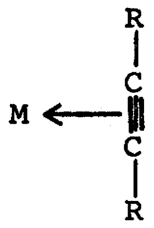


Fig. I

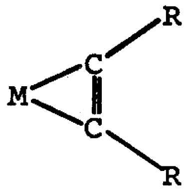


Fig. II

The infrared spectra of acetylene complexes do seem to suggest that bonding of both extremes is possible, since in some compounds there is only a small shift in the $\nu_{C\equiv C}$ of the order 130 → 200 cm^{-1} decrease on complexing, i.e. the triple bond is only weakly perturbed. In other compounds the $\nu_{C\equiv C}$ is lowered by ~ 500 cm^{-1} into the double bond region.

Complexes of the type $Na[(RC_2R')PtCl_3]$ ($\underline{1}$) and $(RC_2R')_2Pt_2Cl_4$ ($\underline{2}$) in which at least one of the groups R is a bulky alkyl show a lowering in $\nu_{C\equiv C}$ of $\sim$200 cm^{-1}. This indicates that the acetylenic bond is not greatly perturbed and the bonding is best approximated by I.

Acetylene complexes of the type $(Ph_3P)_2Pt(RC_2R')$ ($\underline{3}$) show a lowering in $\nu_{C\equiv C}$ of $\sim$500 cm^{-1} which indicates a large perturbation of the triple bond. Such complexes can be represented by II. In these complexes, the greater the electron withdrawing power of the groups R the greater the stability of the complex and the greater the drop in frequency $\nu_{C\equiv C}$. Hence, it is implied that the acetylene is functioning primarily as an acceptor and donation of electron density from the metal into the acetylene antibonding π^* orbitals causes a lowering of the C-C bond order from three towards two.

Thus, infrared data indicate that structures I and II represent two possibilities. Recently it has been suggested[5] that since $\nu_{C\equiv C}$ is lowered over the range 100 → 500 cm^{-1} then I and II are actually extremes of a more gradual transformation. Maitlis *et al.*[6] have also discussed the problem and propose that the bonding can be described by using a single model (Fig. III).

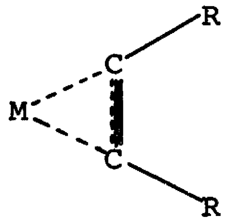


Fig. III

X-ray determinations of acetylene complexes.

The structure of the platinum complex $(Ph_3P)_2Pt(PhC_2Ph)$ (4) has recently been determined.[12] As predicted from the infrared account given above, the structure is between I and II but nearer II, since the C-C bond is only 14° out of the plane formed by the platinum, two phosphorus, and one of the acetylenic carbon atoms. The structure is given in Fig. IV.

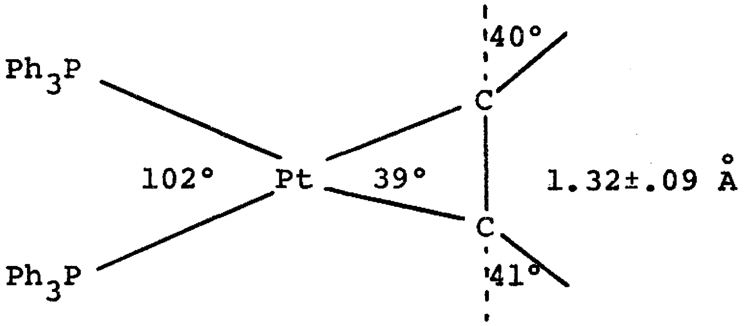


Fig. IV

The structure of the complex $(Bu^tC_2Bu^t)PtCl_2$-(p-toluidine) (5) has also been determined by X-rays[13] and was shown to be closer to that suggested by Fig. I.

A large number of organometallic derivatives have been prepared from the reaction of metal carbonyls with acetylenes.[14] The binuclear cobalt complex $(PhC{\equiv}CPh)Co_2(CO)_6$ (6) was obtained from the following reaction:[15]

$$Co_2(CO)_8 + PhC{\equiv}CPh \longrightarrow (PhC{\equiv}CPh)Co_2(CO)_6$$

Its structure has been determined[16] and is shown in Fig. V.

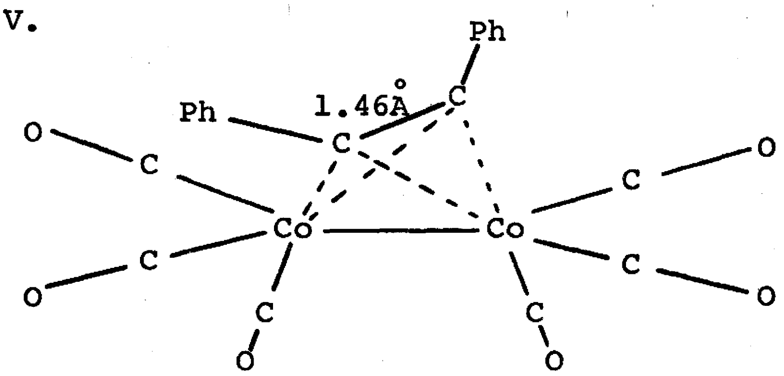


Fig. V

The C-C bond distance of the acetylene is 1.46 Å. Both sets of π- and π*- orbitals of the acetylene are used in bonding to the two cobalt atoms which are bridged by it. The Co-acetylene-Co angle is close to the expected 90°.

Acetylenes normally react with metal carbonyls to give a wide variety of organic products as well as complexes in which two or more acetylene molecules have condensed, with or without inclusion of a metal and/or carbonyl groups to complete a ring.

The reactions of acetylenes with iron dodecacarbonyl have been studied extensively and give a very wide range of products. With diphenylacetylene, a number of complexes have been characterised[17] and their molecular structures determined by X-rays. One of the products is the violet isomer of $Fe_3(CO)_8(PhC_2Ph)_2$ [18] (7), (Fig. VI).

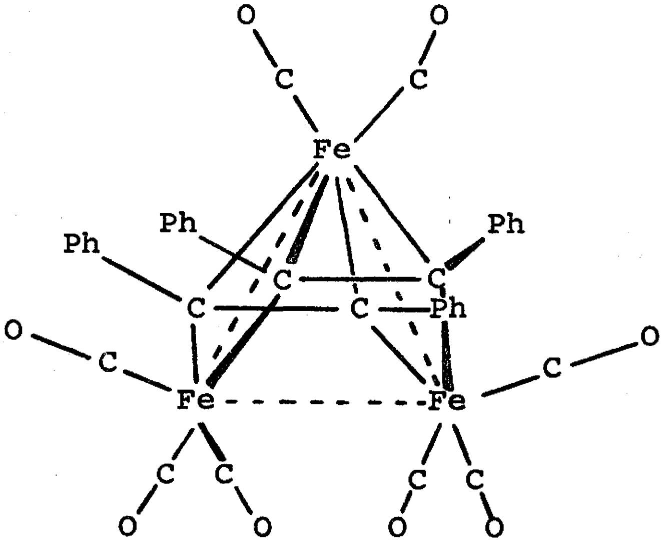


Fig. VI

The acetylenic bond length averages 1.39 Å. The two diphenylacetylene ligands are not joined together but form bridges to the iron atoms on either side of the plane formed by the three metal atoms.

When heated in refluxing benzene, this violet compound undergoes a facile rearrangement to a black compound of the same formula, $Fe_3(CO)_8(PhC_2Ph)_2$ [18] (8). The two acetylenes have bonded together with inclusion of a metal atom to form the stable ferracyclopentadiene ring. Iron carbonyl groups are π-bonded on either side of the planar ferracyclopentadiene ring (Fig. VII).

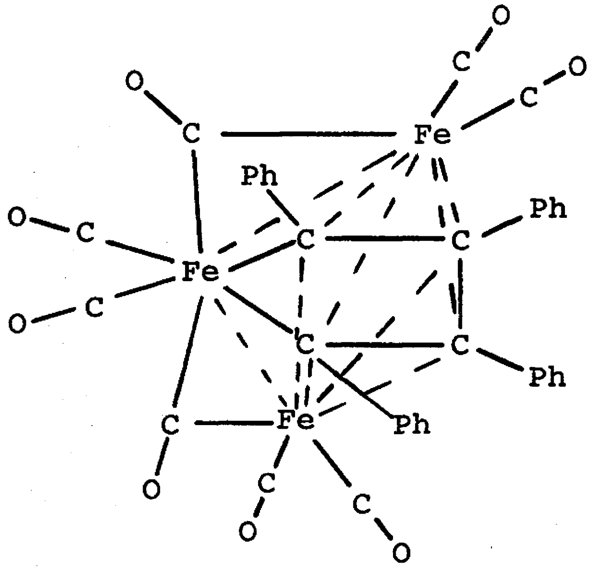


Fig. VII

An interesting complex is $Co_2(CO)_4(HC_2Bu^t)_2C_2H_2$ [19] (9). This is a diallyl complex and its structure illustrates quite nicely how 1,2-di-tert-butylbenzene is formed on decomposition with bromine (Fig. VIII).

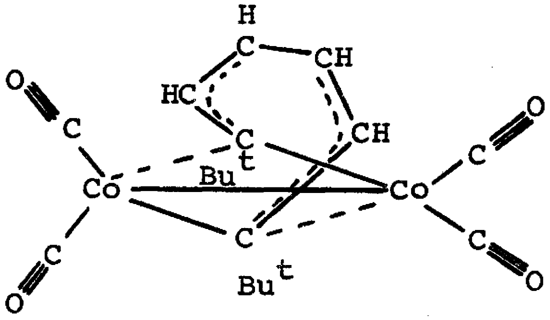


Fig. VIII

Similarly, the related complex $Co_2(CO)_4(HC_2Bu^t)_3$ [20] (10) frees the otherwise inaccessible 1,2,4-tri-tert-butylbenzene.

Cyclic trimerisation of acetylenes.

As has already been mentioned, organometallic complexes of acetylenes have attracted considerable attention in recent years. This is in no small way due to their importance as catalysts and intermediates in acetylene polymerisations. The subject of acetylene polymerisation by transition metal catalysts has been reviewed by various people in recent years.[2,14,21,22,23]

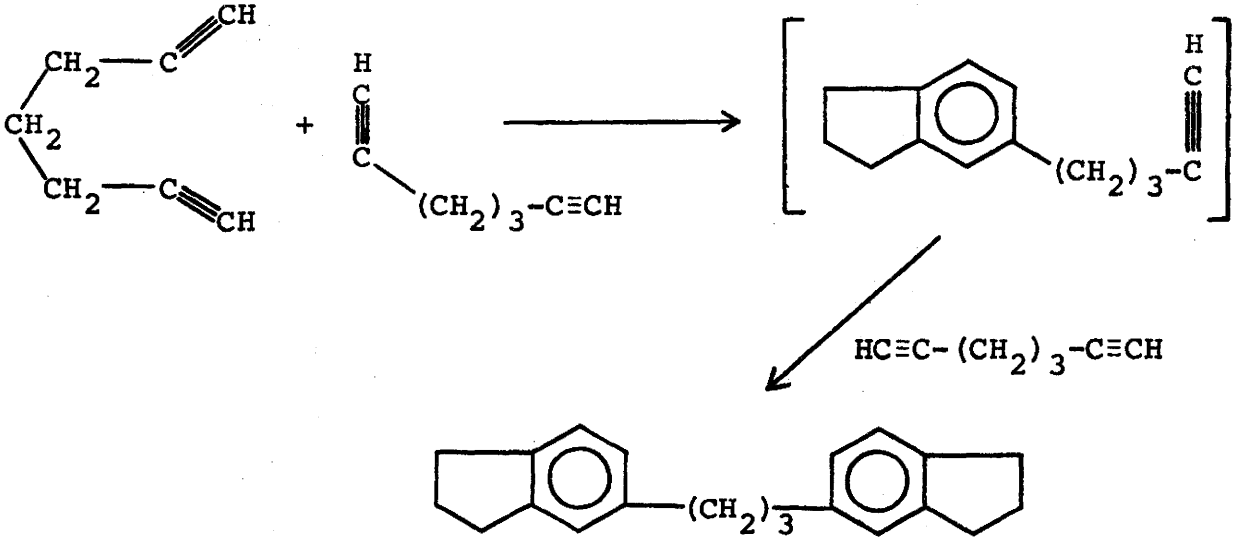
Reppe's discovery of catalysts[24] that allowed the selective preparation of cyclic oligomers from alkynes under mild conditions can be considered the starting point. The availability and continual discovery of a wide variety of catalysts has made cyclisation a process of practical interest. A large number of benzene derivatives which were heretofore either unknown or obtainable only by complicated methods could now be readily synthesised, many in high yields.

1. Catalytic systems

The polymerisation of alkynes by phosphine nickel carbonyls has been studied by several researchers, particularly by Meriwether and co-workers.[3,25] It was found that pretreatment of a solution of the nickel-carbonyl-phosphine complex at reflux with an unreactive disubstituted acetylene enhanced the rate of polymerisation of reactive acetylenes. The active catalyst is assumed to be a phosphine-nickel-acetylene complex.

A large number of monosubstituted acetylenes have been successfully cyclised using these catalysts. Unsymmetrical benzene derivatives are preferred. In addition, linear polymers have been obtained.[25] The ability to form aromatic trimers depends on the substituent and decreases from methyl to n-pentyl. Likewise, alkynes bearing bulky groups give linear polymers, while in fact t-butylacetylene fails to react at all. Besides this apparent steric effect, the yields of benzenes decrease in the sequence R = -COOR, -OR, COR, $-CH_2OH$, $-CH=CH_2$, aryl, n-alkyl, indicating that the presence of polar groups generally facilitates trimerisation. However, acetylenic chlorides and acids poison the catalyst and do not react at all.

With the exception of 2-butyne-1,4-diol[25a] which forms high yields of hexamethylolbenzene, disubstituted acetylenes are not trimerised by phosphine-nickel-carbonyl catalysts. Similarly, the polymerisation of conjugated diacetylenes have been unsuccessful.[25a] An interesting case though is the cyclotrimerisation of unconjugated diacetylenes. In addition to unsubstituted linear polymers, 1,6-heptadiyne forms an aromatic ring structure[25c] (<u>11</u>).

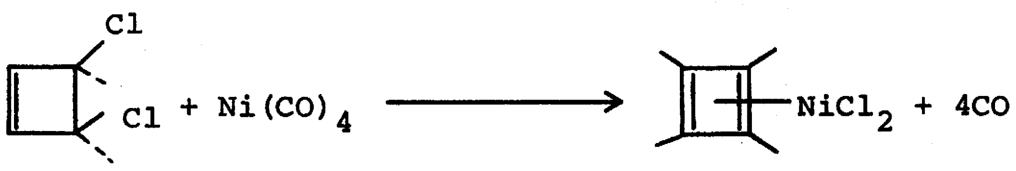


(<u>11</u>)

A number of transition metal carbonyls as well as their acetylene complexes form a large group of active catalysts for the cyclic trimerisation of acetylenes. Hübel and Hoogzand have studied the catalytic effects of some metal-carbonyl compounds on mono-and-disubstituted acetylenes.[26] High yields of benzene derivatives were frequently obtained. The cobalt carbonyls $Co_2(CO)_8$, $[Co(CO)_4]_2Hg$, and $Co(CO)_3NO$ in addition to the alkyne complexes $(RC_2R')Co_2(CO)_6$ and $(RC_2R')Co_4(CO)_{10}$ were found to be excellent catalysts and generally more specific than the phosphine nickel carbonyls. Unsymmetrically substituted benzenes were usually obtained and only occasionally was the symmetrical isomer detected. In contrast, the trimerisation of conjugated diacetylenes was less specific and led to both symmetrical and unsymmetrical forms.[27]

Benzene derivatives containing bulky groups have been conveniently prepared in the presence of cobalt carbonyls. 1,2,4-tri-t-butyl-[20] and 1,2,4,5-tetra-t-butylbenzene[28] have both been obtained in this way (see also p. 8, Fig. VIII) while cyclisation of di-isopropyl acetylene gave hexaisopropylbenzene.[29] In this latter molecule rotation of the isopropyl groups is hindered almost completely for steric reasons.

Criegee and Schroeder were the first to prepare a derivative of cyclobutadiene[30] by dehalogenation of a 3,4-dihalocyclobutene:

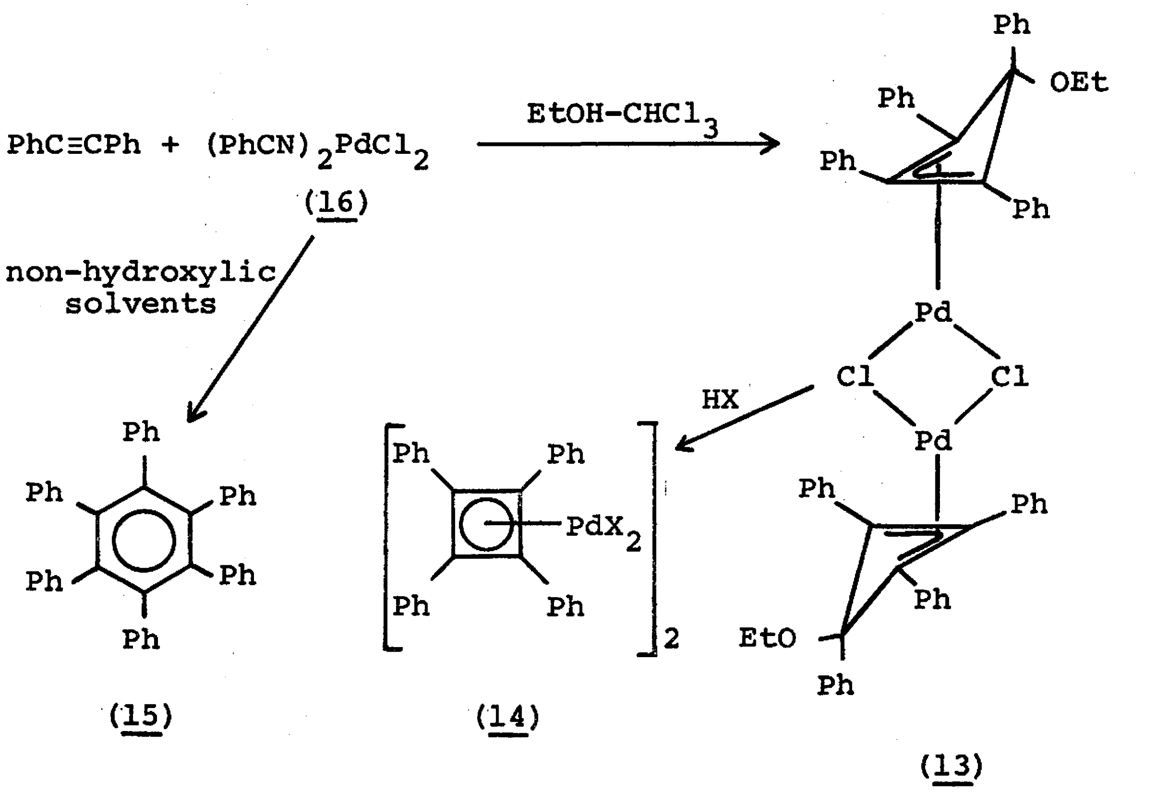


(12)

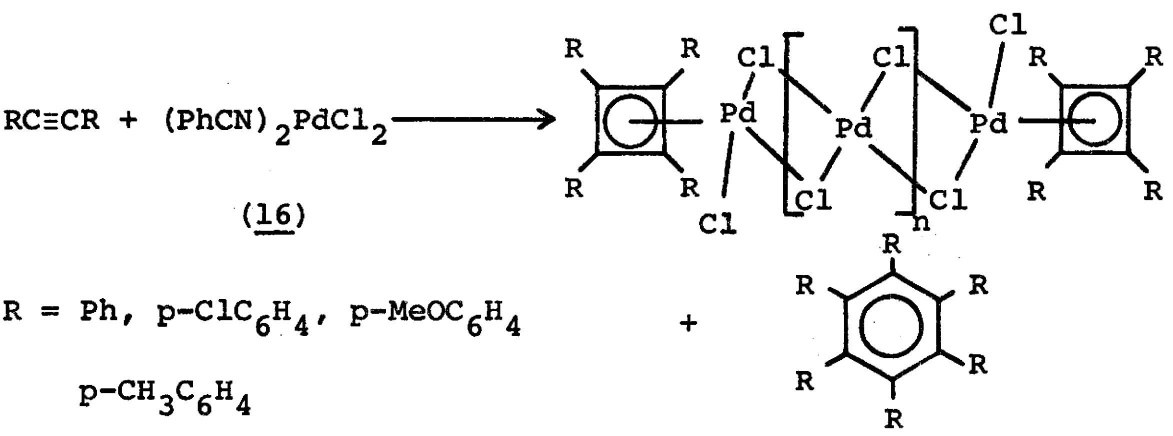
In recent years, a number of cyclobutadiene-metal complexes have been prepared from alkynes. Complexes of Fe,[31,32] Co,[32,33,34] Mo,[34,35] W,[34] Pd[36,37,38] are known.

Malatesta and co-workers[39] first studied the reaction between tolan (diphenylacetylene) and palladium chloride in ethanol, the product of which was suggested to be a σ- and π-bonded ethoxytetraphenylcyclobutene palladium chloride dimer. Subsequent investigations[37,40] and an X-ray structure determination[41] showed the complex to be endoethoxytetraphenylcyclobutenyl palladium chloride dimer (13). Treatment of the complex with hydrogen halide gives the cyclobutadiene complex (14).

Blomquist and Maitlis[40] have shown that in non-hydroxylic solvents the trimerisation of tolan to hexaphenylbenzene (15) was catalysed by bis(benzonitrile)-palladium chloride (16). In ethanol-chloroform solvent they were able to confirm the results of Malatesta described above. The tetraphenylcyclobutadiene complex (14) was not an intermediate in the trimerisation reaction as it failed to react with excess tolan to give hexaphenylbenzene.



Under some conditions tetraphenylcyclobutadiene palladium chloride (14) formed directly[36] in addition to the hexa-substituted benzene (15). The relative proportions of products depended on the method of addition and the solvent. High dilution and addition of the acetylene to $(PhCN)_2PdCl_2$ (16) favoured the formation of complex.



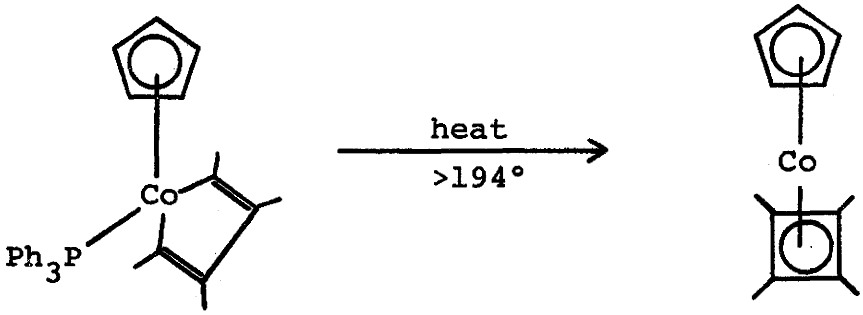
R = Ph, p-ClC_6H_4, p-$MeOC_6H_4$
p-$CH_3C_6H_4$

Five-membered rings have also been formed in the cyclisation of acetylenes. A number of substituted cyclopentadienones have been obtained from the catalytic action of metal carbonyls on disubstituted acetylenes.[17,29,31]

Formation of eight-membered and larger rings from acetylene are known from the initial work of Reppe[24] and Schrauzer.[42]

Metalacyclopentadiene complexes of Ti,[43,44] Zr,[45] Fe,[17,46,47] Os,[48,49] Co,[50] Rh,[51,52,53] and Ir[51] have been prepared. The structures have generally been proposed on the basis of spectral evidence or the method of synthesis. Several structures have also been proven by X-rays.[54]

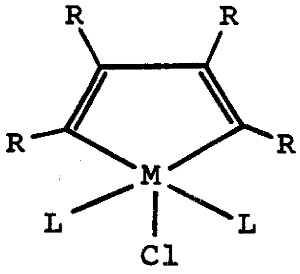
Metalacyclopentadiene and cyclobutadiene complexes can be considered valence tautomers of one another. It is sometimes difficult to distinguish between the two possibilities. However, Yamazaki and Hagihara have reported the conversion of one form into the other.[50]



(17) (18)

This was accomplished by heating (17) above its melting point to form the known cyclobutadiene complex (18).[32,33]

Collman and co-workers[51] have described the synthesis of metalacyclopentadiene complexes of iridium and rhodium. The metalacycles (19) and (20) were found to catalyse the trimerisation of dimethyl acetylenedicarboxylate. The iridacycle is an effective catalyst above 100° while lower temperatures are required for the rhodium analogue. These metalacycles possess a latent site of unsaturation and readily take up 1 mole of CO. The vacant coordination site has been shown to be essential to the catalytic activity.

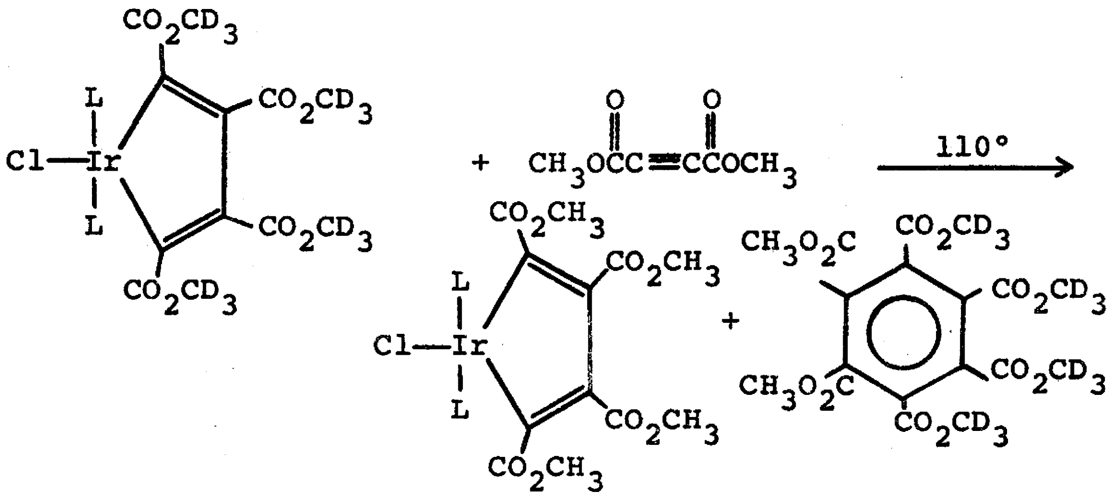


(19) M = Ir, L = Ph_3P

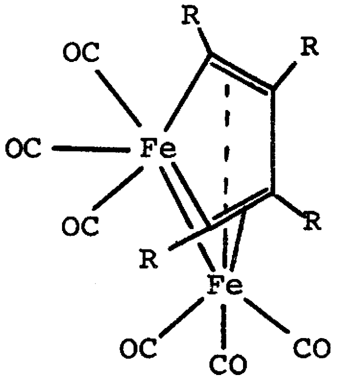
(20) M = Rh, L = Ph_3As

R = CO_2CH_3

Apparently the metalacycle unit combines with another mole of acetylene as evidenced by the reaction outlined below using a perdeuterioiridacycle.



In the case of the binuclear iron complex (21), Hübel[26] concluded that (21) was not a catalytic intermediate but decomposed to form the active catalyst.

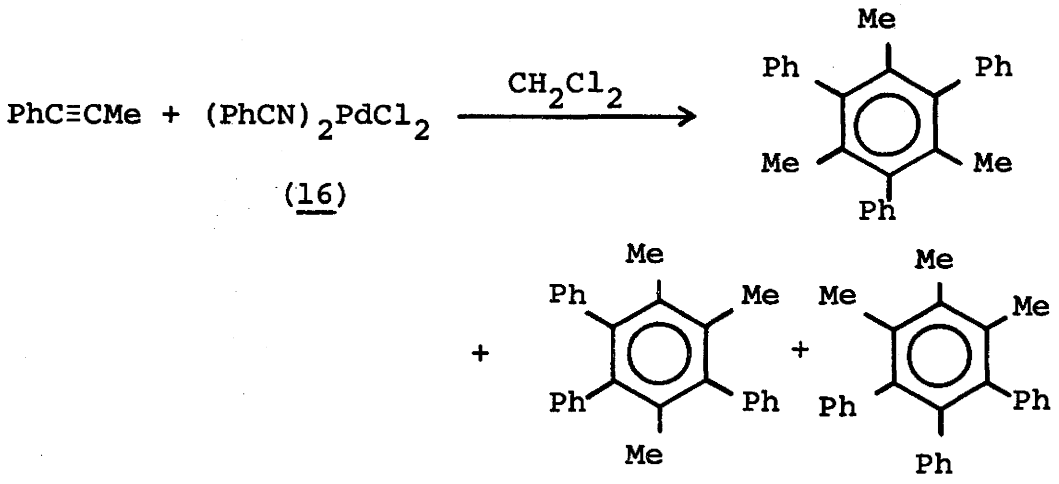


$R = C_6H_5$

(21)

Treatment of (21) with di(p-chlorophenyl)acetylene resulted in a 49% yield of hexa(p-chlorophenyl)benzene but only 4% of the mixed trimer di(p-chlorophenyl)tetraphenylbenzene. Similarly, the coordinatively saturated cobalt complex (17) produced hexaphenylbenzene in 8% yield when refluxed with tolan in toluene.

Recently, Dietl and Maitlis[55] reported the catalytic action of bis(benzonitrile)palladium chloride (16) on methylphenylacetylene. In methylene chloride a mixture of organic trimers was obtained which were separated and characterised spectroscopically.



(16) (22)

(23) (24)

The isomers (22) and (23) had previously been obtained from the trimerisation of methylphenylacetylene with $Hg[Co(CO)_4]_2$.[26] The isomer (24), however, had never been reported and is a very novel product since its formation must involve cleavage of a C≡C bond, at least formally.

In benzene solution, methylphenylacetylene reacted with (16) to give the three isomers (22), (23), and (24) and a complex (61%) which analysed for $[(PhC_2Me)_3PdCl_2]_2$ (25). The complex decomposed in chloroform or methylene chloride solution to give $PdCl_2$ and the isomers (22) and (23). Likewise, when treated with triphenylphosphine, bis(triphenylphosphine)palladium chloride (26) was obtained in addition to (22) and (23). None of the isomer (24) was detected.

Maitlis and co-workers[56] have extended their studies by examining the trimerisation of 2-butyne (27) with bis(benzonitrile)palladium chloride (16). An excess of (27) reacted with (16) in benzene at ∿10° to give a little hexamethylbenzene and a complex which analysed correctly for $[(MeC_2Me)_3PdCl_2]_2$. An open chain structure was proposed on the basis of spectroscopic evidence and its reactions (Fig. IX).

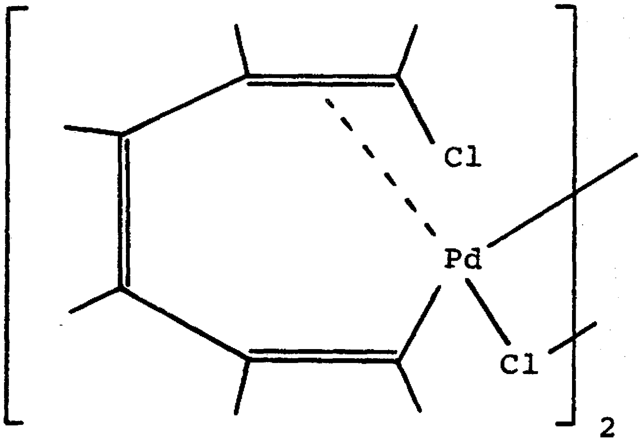


Fig. IX

2. Mechanisms

A number of mechanisms have been advanced to account for the catalytic trimerisation of acetylenes. Initially, Bergmann[57] suggested that cyclooctatetraene is formed in the Reppe synthesis by dimerisation of cyclobutadiene. Longuett-Higgins and Orgel[58] expressed a similar opinion to account for the low yield of benzene which, for thermodynamic reasons, would be the expected product. The cyclobutadiene hypothesis has not received wide support since cyclobutadiene complexes[59] have been shown to be stable under the conditions for acetylene trimerisation. Such a mechanism cannot be ruled out, however, as certain workers[29,60] have obtained results which are difficult to explain without the hypothesis that cyclobutadiene is produced as an intermediate.

In a detailed study of the Reppe synthesis, Schrauzer[1] and co-workers found that the formation of cyclooctatetraene was dependent on the nature of the catalyst and the solvent. The only active nickel catalysts were those with an octahedral environment. Moderately polar solvents in which the acetylenes could undergo ligand-exchange reactions and displace the solvent molecules surrounding the Ni(II) ion were found to be best. With complexing solvents such as pyridine or benzonitrile, no cyclooctatetraene was formed.

Schrauzer suggested that for cyclooctatetraene formation the Ni(II) ion is "solvated" by the weakly coordinating acetylene molecules. In the resulting octahedral complex the acetylenes assume an arrangement which favors the formation of cyclooctatetraene. Such a π-complex multicentred mechanism is indicated in Fig. X.

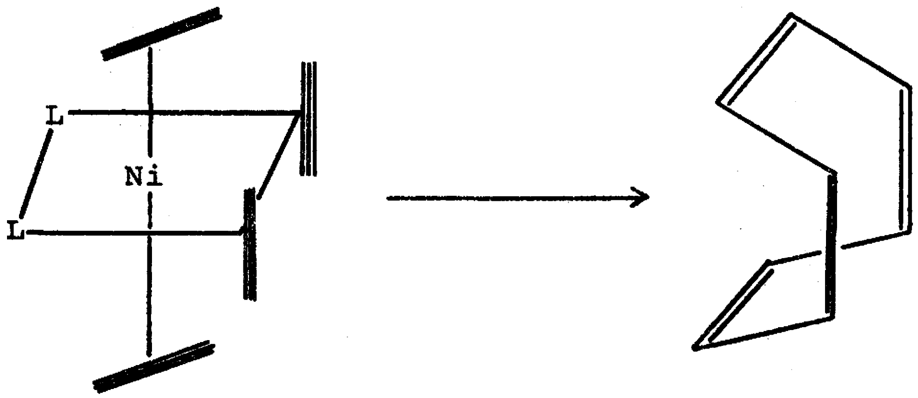
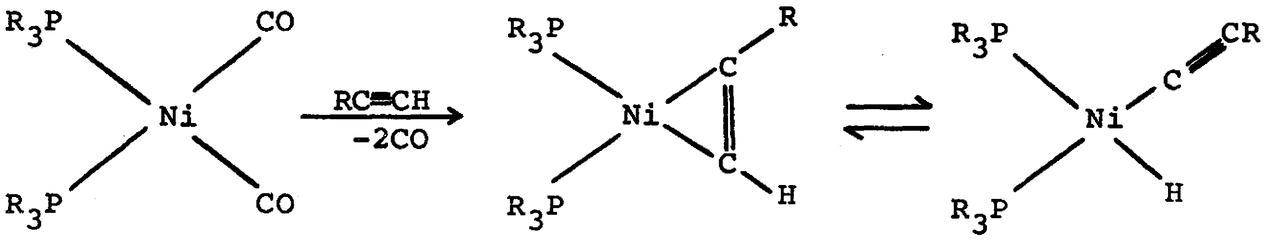


Fig. X

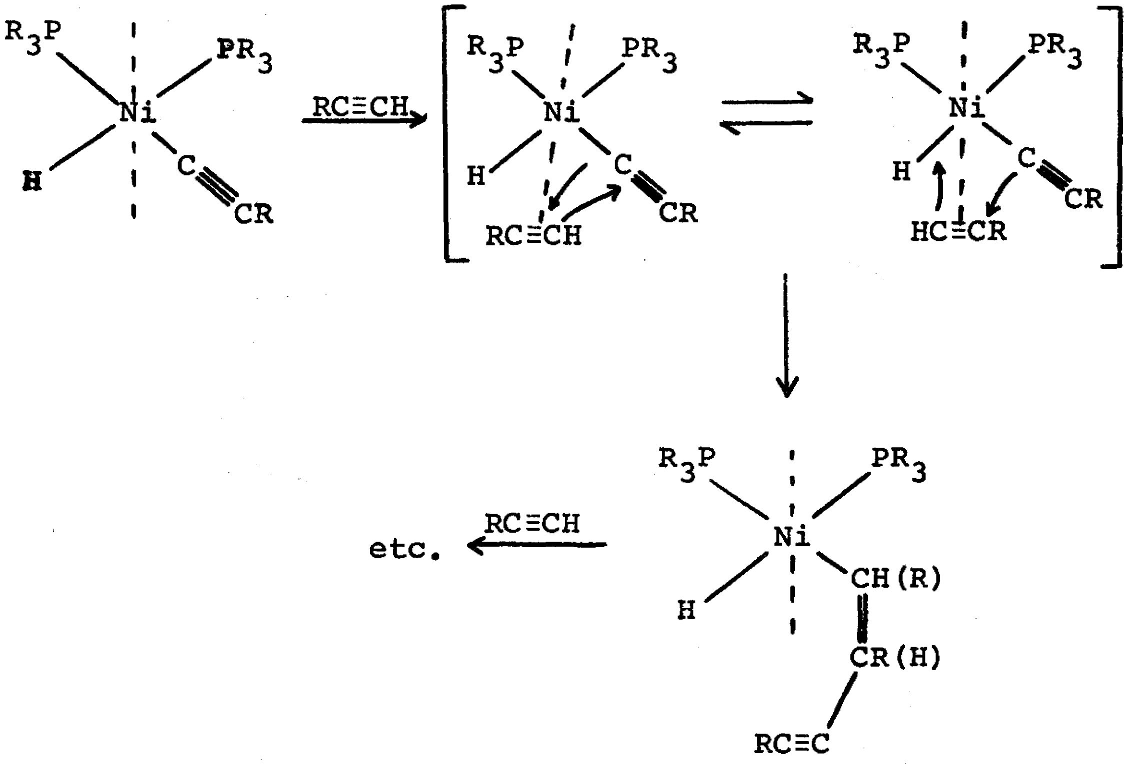
Cyclooctatetraene formation is inhibited when the reaction is carried out in the presence of one mole of triphenylphosphine. This strongly coordinating ligand apparently blocks one of the coordination sites and only three acetylenes can couple to give benzene in high yield. With strong chelating ligands such as α,α'-dipyridyl the catalyst is completely poisoned.

Meriwether[3] proposed a different interpretation based on the oxidative addition of the acetylenic C-H bond to the metal so as to form an acetylide-hydride complex (28) which is considered to be the active catalyst for both linear and cyclic polymerisation.

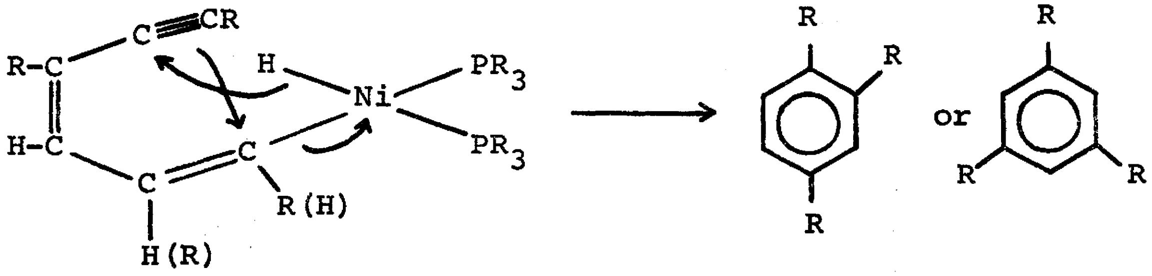


(28)

The nickel atom is capable of coordinating a second acetylene molecule on a vacant p_z orbital; chain growth then proceeds by a series of cis insertions between the nickel and acetylide carbon atoms.

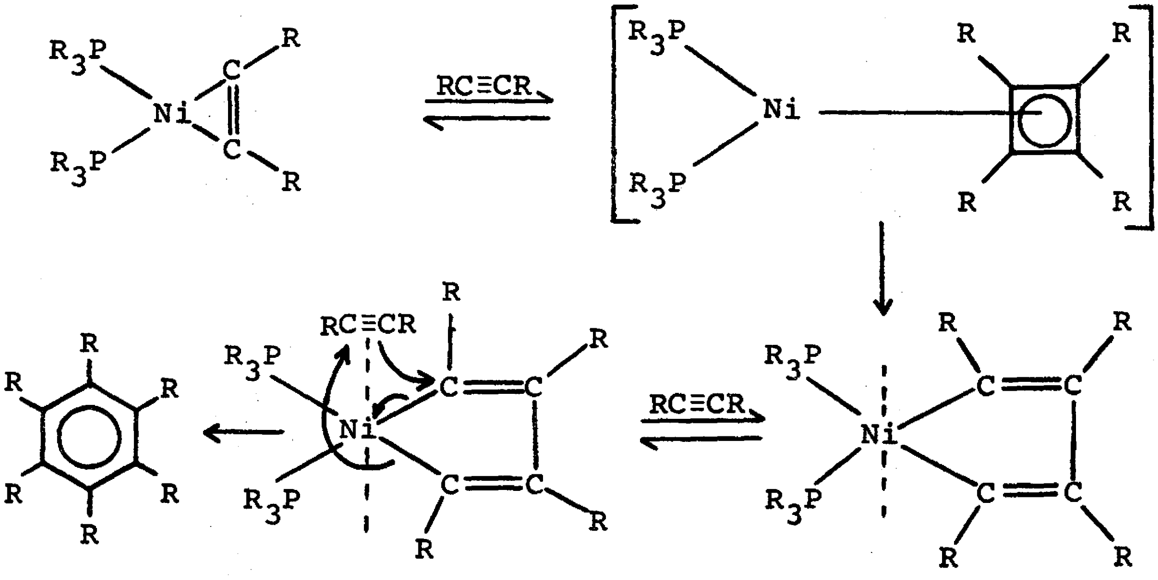


Aromatisation can occur when the first and the sixth carbon atoms of the chain approach within bonding distance. A concerted hydrogen transfer followed by ring closure would give the aromatic products.



(29)

Since a hydrogen transfer is the characteristic feature of this mechanism, the cyclotrimerisation of disubstituted acetylenes cannot be explained. Meriwether proposed an intermediate metalacyclopentadiene complex (30) for the cyclotrimerisation of disubstituted acetylenes, generally obtained using bis(acrylonitrile)-nickel-phosphine catalysts

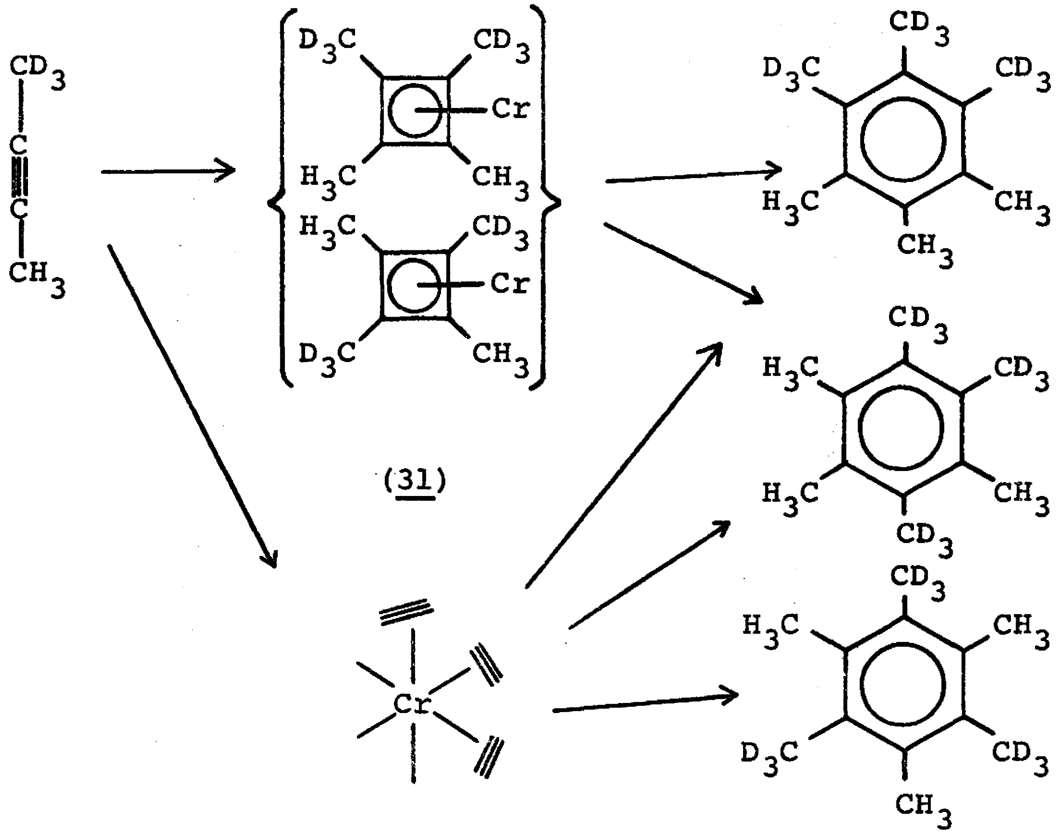


+ $(R_3P)_2Ni$

(30)

Similar metalacycles have been described recently[40,50,52,53] and have been proposed as intermediates in the trimerisation of acetylenes.

Whitesides and Ehmann[61] have studied the cyclotrimerisation of 2-butyne-1,1,1-d_3 on a chromium catalyst and have found evidence which excludes the formation of a cyclobutadiene intermediate. The cyclobutadienes (31) must be formed with equal probability via head-to-head and head-to-tail combinations. Reaction with a third molecule of the acetylene would then lead to a statistical distribution of the three hexamethylbenzenes. If cyclotrimerisation proceeds through a concerted mechanism then only two of the hexamethylbenzenes can arise. They found that none of the isomer with three adjacent labelled methyl groups was formed and therefore concluded that cyclobutadiene was not an intermediate. (However, see p. 16.)



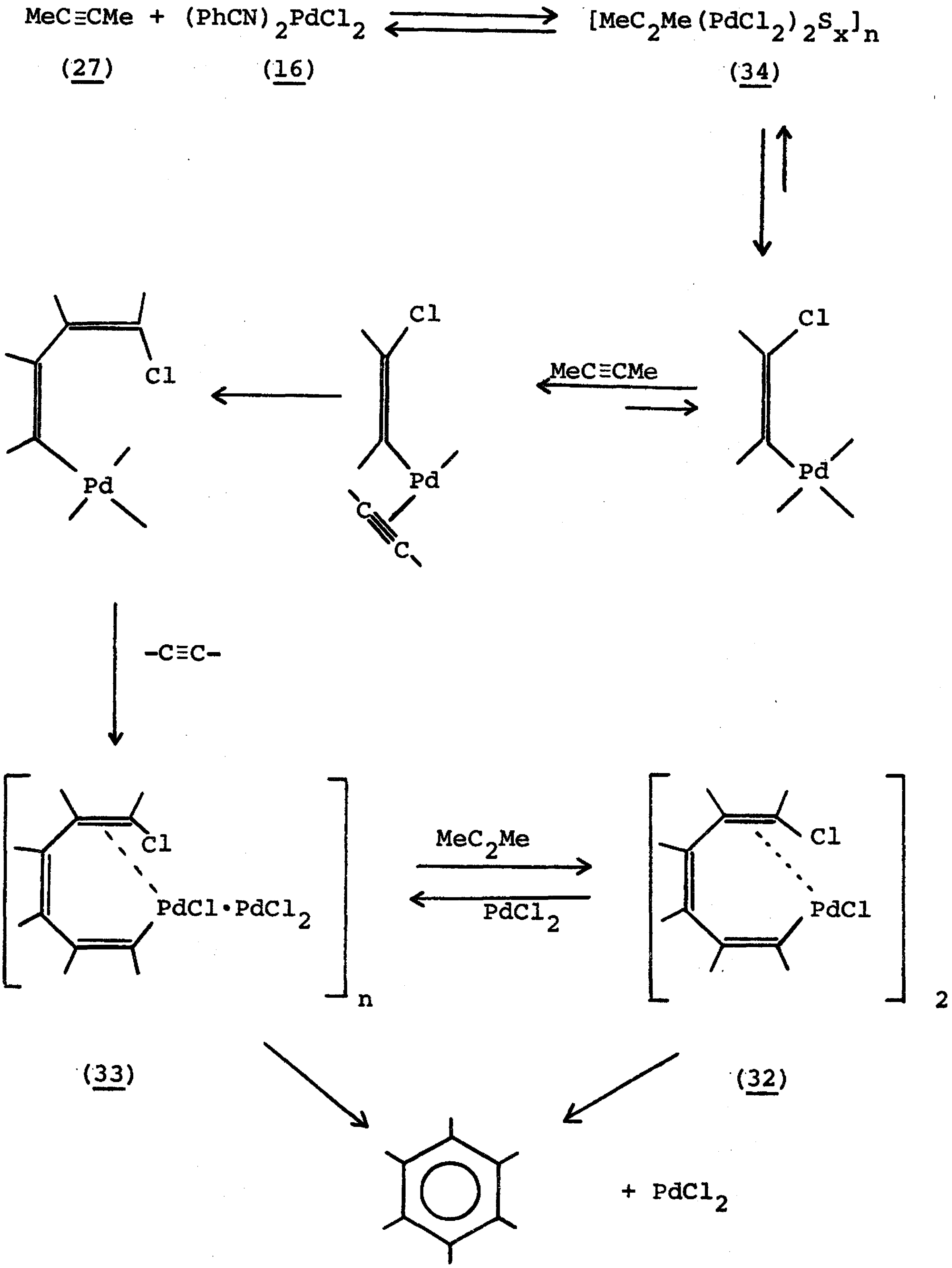
(31)

In the trimerisation of 2-butyne (27) with (16), Maitlis and co-workers[56] have reported evidence for intermediates and a reaction mechanism different from any considered to date. At -50° a π-complex was formed which reacted at -25° with more 2-butyne to give an intermediate proposed to be a 2-chloro-3,4,5,6-tetramethyl-2-trans-4-

cis-6-trans octatriene σ-bonded to a PdCl at the 7-position and π-bonded to the PdCl at the other end. At higher temperatures the complex decomposed to hexamethylbenzene.

At 10° in benzene, bis(benzonitrile)palladium chloride (16) reacted with an excess of 2-butyne (27) to give the complex $[(Me_2C_2)_3PdCl_2]_2$ (32) (Fig. IX). The complex (32) reacted with (16) (1:2 molar ratio) to give a new complex which was too labile to be isolable and which was assigned the molecular formula $[(Me_2C_2)_3Pd_2Cl_4]_n$ (33). Complex (32) decomposed via complex (33) to hexamethylbenzene.

The rate of formation of (33) was found to be independent of the concentration of 2-butyne which suggested that the rate determining step is probably a rearrangement. A reasonable rearrangement would be cis insertion of the acetylene in the π-complex (34) into a PdCl bond, which would then be followed by two further very fast cis insertions of coordinated acetylenes into the Pd-C (vinyl) bond, eventually yielding (33). The extra $PdCl_2$ likely assists these processes but the method is not yet clear. The reaction largely finishes after three moles of the acetylene have been added for steric reasons. The reaction is envisaged schematically as follows:


MeC≡CMe + (PhCN)₂PdCl₂ ⇌ [MeC₂Me(PdCl₂)₂Sₓ]ₙ
(27)
(16)
(34)
Cl
Cl
Cl
MeC≡CMe
Pd
Pd
Pd
C
C
-C≡C-
Cl
PdCl·PdCl₂
n
MeC₂Me
PdCl₂
Cl
PdCl
2
(33)
(32)
+ PdCl₂

Purpose of current work.

As can be seen from the foregoing discussion, the polymerisation of acetylenes can proceed through a variety of mechanisms. Due to the complexity of catalysts and products obtained in these reactions it is often difficult to predict which mechanistic path has been followed.

In particular, we have been concerned with the mechanisms of the palladium-catalysed polymerisations of acetylenes. When this work was started, the palladium-acetylene complex $[(MeC_2Me)_3PdCl_2]_2$ (32) had recently been prepared in these laboratories. It was decided to study some of the reactions of this complex in the hope of learning the structure and bonding in the complex. A knowledge of the structure and bonding in (32) should shed some light on the mechanism of the palladium catalysed reaction and, hopefully, explain the origin of the interesting isomer (24) obtained from the palladium catalysed reaction of methylpenylacetylene.[55]

RESULTS

RESULTS

Reaction of 2-butyne with palladium chloride.

2-Butyne (27) and palladium chloride reacted together in benzene at about 10° to give a complex which contained three moles of the acetylene per palladium atom and which analysed for $[(Me_2C_2)_3PdCl_2]_2$ (32). Bis(benzonitrile)palladium chloride (16) was used as the source of palladium chloride because of its ready solubility in benzene and other organic solvents. A small amount of hexamethylbenzene was isolated in addition to the bright yellow microcrystalline complex (32). The complex (32) was stable for about six weeks when kept at -10°.

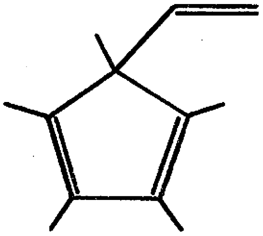
Reduction of the mother liquors from the synthesis of complex (32).

The mother liquors remaining after the isolation of complex (32) were treated with an excess of anhydrous hydrazine to free any organic components which may have been complexed to palladium. Removal of the reduced metal and concentration of the filtrate followed by chromatography over alumina gave an oil whose complicated nmr spectrum was the same as the spectrum of the mother liquors before reduction. The oil could be separated into four components by preparative vpc. The first fraction represented about 10% of the mixture and was identified by nmr as vinylpentamethylcyclopentadiene (35). The second fraction represented about 7% of the mixture. The mass spectroscopic molecular weight was 217, whereas a value of 252 was expected. The difference of 35 mass units suggests that chlorine is lost very readily in the mass spectrometer. Component three was 25% of the mixture and analysed for $C_{16}H_{22}$; the mass spectroscopic molecular weight was 214. Fraction four was the major component and represented the remainder or 55% of the mixture. Analysis showed the compound to have a molecular formula of $C_{16}H_{25}Cl$ and both mass spectroscopic and osmometric molecular weight determinations agreed with this. The ^{1}H nmr spectrum in chloroform showed a small resonance at τ 4.85 and a series of sharp peaks in the methyl region of the spectrum between τ 8.09 and 8.57; no assignments were made. The spectrum was almost exactly identical with the spectrum of fraction two, apart from minor differences, suggesting that the second and fourth fractions were isomers. The ultraviolet spectrum of fraction four had shoulders at 2610 Å (ε = 4355) and 2330 Å (ε = 8710). The infrared spectrum (liquid film) showed, besides other bands, absorptions at 1645(m) (non-conjugated C=C) and 740(m) (ν_{C-Cl}) cm^{-1}.

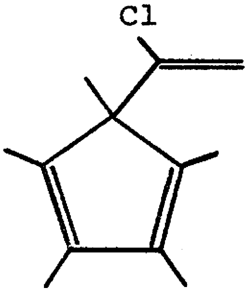
Reactions of $[(Me_2C_2)_3PdCl_2]_2$, complex (32).

Reaction of complex (32) with triphenylphosphine.

Triphenylphosphine reacted with (32) in both benzene and $CDCl_3$ to give the two vinylpentamethylcyclopentadiene derivatives (35) and (36), and a small amount of hexamethylbenzene.



(35)



(36)

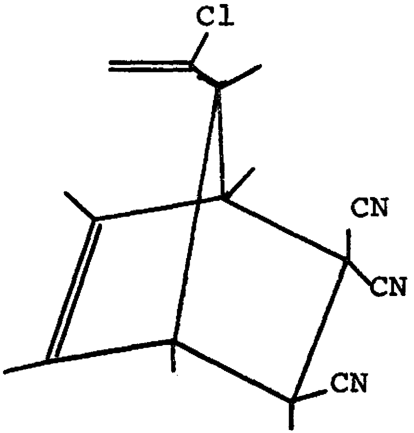
The structures of the two compounds were assigned on the basis of their analyses and spectroscopic properties. The 100 MHz ^1H nmr spectra in $CDCl_3$ (Appendix I) showed the following resonances: for (35), at τ 9.00 (singlet, bridgehead methyl), 8.34 (doublet, J = 0.9Hz, diene methyls), 8.22 (doublet, J = 0.9Hz, diene methyls), and 4.96 (multiplet, vinyl protons), with intensity ratios 3:6:6:3. (In benzene at 60MHz peaks were observed at τ 8.76 (singlet, 3H), 8.10 (singlet, 12H), and 4.66 (multiplet, 3H).) For (36), resonances appeared at τ 8.90 (singlet, 3H), 8.33 (doublet, J = 1.0Hz, 6H), 8.22 (doublet, J = 0.85Hz, 6H), 4.76 (doublet, J = 1.3Hz, 1H), and 4.71 (doublet, J = 1.3Hz, 1H). (In benzene at

60MHz resonances appeared at τ 8.79 (singlet, 3H), 8.10 (singlet, 12H), and 4.61 (double doublet, 2H).) The small splittings observed in the resonances of the diene methyls are due to homoallylic coupling between inequivalent methyls. The chlorovinyl group in compound (36) can be considered a disubstituted olefin. Therefore, the protons can be geminal, cis, or trans to each other. From a comparison of the spectra of various disubstituted olefins it has been found that the geminal coupling constant has the smallest value and the trans coupling constant the largest, and that J_{HH}^{gem} (0 to 2.5 Hz) << J_{HH}^{cis} (4.0 to 12.0 Hz) < J_{HH}^{trans} (12 to 19 Hz).[65] On the basis of the observed value of 1.3 Hz for J, the chlorovinyl group was assigned as having the protons geminal. The infrared spectra of (35) and (36) also agreed well with the proposed structures and showed bands, apart from those due to vibrations associated with the methyls, at 3080(m), 3050(w) (vinylic CH), 1655(w), 1625(s), and 906(s) cm^{-1} for (35), and at 3110(w), 1660(m), 1625(s), 1620(sh), 882(vs), and 708(s) (ν_{C-Cl}) cm^{-1} for (36). The ultraviolet spectrum of (35) in n-hexane had λ_{max} at 2400 Å (ε = 3780) while that of (36) had λ_{max} at 2500 Å (ε = 4750). These values are consistent with those normally found for cyclopentadienes. Also, the nmr and uv data for compound (35) are in agreement with the values reported by Criegee and Grüner.[63] High resolution mass spectra of the two compounds were run and gave accurate molecular weights. For the vinylpentamethylcyclopentadiene (35) a molecular ion peak was observed at m/e 162.139930 ($C_{12}H_{18}$). In addition low resolution mass spectra showed peaks at m/e 147 ($C_{11}H_{15}$) due to loss of a methyl and m/e 119 (C_9H_{11}, dimethyltropylium?) due to loss of C_3H_7. No detailed structural information was obtained apart from the fact that the cracking pattern was similar to the isomeric hexamethylbenzene. The molecular ion peaks for chlorovinylpentamethylcyclopentadiene (36) were observed at m/e 196.103268 ($C_{12}H_{17}{}^{35}Cl$) and 198.100317 ($C_{12}H_{17}{}^{37}Cl$). In addition low resolution mass spectral peaks were observed at m/e 181, 183 ($C_{11}H_{14}Cl$) due to loss of a methyl and m/e 161 ($C_{12}H_{17}$) due to loss of chlorine.

The yield of (35) and (36) was found to be temperature dependent: whereas (35) was formed exclusively at low temperatures, (36) was favoured at high temperatures. The results of reactions in benzene and $CDCl_3$ are presented in Table I.

The chlorovinylpentamethylcyclopentadiene (36) took up three moles of hydrogen, providing evidence for the three double bonds. The mass spectrum of the saturated chlorocompound had molecular ion peaks at m/e 204 ($C_{12}H_{23}{}^{37}Cl$) and 202 ($C_{12}H_{23}{}^{35}Cl$). The hydrocarbon (35) did not undergo this reaction under the conditions employed. Instead, a white insoluble polymeric solid was obtained.

Chlorovinylpentamethylcyclopentadiene (36) formed a 1:1 adduct with tetracyanoethylene (TCNE). Although the violet solid could not be purified from excess TCNE the 60MHz ^1H nmr clearly showed that the adduct (37) had been formed.



(37)

In benzene resonances were observed at τ 4.87 (doublet, J = 3Hz, 1H), 5.67 (doublet, J = 3Hz, 1H), 8.46 (singlet, 6H), 8.56 (singlet, 3H), and 8.66 (singlet, 6H). In $CDCl_3$, the resonances appeared at τ 4.50 (doublet, J = 3Hz, 1H), 5.15 (doublet, J = 3Hz, 1H), 8.15 (singlet, 6H), 8.32 (singlet, 6H), and 8.41 (singlet, 3H). A solvent effect is readily apparent, in particular with the singlets of intensity 3H. This phenomenon is not unusual and in fact has already been observed in the spectra of compounds (35) and (36), (see p.29).

In addition to the organic products of hexamethylbenzene, 1-vinyl-1,2,3,4,5-pentamethylcyclopentadiene (35),[64] and 1-(1-chlorovinyl)-1,2,3,4,5-pentamethylcyclopentadiene (36), bis(triphenylphosphine)palladium chloride (26) was also obtained from the reactions of

$[(Me_2C_2)_3PdCl_2]_2$ (32) with triphenylphosphine. The reactions leading to $(Ph_3P)_2PdCl_2$ (26), hexamethylbenzene, and (35) (i.e. the lower temperature reactions) were essentially quantitative. At higher temperatures, another complex besides $(Ph_3P)_2PdCl_2$ (26) could be isolated. Although not conclusive, the evidence strongly suggests that $(Ph_3P)_4Pd$ was formed, to some extent at least, presumably according to:

$$[(Me_2C_2)_3PdCl_2]_2 + Ph_3P \longrightarrow (Ph_3P)_2PdCl_2 + (Ph_3P)_4Pd$$

(32) (26)

$$+\ 2\ C_5Me_5CCl{=}CH_2 + H_2(?)$$

(36)

This was isolated as the more stable carbon disulphide adduct $(Ph_3P)_2PdCS_2$ (38).[62] Attempts to purify this compound were unsuccessful and the analytical results suggested that the adduct was contaminated, most likely with $(Ph_3P)_2PdCl_2$ (26) and triphenylphosphine. After a few days the solid was observed to have undergone a colour change from yellow to dark brown by air oxidation.

Reaction of complex (32) with triphenyl-arsine and -stibine.

Reactions of complex (32) with excess triphenylarsine and -stibine were carried out in benzene and chloroform at different temperatures. In each case an essentially similar reaction occurred with formation of hexamethylbenzene, (35), (36), and $(Ph_3E)_2PdCl_2$ (39), (E = As, Sb). The relative proportions of organic products were estimated by nmr, and the results recorded in Table I. As with the triphenylphosphine reaction, the reactions leading to $(Ph_3E)_2PdCl_2$ (39), (35), and hexamethylbenzene were essentially quantitative.

The results of the reactions with excess Ph_3E (E = P, As, Sb) in chloroform and benzene at different temperatures are grouped together in Table I for comparative purposes. The most readily apparent feature of the results is that the chlorovinylpentamethylcyclopentadiene (36) is a significant product only at higher temperatures, being greatest in the reactions with Ph_3P and least in the reactions with Ph_3Sb. The complex (32) normally reacts with chloroform to give hexamethylbenzene. The formation of this product has been largely suppressed in these reactions, with the possible exception of the reactions with Ph_3As. Another interesting feature is the consistency of the results. The amount of hexamethylbenzene formed remains fairly constant for a given base while it appears that (36) is largely formed at the expense of (35). At low temperatures (35) and about 15% hexamethylbenzene are the only products and the formation of (36) has been completely suppressed.

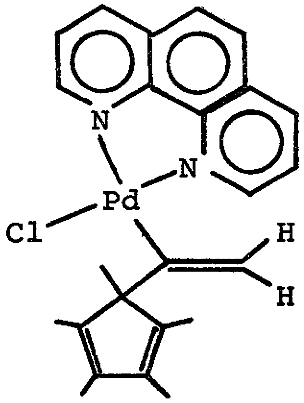
Base	Temp. °	CDCl$_3$			C$_6$H$_6$		
		HMB* %	35 %	36 %	HMB %	35 %	36 %
Ph$_3$P	0	25	65	10	10	60	30
	20	15	65	20	10	45	45
	40	15	60	25	10	25	65
	50	15	60	25			
	65				15	5	80
Ph$_3$As	0	15	80	5	35	45	20
	20	25	70	5	40	40	20
	40	30	60	10	45	30	25
	50	30	50	20			
	65				45	30	25
Ph$_3$Sb	0	15	85	-	10	90	-
	20	10	90	trace	10	85	5
	40	15	80	5	20	75	5
	50	15	80	5			
	65				30	55	15

*HMB = hexamethylbenzene

Table 1. Relative distribution of products from the reaction of $[(Me_2C_2)_3PdCl_2]_2$ (<u>32</u>) with Ph_3E

Reaction of complex (32) with o-phenanthroline.

o-Phenanthroline reacted rapidly with complex (32) in benzene at 25° to give a product from which was isolated a bright yellow complex (40).



(40)

The 60MHz ^1H nmr in $CDCl_3$ showed resonances at τ 1.94 (multiplet, 8H), 5.00 (doublet, 1H), 5.20 (doublet, 1H), 8.08 (singlet, 6H), 8.36 (singlet, 6H), and 8.63 (singlet, 3H). At 100MHz in $CHCl_3$ (Appendix I) resonances were observed at τ 5.11 (doublet, J = 2Hz, 1H), 5.30 (doublet, J = 2Hz, 1H), 8.18 (singlet, 6H), 8.36 (singlet, 6H), and 8.62 (singlet, 3H). The vinylic protons were observed to decouple in a decoupling experiment. An expanded spectrum showed further splittings of the diene methyls and is explained as being due to homoallylic coupling of inequivalent methyl groups. A strong band in the far infrared at 316 cm^{-1} was assigned to a terminal palladium-chlorine stretching frequency.

Reactions of (o-phen) $C_{12}H_{17}PdCl$, complex (40).

Reaction of complex (40) with triphenylphosphine.

The complex (40) reacted with an excess of triphenylphosphine in benzene either at reflux or at room temperature to give a yellow solution. Removal of the solvent followed by the addition of petroleum ether precipitated a pale yellow complex which was not identified or further purified. The 60MHz ^1H nmr in $CDCl_3$ showed resonances at τ 4.51, 4.65, 6.85, 8.40, 8.52, and 9.05 in addition to the low field resonances around τ 2.4 due to the o-phenanthroline and triphenylphosphine protons. All of the peaks were sharp with the exception of the one at τ 6.85 which was broad. The relative intensities were approximately 1:1:3:6:6:6. Although no detailed structural information was obtained, it is possible that the Ph_3P simply replaced the chlorine in complex (40). Also, the compound isolated was probably a mixture of two or more products.

Reaction of complex (40) with acids.

Trifluoroacetic acid reacted with complex (40) in chloroform solution at -10°. Following removal of the residue, the ^1H nmr spectrum of the filtrate showed the presence of a large amount of hexamethylbenzene. Additional crowded peaks to high field of hexamethylbenzene were not identified.

Hexamethylbenzene was also formed when the complex (40) was reacted with anhydrous and aqueous hydrogen chloride. However, as above, other products were not identified.

Reaction of complex (40) with cyanide.

Aqueous cyanide and complex (40) were reacted in a 1:1 ether-water mixture. A colourless oil was obtained but was not identified. The ^1H nmr in $CDCl_3$ contained numerous sharp peaks in the methyl region of the spectrum in addition to smaller lower field resonances.

Reaction of complex (40) with hydrazine.

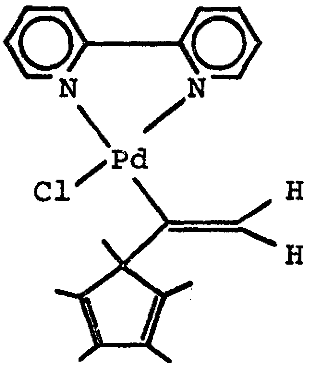
Hydrazine was reacted with the complex (40) in benzene solution. Metallic palladium was removed by filtration and evaporation of the filtrate gave an oil which was not identified and whose nmr spectrum was crowded in the methyl region.

Reaction of complex (40) with halogen.

Iodine reacted with complex (40) in chloroform to give a little hexamethylbenzene, identified by nmr. However, additional peaks in the nmr spectrum were unassigned and were observed to comprise the major product(s) of the reaction.

Reaction of complex (32) with 2,2'-dipyridyl.

2,2'-Dipyridyl also reacted with complex (32) in benzene in a manner similar to that described above to give the yellow product (41).

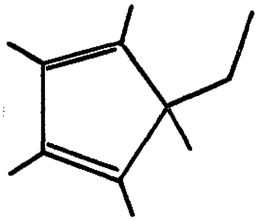


(41)

The 60MHz ^{1}H nmr in $CDCl_3$ contained resonances at τ 1.99 (multiplet, 8H), 5.10 (doublet, 1H), 5.28 (doublet, 1H), 8.10 (singlet, 6H), 8.40 (singlet, 6H), and 8.71 (singlet, 3H). The complex was not as stable as the related o-phenanthroline complex as evidenced by its slow discolouration over a few weeks.

Reaction of complex (32) with lithium aluminum hydride.

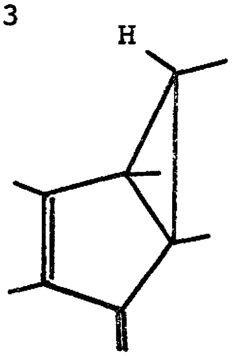
At -30° complex (32) was added to a suspension of $LiAlH_4$ in ether. After stirring and allowing to warm to room temperature a black residue of metallic palladium was filtered off. The solvent was removed by evaporation leaving a pale yellow oil and a small amount of a white solid identified as hexamethylbenzene. The oil was separated into three components by preparative vpc and two of the three products identified by analysis and/or nmr. Fraction 1 represented about 90% of the material; it was identified as 1-ethyl-1,2,3,4,5-pentamethylcyclopentadiene (42).



(42)

The 100MHz ^{1}H nmr in $CDCl_3$ showed resonances at τ 8.28 (singlet, 6H), 8.36 (singlet, 6H), 8.60 (quartet, J = 7Hz, 2H), 9.16 (singlet, 3H), and 9.74 (triplet, J = 7Hz, 3H).

Fractions 2 and 3 were present in approximately equal amounts, i.e. about 5% each. Fraction 2 was not identified. The third product was identified as pentamethyl-4-methylene-6H-bicyclo[3.1.0]hex-2-ene (43) by its nmr spectrum which was similar to that reported by Criegee and Grüner.[63]



(43)

The 100MHz ^{1}H nmr in $CDCl_3$ showed resonances at τ 5.34 (doublet, J = 2Hz, 2H), 8.25 (singlet, 3H), 8.40 (singlet, 3H), 8.86 (singlet, 3H), 8.95 (singlet, 3H), 9.05 (doublet, J = 6Hz, 3H), and

9.33 (quartet, J = 6Hz, 1H).

Reaction of complex (32) with hydrazine.

At 5° a benzene solution of the complex (32) was treated with an excess of anhydrous hydrazine resulting in the precipitation of metallic palladium. The filtrate yielded a pale yellow oil which proved to be vinylpentamethylcyclopentadiene (35) when examined by nmr.

Reaction of complex (32) with halogens.

A solution of bromine in chloroform was mixed with complex (32) at -78° in an nmr tube. At -50° the 100MHz ^{1}H nmr spectrum (Appendix II) consisted of six broad peaks at τ 7.87, 8.03, 8.19, 8.29, 8.45, and 8.71 which were unassigned. The spectrum remained fairly constant and exhibited no appreciable changes up to a temperature of -15°. At this temperature a new peak began to grow at τ 7.78 due to the formation of hexamethylbenzene. At 0° the decomposition was more rapid as evidenced by the quick growth of the singlet at τ 7.78 and the simultaneous decrease of the other peaks in the spectrum. No detectable intermediates were observed during this transformation. The final spectrum at room temperature showed only the sharp singlet of hexamethylbenzene.

Reaction of (32) with iodine also resulted in the formation of hexamethylbenzene.

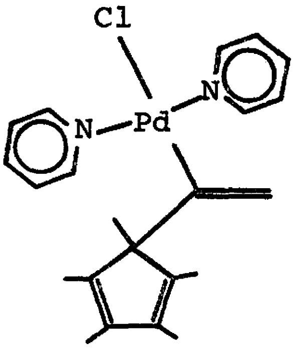
Reaction of complex (32) with pyridine.

Pyridine reacted rapidly with a benzene solution of complex (32) at 25° (4:1 mole ratio) to give a brown solution, from which was isolated a small amount of an unidentified ochre solid. Evaporation of the filtrate gave an orange-yellow oil which slowly crystallised. This orange complex (44) was probably a mixture but repeated attempts at recrystallisation were unsuccessful. The ^{1}H nmr in $CDCl_3$ was not too informative and showed a series of broad resonances at τ 5.87, 6.70, 7.37, 8.00 (sharp), 8.23 (very broad), 9.00, and 9.37 in addition to the pyridine protons. The relative intensities of 1:1:3:18:48:1:1 in addition to the complexity of the spectrum give an idea of the problems involved in interpreting this spectrum. The complex was not too stable in chloroform as it decomposed within about 10 minutes at 34°. A much better, although still complicated spectrum was obtained in pyridine solution. The spectrum was similar to that in chloroform, the main differences lying in the resolution and chemical shifts, the latter attributable to a solvent effect. Well resolved broad peaks were observed at τ 5.17, 5.50, 5.60, 6.29, 7.06, 7.63, 7.88, 8.87, 8.36, 8.48, 9.01, and 9.30, with relative intensities approximately 6:1:1:3:3:6:3:4:12:1:3. Again, it was difficult to meaningfully interpret this spectrum.

Reaction with a 2:1 mole ratio resulted in a red solution from which was isolated an unidentifiable insoluble red material. Evaporation of the filtrate gave a small amount of the orange product described above.

Similar results were obtained when a 1:1 ratio of reactants was used. However, very little of the orange complex was obtained.

In chloroform solution at -30°, pyridine reacted with complex (32) (4:1 mole ratio) to give a yellow solution. After warming to room temperature, a small amount of bis(pyridine)palladium chloride was isolated, identified by analysis. Removal of the solvent gave a greasy solid which, when washed with petroleum ether gave an orange product (45). Again, the product could not be recrystallised. The ^1H nmr in $CDCl_3$ showed resonances at τ 4.68 (doublet, 1H), 5.23 (doublet, 1H), 8.24 (singlet, 6H), 9.16 (singlet, 3H), and 9.23 (singlet, 6H), in addition to the pyridine resonances at low field. Such a spectrum implied a complex $(py)_2\ C_{12}H_{17}PdCl$ (45), analogous to the complex (40).



(45)

The upfield shift of the diene methyls adjacent to the bridgehead is readily explained. From a model of the complex it is seen that these methyls interact quite strongly with the pyridines if the pyridine rings are coplanar with the rest of the structure. Much of this interaction can be relieved if the pyridine rings are rotated 90° so that they lie perpendicular to the rest of the structure. In such a conformation, the two methyls lie above the plane of the pyridine rings and hence are largely shielded and an upfield shift in the nmr is observed.

Experiments were also carried out by mixing calculated amounts of the reactants in either benzene or chloroform and recording the ^1H nmr spectra of the solutions. The spectra observed from the benzene solutions were more complicated and less informative than the chloroform solutions. A Pd:pyridine ratio of 1:4 in benzene afforded a spectrum which was identical to that of the orange complex (44) (pyridine solution) described previously, although the peaks had slightly different chemical shifts, attributable to a solvent effect. Other reactions employing ratios of 1:2 and 1:1 gave spectra which were crowded with numerous peaks. Identification of products or assignments to the resonances was not possible in either case.

In $CDCl_3$ the 1:4 ratio reacted to give the complex

(45), observed by its nmr spectrum. After 24 hours additional resonances corresponding to vinylpentamethylcyclopentadiene (35) appeared in the spectrum. At 100MHz, the spectrum of a 1:4 mixture of complex (32) and pyridine in chloroform showed resonances at τ 4.82 (doublet, J = 1.9Hz, 1H), 5.37 (doublet, J = 1.9Hz, 1H), 8.36 (singlet, 6H), 9.27 (singlet, 3H), and 9.32 (singlet, 6H). The two low field protons readily decoupled when a decoupling experiment was done.

When a 1:2 ratio of reactants was mixed in $CDCl_3$ two of the products were observed to be hexamethylbenzene and vinylpentamethylcyclopentadiene (35). Other products were not identified.

Hexamethylbenzene was formed when a 1:1 ratio of reactants was mixed in $CDCl_3$. This was probably due to the known decomposition of complex (32) in chloroform.[56]

Reaction of complex (32) with aniline.

In benzene solution at 25°, complex (32) reacted with aniline (1:4 mole ratio) to give an ochre solid (46) which analysed for $C_{33}H_{42}N_3Cl_4Pd_2$. This was probably a mixture and corresponds to $(an)_2$* $PdC_{12}H_{17}Cl \cdot anH^+PdCl_3^- \cdot 1/2\ C_6H_6$. The complex was too insoluble to get an nmr spectrum. Its infrared spectrum contained numerous peaks but was too complicated to make any definite assignments. In addition

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* an = aniline

to (<u>46</u>) an oil was obtained from the filtrate. Hexamethylbenzene and vinylpentamethylcyclopentadiene (<u>35</u>) were identified from the 60MHz ^1H nmr spectrum of the oil in $CDCl_3$. Other peaks appeared in the spectrum too, but were not identified.

Similar results were obtained when a 1:1 ratio of reactants was used. An insoluble ochre solid, which was not analysed but whose ir spectrum was identical to complex (<u>46</u>), was isolated from the reaction mixture. Evaporation of the filtrate left an oil whose ^1H nmr spectrum showed, as usual, some hexamethylbenzene and compound (<u>35</u>). The major components were not identified, however, and appeared as numerous sharp peaks in the methyl region of the spectrum.

Complex (<u>32</u>) and aniline were reacted in varying mole ratios in benzene and deuterochloroform solutions and the products observed by recording the nmr spectra. Reactions in which palladium:aniline ratios of 1:4 and 1:2 in $CDCl_3$ were used resulted in the formation of hexamethylbenzene, vinylpentamethylcyclopentadiene (<u>35</u>), and other unidentified products. The reactions in benzene resulted in complicated nmr spectra and were inconclusive.

<u>Reaction of complex (32) with p-toluidine.</u>

p-Toluidine reacted with complex (<u>32</u>) in benzene at 25° to give a brown solution. A pale yellow precipitate

(47) was isolated and analysed for $C_{40}H_{54}N_4Cl_4Pd_2$. This was probably a mixture and corresponds to $(p\text{-tol})_2$* $PdC_{12}H_{17}Cl\cdot(p\text{-tol})\cdot(p\text{-tol}\ H^+PdCl_3^-)$. The complex slowly darkened on exposure to the atmosphere. An oil was obtained on evaporation of the solvent from the filtrate. Hexamethylbenzene and (35) were identified by nmr while additional products were not identified.

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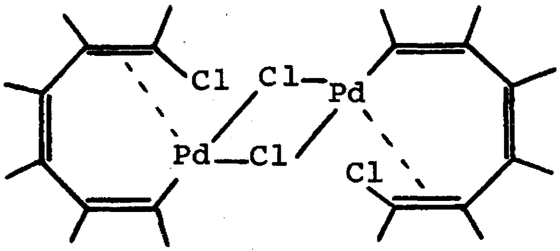
* p-tol = p-toluidine

DISCUSSION

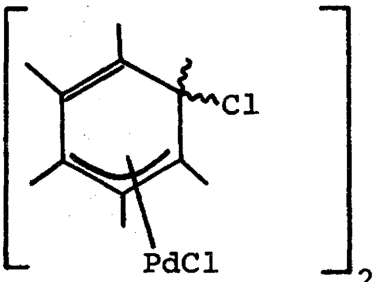
DISCUSSION

1. Structure of $[(Me_2C_2)_3PdCl_2]_2$ (32).

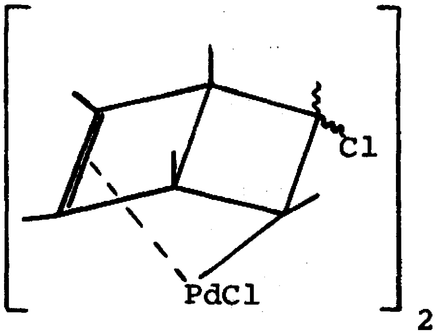
The present work was undertaken with the purpose of finding chemical evidence for the structure of the complex (32). The spectroscopic evidence implies that the complex is highly asymmetric, that it contains both a coordinated and an uncoordinated double bond, possesses an asymmetric $PdCl_2Pd$ bridge, and yet has no terminal PdCl bonds. A number of structures have been proposed (i-v) and each of these is considered below.



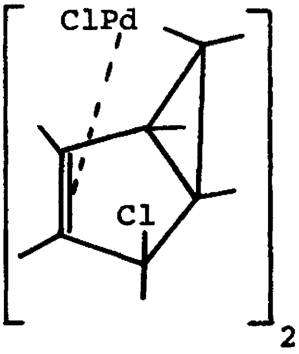
(i)



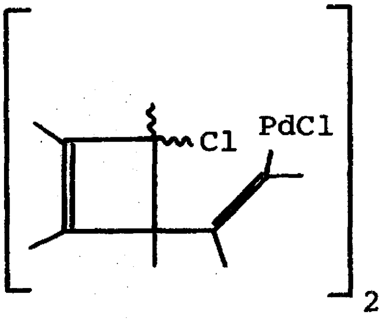
(ii)



(iii)

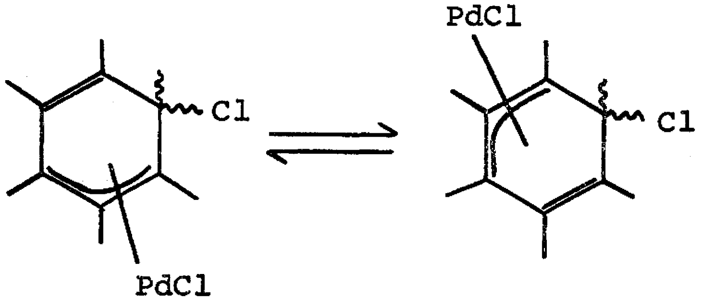


(iv)



(v)

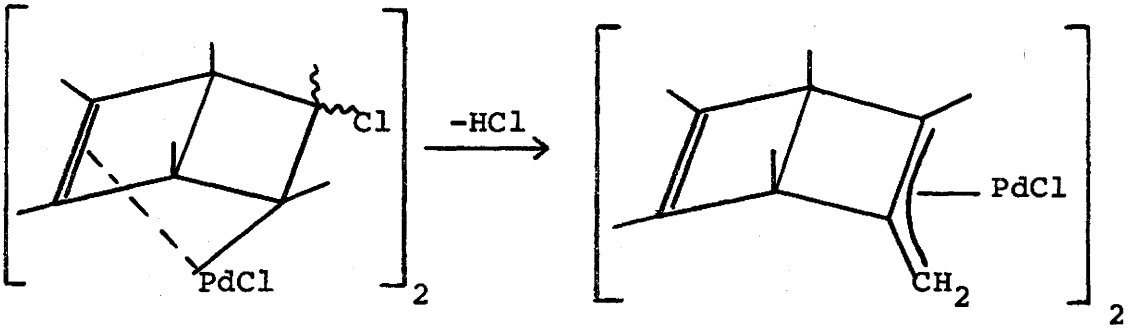
Each of the five structures exhibits the high degree of asymmetry required by the spectra. Models of the structures were prepared and from these a number of interesting observations were made. From a consideration of bond lengths and bond angles for (iv) and (v) it was seen that there could be little effective coordination between the metal and double bond. In these cases the distance from the palladium to each double bond is at least 3.0 Å compared with Pd-C distances of between 2.1 and 2.25 Å normally found in π-bonded olefinic or allylic complexes.[66] Although this objection does not apply to the structure (ii), a model indicates this to be essentially a planar molecule. As a result, it is unlikely that the π-allylic group would remain localised as shown. Instead it would be expected to exhibit fluxional behaviour between the forms



(iia) (iib)

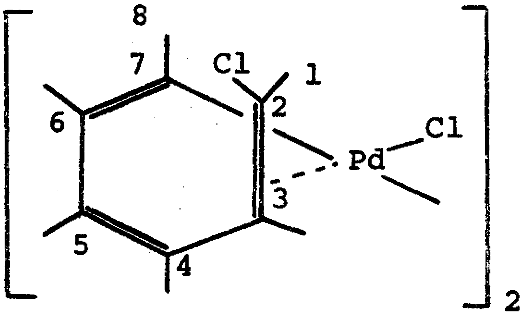
with a resultant simplification of the ^1H nmr at ambient temperatures.

The structure (iii) does not possess an uncoordinated double bond. Furthermore, a complex of this type would be expected to lose HCl to give the complex (48) already obtained by Shaw and Shaw.[67]

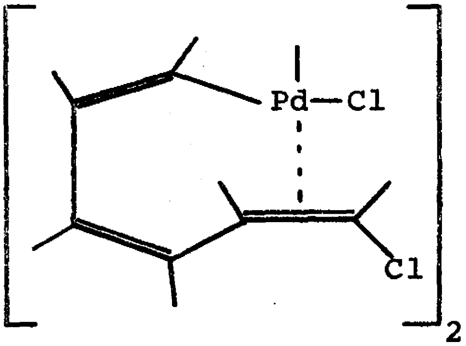


(iii) (48)

The structure (i) is the only structure which satisfies all of the spectral requirements; none of the above objections apply to it. Models show this to be a relatively strain-free molecule, capable of existing in two conformers, one with the coordinated double bond perpendicular, and the other with it coplanar, to the coordination plane of the metal. Interconversion between these two conformers can occur by rotation of the C_2C_3 bond about its axis to the metal and a twisting of the C_3C_4 bond. The two conformers are conveniently written as follows:



(32a)



(32b)

2. Reactions of $[(Me_2C_2)_3PdCl_2]_2$ (32).

The reaction of $[(Me_2C_2)_3PdCl_2]_2$ (32) with triphenyl-phosphine, -arsine, and -stibine gave hexamethylbenzene, vinylpentamethylcyclopentadiene (35), and 1-chlorovinylpentamethylcyclopentadiene (36). At higher temperatures, the chlorovinylpentamethylcyclopentadiene (36) was the main product; below 0°, vinylpentamethylcyclopentadiene (35) and hexamethylbenzene were the only organic products. The complex (32) was decomposed by acids and by halogen to hexamethylbenzene; hydrazine gave vinylpentamethylcyclopentadiene (35); and lithium aluminum hydride gave largely ethylpentamethylcyclopentadiene (42). o-Phenanthroline reacted with (32) to give the stable complex 1-(chloro-(o-phenanthroline)-palladium)vinyl-1,2,3,4,5-pentamethylcyclopentadiene (40). Similar complexes were obtained with bipyridyl and pyridine. The reactions are summarised in Fig. XI.

3. Proposed Mechanisms.

None of the reactions of complex (32) led to an acyclic organic product. It must be assumed that cyclisation occurs very readily under the influence of most reagents. This probably takes place via a ligand- or solvent-assisted cis-insertion of the π-bonded olefin into the Pd-C σ-bond.[68] It has generally been found that in order for this to occur, the coordinated double bond and

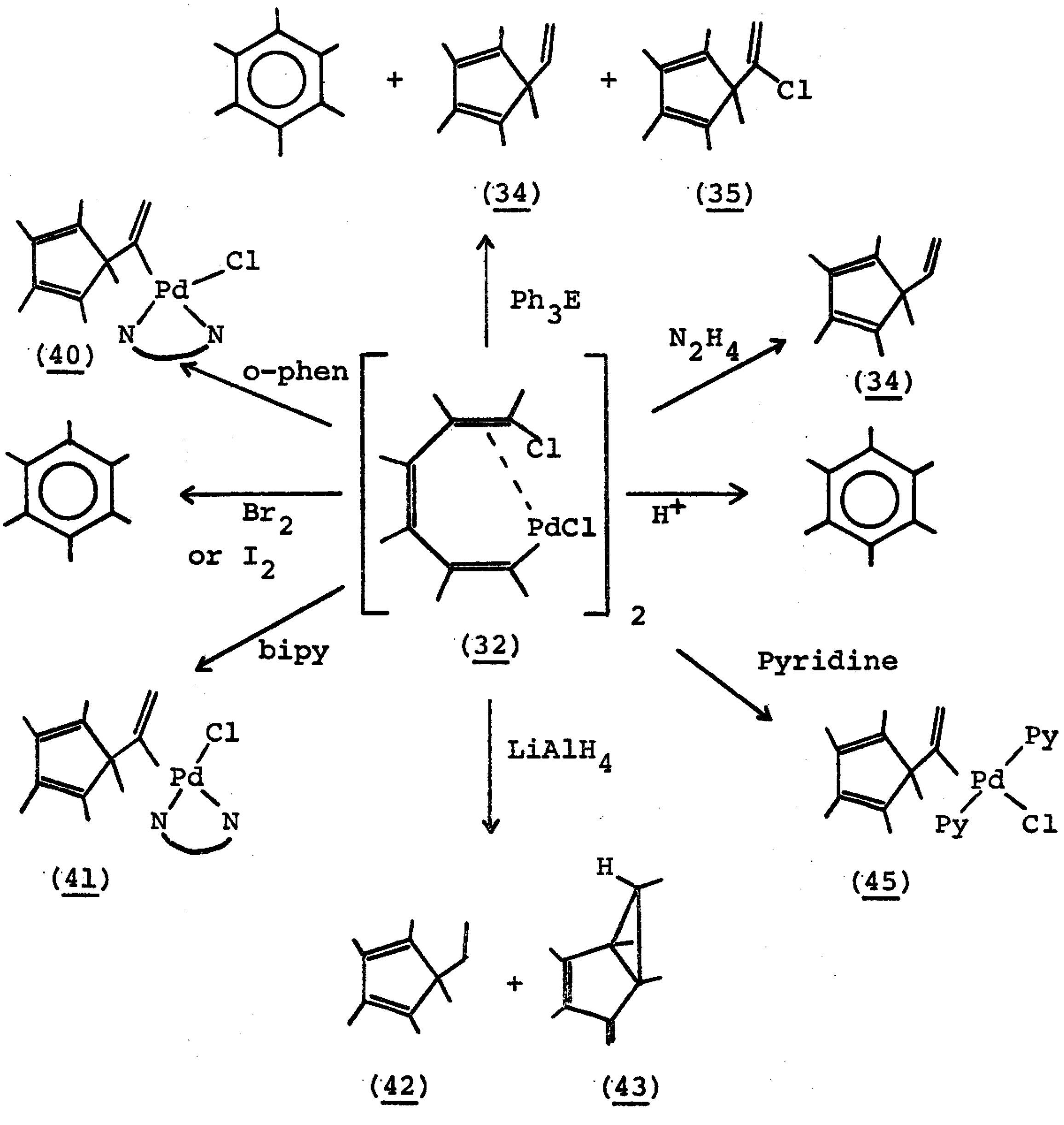
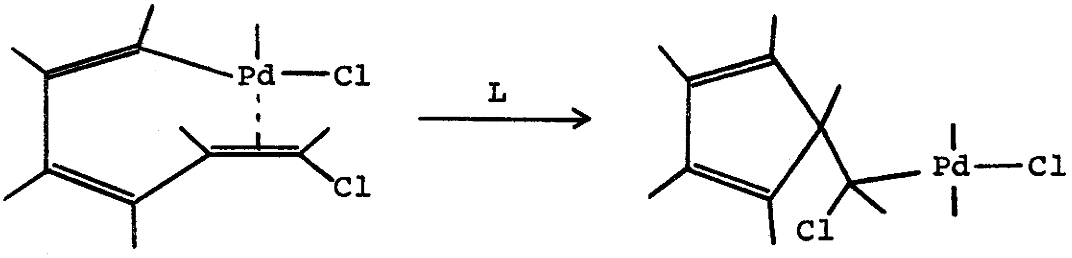


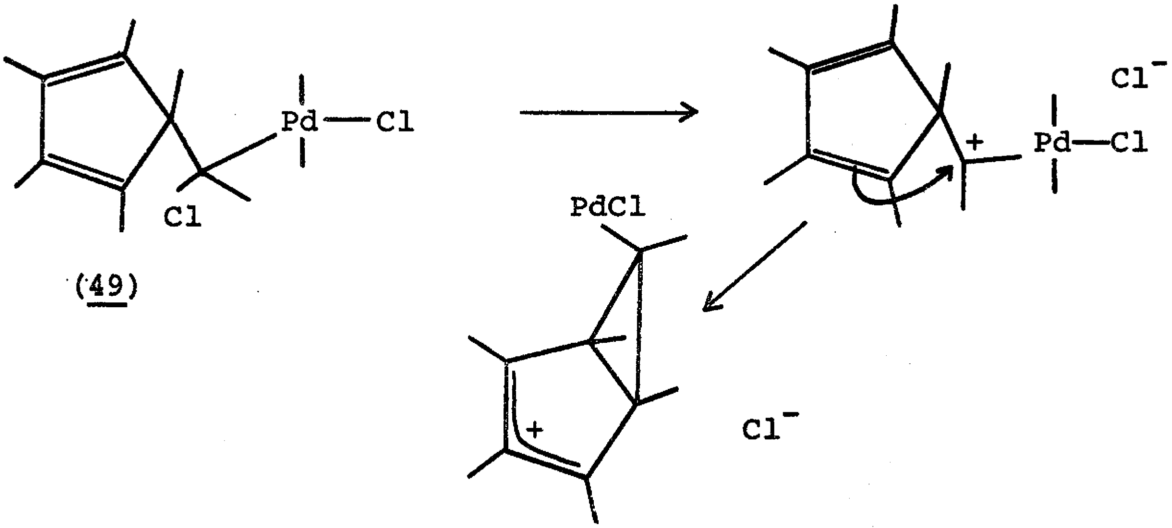
Fig. XI Reactions of Complex (32)

the metal-carbon bond must be coplanar.[69,70] This requirement is met in the structure (32b) and as a result pentamethylcyclopentadienyl products can easily arise.



(32b) (49)

The product (49) contains an active chlorine which probably ionises. Further rearrangement likely occurs to give a more stable product, presumed to be the bicyclohexenyl complex (50).[72]

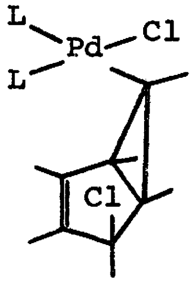


(49)

(50)

The reactions with triphenyl-phosphine, -arsine, and -stibine have been studied in considerable detail. In particular, the reactions with -phophine and -arsine were studied from -60° to +20° by nmr by Dr. Reinheimer.[71] These findings have provided much of the evidence for the mechanisms and intermediates described below.

At low temperatures, the bicyclohexenyl complex (50) presumably exists as (51). Although the stereochemistry is not known, the reaction scheme is simplified if it is assumed that the metal lies above the ring and that the chlorine is endo to the metal.

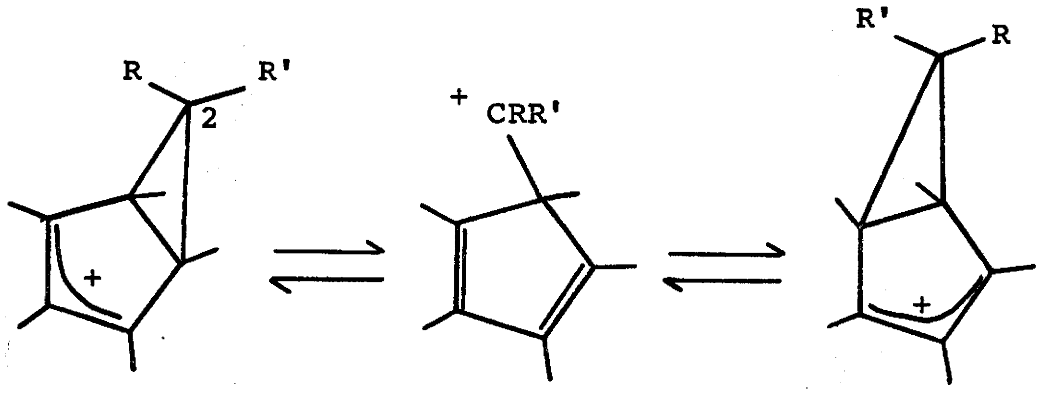


$L = Ph_3P$

$L = Ph_3As$

(51)

At temperatures of -60° with P:Pd ratios of between 1 and 6, reaction had already occurred with the formation of a new species for which structure (51) is proposed. As the temperature was raised, and in the absence of an excess of Ph_3E (E = P, As), a reversible coalescence of the five cyclopentyl methyls was observed. Childs and Winstein[72] and Koptyug et al.[73,74] have described a similar process for the bicyclo[3.1.0]hexenyl cations (52) at low temperatures.



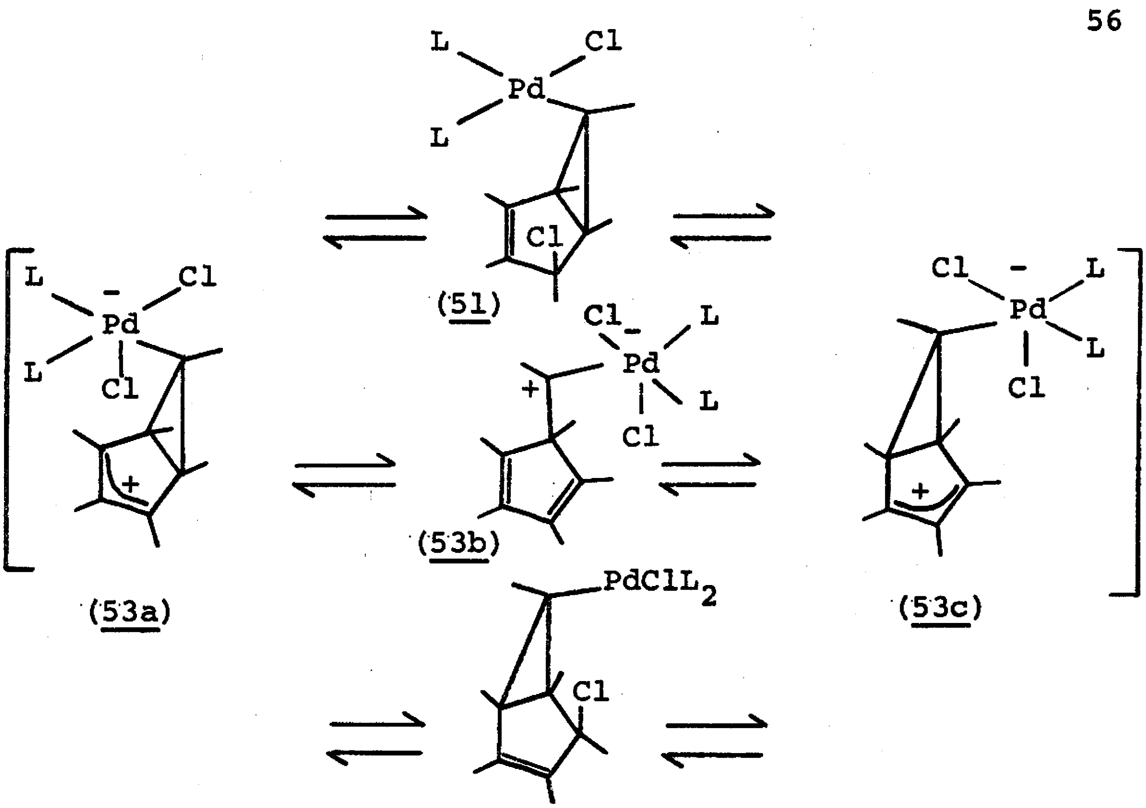
(52)

R = R' = Me

R(endo) = H,   R'(exo) = Me

This five-fold degenerate scrambling is believed to arise via a suprafacial concerted 1,4-sigmatropic shift of the C_2 methyl. Furthermore, it has been shown that no inversion occurs at C_2 during this process.[72]

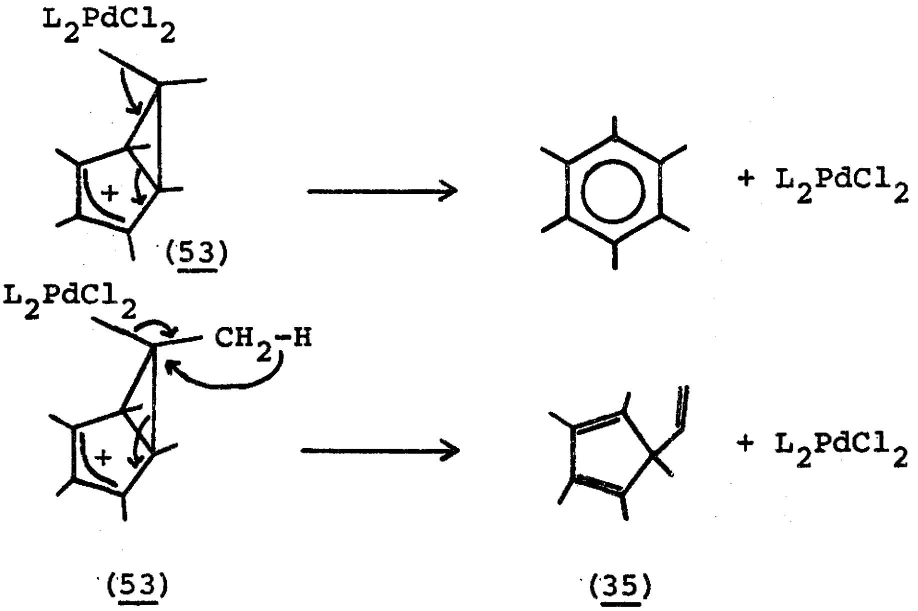
The species (51) being considered here behaves in a similar manner. In order for the sigmatropic rearrangement to occur, the chlorine on the ring must be removed. If the complex has the indicated stereochemistry, then this chlorine is close to the fifth coordination position of the metal and is within bonding distance of it. The proposed sequence is outlined as follows:



(51) (53a) (53b) (53c)

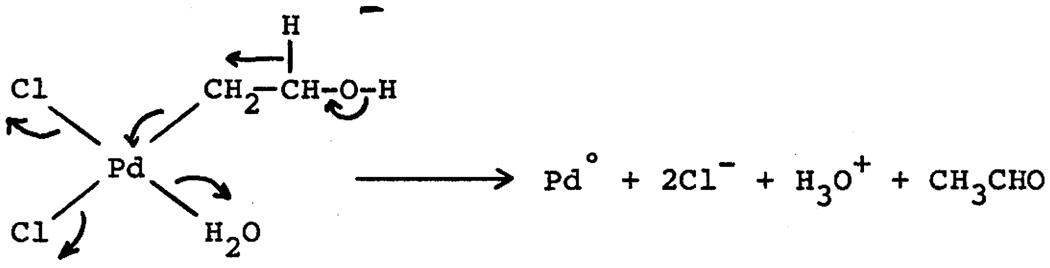
Stabilisation of the positive charge on the carbon in (53b) can occur by back-donation from the metal.

The final step in this decomposition leads directly to the products.



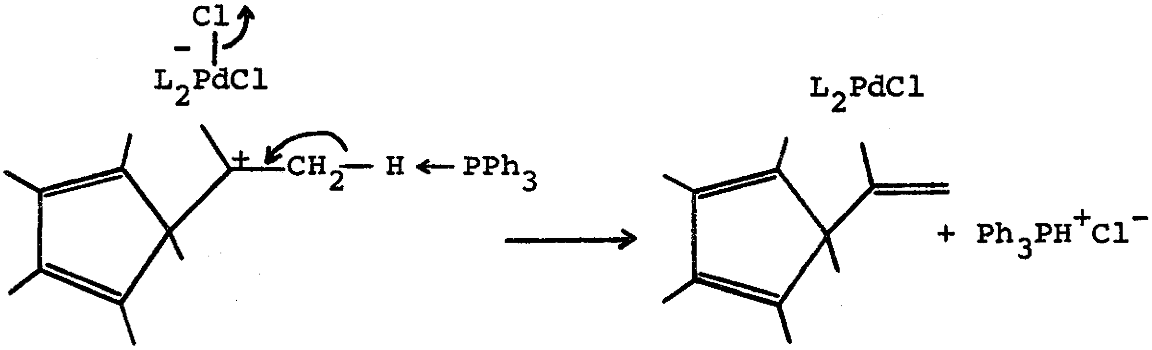
(53) (53) (35)

The reaction leading to (35) must involve a 1,2-hydride shift. There are many well-known palladium-catalysed reactions of this type,[75] for example the formation of acetaldehyde from ethylene.



(54)

In the presence of an excess of triphenylphosphine the further reaction of (51) was different. No averaging of the cyclopentenyl methyls occurred; instead, (51) underwent an irreversible change, presumably via (53), to a new species (55).[71]

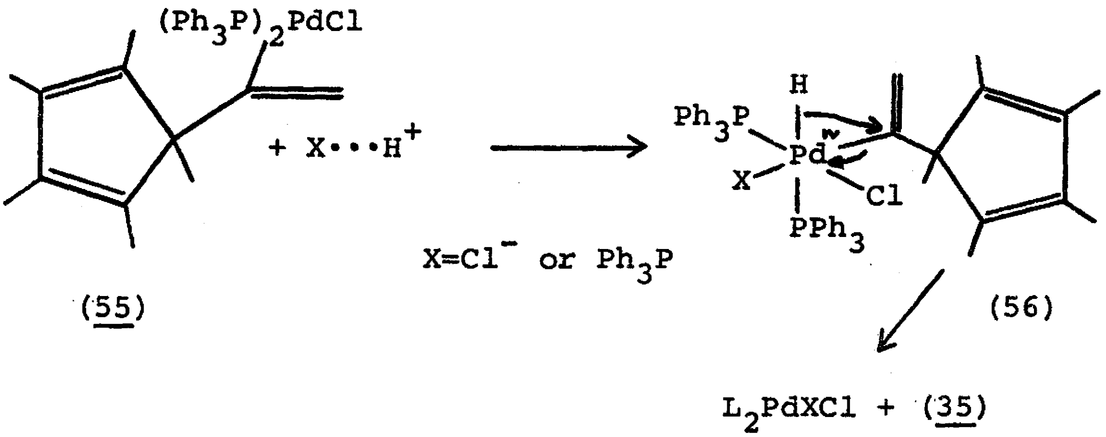


(53) (55)

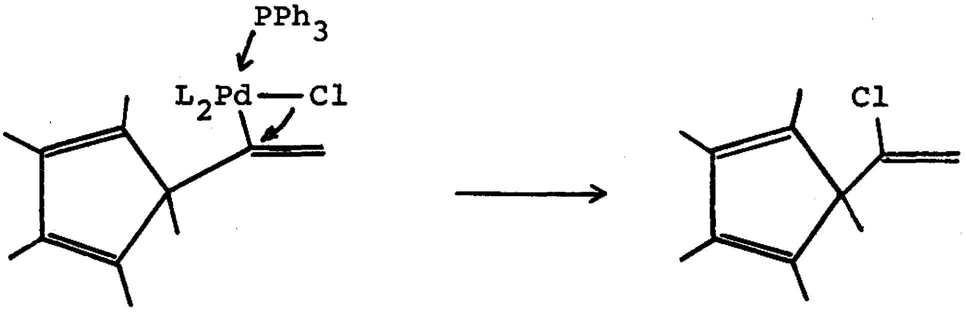
The species (55) is seen to arise in the presence of a base, such as triphenylphosphine, which is strong enough to abstract a proton from the C_2 methyl. Triphenylarsine is not a strong enough base to effect this removal.[71]

The formation of hexamethylbenzene can arise from a reversal of the above reactions; namely, (<u>55</u>) ⟶ (<u>53</u>) ⟶ hexamethylbenzene.

The formation of vinylpentamethylcyclopentadiene (<u>35</u>) can also arise by the above route. Alternatively, oxidative addition of $X\cdots\cdots H^+$ to the palladium to form the intermediate (<u>56</u>), followed by an internal hydrogen transfer, leads to products. Similar mechanisms have been reported for some Pt(II) complexes.[76]



The chlorovinylpentamethylcyclopentadiene (<u>36</u>) appears to be formed at the expense of vinylpentamethylcyclopentadiene (<u>35</u>) in the higher temperature reactions. The mode of formation of (<u>36</u>) is not too clear due to a lack of details. Conceivably this could arise by the decomposition of some intermediate such as (<u>55</u>) in the presence of excess phosphine.

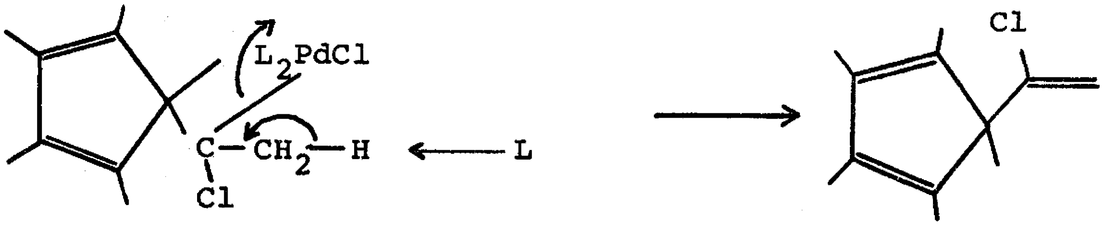


(55)

(36)

+ $(Ph_3P)_xPd$

Attack by triphenylphosphine at the metal accompanied by a chloride shift would lead directly to the products. Alternatively, the product (36) may arise prior to the formation of the intermediate (55). Cyclisation of the complex (32) is believed to occur by a cis-insertion of the coordinated double bond into the Pd-C bond to give a product (49) (see p. 53). Proton abstraction and elimination of L_2PdCl as shown below gives the chloro-compound (36).



(49)

(36)

L = Ph_3P

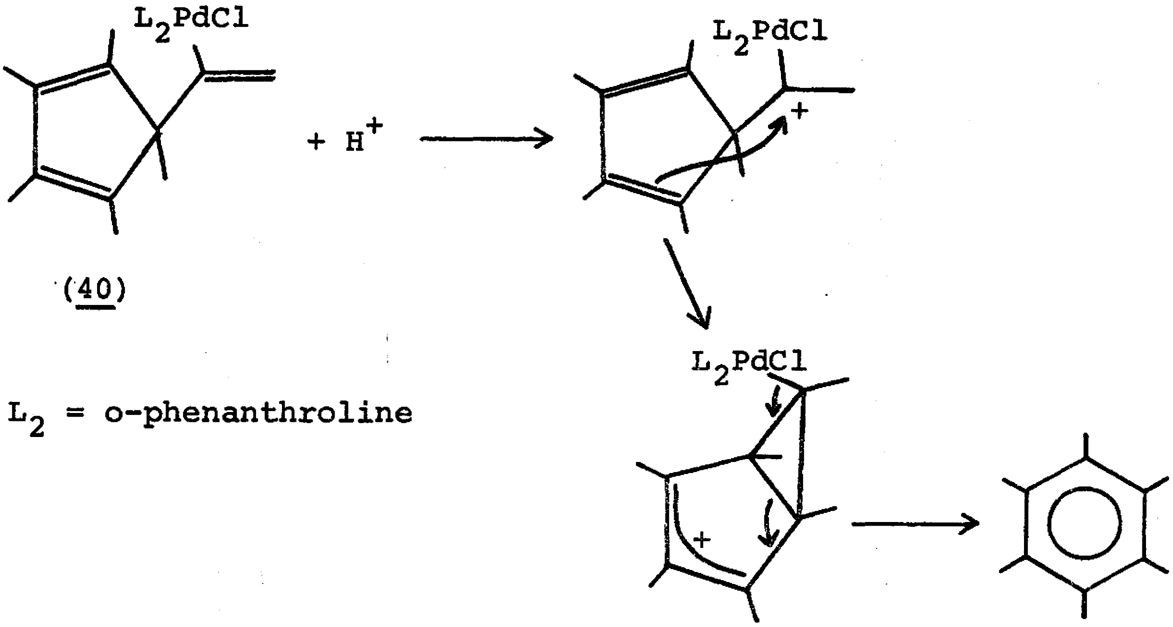
+ L_2PdCl^- LH^+

$\downarrow L$

$(L)_xPd^\circ$ + HCl

The reactions with other bases provide some evidence for the intermediate complex (55). In particular, the chelating diamines o-phenanthroline and bipyridyl reacted with complex (32) to give fairly good yields of a complex which was assigned the structure (55) (L_2 = o-phenanthroline, bipyridyl) on the basis of analysis and spectroscopic data. A similar product was obtained with pyridine, but only in an impure state. Furthermore, this latter product was observed to partially decompose to give vinylpentamethylcyclopentadiene (35).

The o-phenanthroline complex (40) was reacted with a number of reagents with the purpose of finding additional proof for the structure of this intermediate. In particular, it was hoped that reactions of the complex (40) would give vinylpentamethylcyclopentadiene (35). In fact, none of the organic product (35) was formed in any of the reactions investigated. The reaction with acids gave hexamethylbenzene in addition to small amounts of unidentified materials. The formation of hexamethylbenzene is explained in terms of the protonation of the vinylic group followed by formation of the bicyclohexenyl complex (53) which can decompose to the observed product.



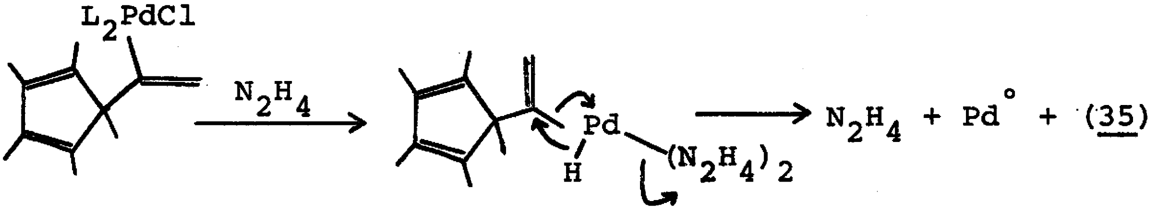
(40)

L_2 = o-phenanthroline

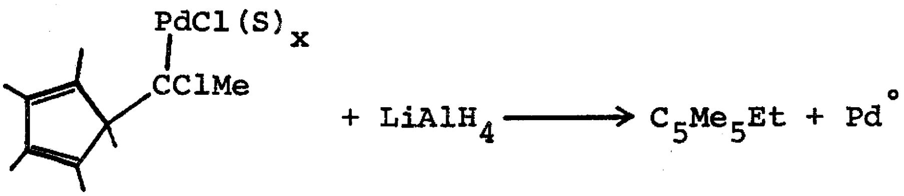
(53)

The reaction of complex (40) with different bases led to products which were unidentified. These products were generally oils and hexamethylbenzene was not formed in the reactions.

The intermediate (55) is probably formed in other decomposition reactions which lead to pentamethylcyclopentadiene derivatives. For example, vinylpentamethylcyclopentadiene (35) is the product of reaction of complex (32) with hydrazine. This can be explained by the formation of (55) (L = N_2H_4) which could react further to form a hydride (57). Intramolecular hydrogen transfer and subsequent decomposition gives the observed product.

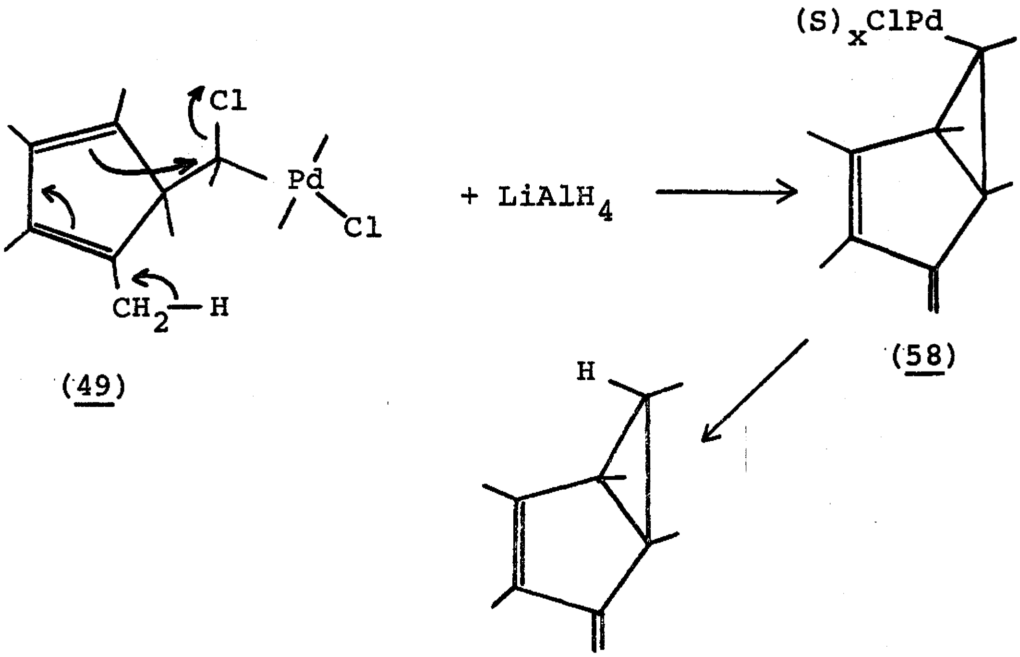


However, with lithium aluminum hydride the reaction path is likely to be different. Following ring closure to (49), reduction of the carbon-bonded chlorine and the palladium-carbon bond can lead directly to the major product, ethylpentamethylcyclopentadiene (42).



(49) (42)

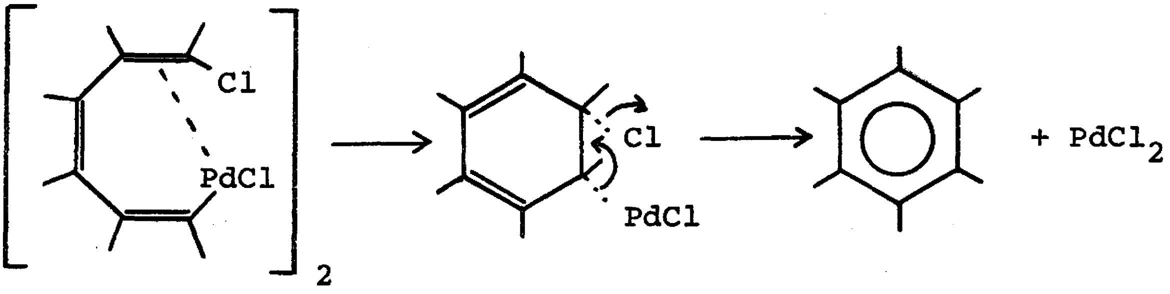
Alternatively, the hydride acting as base may first cause loss of HCl to give a bicyclic species (58), which is then cleaved at the Pd-C bond to give the homofulvene (43).



(49) (58) (43)

Addition of hydride (2H) to (43) may also give rise to ethylpentamethylcyclopentadiene (42).

The paths of decomposition of complex (32) to hexamethylbenzene almost certainly depend on the conditions used. In acid media the reaction presumably goes via the path previously described for the acid-catalysed decomposition of the o-phenanthroline complex (40). However, the reaction with halogens is not well understood. One possibility would be a concerted ring closure to the cis-cyclohexadiene (59) followed by a cis-elimination of $PdCl_2$.



(32) (59)

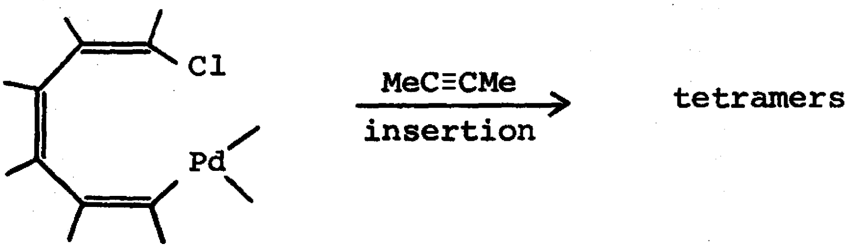
There are objections to this route though in that the role of the solvent or reactants is not explained. Furthermore, the origin of the anomalous isomers obtained from the trimerisation of unsymmetrical acetylenes[55] is not explained.

The complexes obtained from reaction of (32) with aniline and p-toluidine were not fully characterised. By analogy with the intermediate (55) it is conceivable that these ligands formed similar complexes. The origin of vinylpentamethylcyclopentadiene (35) and hexamethylbenzene in these reactions is believed to arise via intermediates such as (55) (L = aniline, p-toluidine).

4. Other products.

The complex $[(Me_2C_2)_3PdCl_2]_2$ (32) was obtained in 50% yield from the reaction of 2-butyne with palladium chloride in benzene. Other complexes, hexamethylbenzene, and possibly other organic oligomers were found to compose the remaining material. Reduction of this mother liquor with hydrazine gave, apart from the hexamethylbenzene, four products. Vinylpentamethylcyclopentadiene (35) (10%) presumably arose from residual amounts of the complex (32). This reaction path has already been discussed. The remaining three products were found to be tetramers. Two of these had the composition $C_{16}H_{25}Cl$ (ca. 7% and 55%) and were isomers, while the third had the composition $C_{16}H_{22}$ (25%). Their structures are not known.

The origin of the tetramers is not known. It was mentioned in the Introduction (p. 24) that $[(Me_2C_2)_3PdCl_2]$ (32) is believed to arise from a palladium-acetylene π complex by a series of cis-insertions. Conceivably, this mechanism could be extended to account for the tetramers.



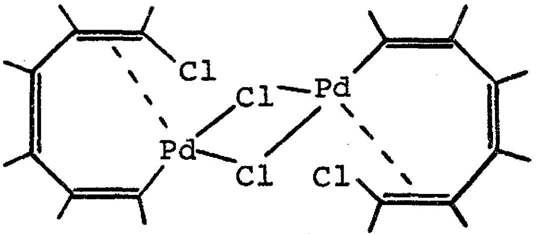
(32)

However, due to steric hindrance about the metal in (32) it is believed that this reaction terminates following the combination of three moles of the acetylene. Furthermore, tetramerisation has been found to occur only under certain conditions, that is, the reaction in benzene at 5°. In addition, it is not known whether these tetramers are formed as organic products or as complexes. Alternatively, these products may arise from side reactions.

CONCLUSION

CONCLUSION

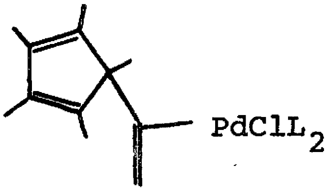
The reaction of 2-butyne with palladium chloride gives a complex $[(Me_2C_2)_3PdCl_2]_2$ (32). Spectroscopic data indicate that (32) is a highly asymmetric molecule. A number of structures have been considered but the one most favoured is the following acyclic molecule:



(32)

The complex (32) cyclises readily as evidenced by the formation of five- and six-membered ring systems in all of its reactions.

Reaction mechanisms have been proposed to explain the formation of pentamethylcyclopentadiene derivatives and other products. Evidence has been obtained for intermediates such as (55).



(55)

Firstly, (55) (L = Ph_3P or pyridine) was observed in the nmr in the presence of an excess of phosphine or pyridine. Secondly, complexes (55) have been isolated with the chelating agents o-phenanthroline and bipyridyl. In addition, with pyridine the complex (55) was isolated in an impure state.

Tetramerisation as well as trimerisation was found to occur in the benzene reaction of 2-butyne with palladium chloride. Tetrameric products were not observed when this reaction was done in chloroform, nor were they formed when complex (32) was used as a trimerisation catalyst. Their origin has not been established, although they may arise from the further reaction of complex (32) with more 2-butyne, or they may be formed from one or more side reactions.

EXPERIMENTAL

EXPERIMENTAL

Experimental Procedures

Melting points

These were determined using a Thomas Hoover capillary melting-point apparatus and are uncorrected.

Infrared spectra

Solid compounds were made up as potassium bromide discs (unless otherwise indicated) while liquids were run as a film between potassium bromide plates. Spectra were recorded on a Beckmann IR5 spectrophotometer. Far infrared spectra were recorded on a Beckmann IR12 spectrophotometer.

Ultraviolet spectra

Solutions of compounds were made up using spectranalysed solvents and placed in quartz cells having a 1.0 cm path length. Spectra were recorded on a Cary 14 Ultraviolet-Visible recording spectrophotometer.

Mass spectra

These were run on a Hitachi Perkin-Elmer RMU-6A spectrometer at 200° and a CEC 110B high resolution mass spectrometer.

Nuclear magnetic resonance spectra

Proton magnetic resonance spectra were run on Varian A60 60MHz, Varian T60 60MHz, and Varian HA100 100MHz spectrometers. Hexamethylbenzene (τ7.77) was usually used as an internal reference and this was calibrated against solvent (benzene, chloroform) or tetramethylsilane.

Analyses were by A. B. Gygli, Toronto, and by A. Bernhardt, Germany.

Reagents

Reagent grade solvents were used at all times. Benzene was dried over lithium aluminum hydride and freshly distilled before use. Nitrogen (Purified Grade) was dried by passage through concentrated sulphuric acid and phosphorus pentoxide. The petroleum ether used was that fraction with boiling point range 30-60°. 2-Butyne was obtained from the Air Reduction Company, New York, was purified by distillation, and freed of dimethyl sulphide by stirring with palladium chloride and redistilling. Palladium chloride was obtained on loan from Johnson, Matthey, and Mallory, Ltd. Alumina (80-200 mesh) was supplied by Fisher.

Experimental Techniques

All reactions were carried out under a nitrogen atmosphere. Solutions were stirred magnetically using

25 mm Teflon-coated stirring bars, and solids were isolated by filtration. Solvents were removed under vacuum on a rotary vacuum evaporator. Organic products were prepurified by adsorption elution chromatography on a column 35 cm in length and 2 cm in diameter. Products were then separated and collected by preparative vapor phase chromatography using a Varian A90-P3 gas chromatograph. A 5' x 1/4" 20% SE-30 on 60/80 Chromosorb W column or a 15' x 3/8" 15% Carbowax 20M on 60/80 Chromosorb W column was used. Analytical vapor phase chromatography was carried out using a Varian Aerograph. Five foot columns of 5% SE-30 and 5% Carbowax on 60/80 Chromosorb W were used.

Low temperature nuclear magnetic resonance experiments were carried out by mixing the reactants in an nmr tube at -78° then following the reaction in the spectrometer at successively higher temperatures.

Preparation of dichlorobis(benzonitrile)palladium (16).

Palladium chloride (4 g, 23 mmoles) was dissolved in benzonitrile (100 ml) by stirring with heating to 115-120° for 2 hours. The hot solution was filtered and poured into light petroleum (1000 ml). The yellow precipitate (8 g, 90%) was filtered and washed with petroleum ether, and air-dried.

Reaction of 2-butyne with palladium chloride in benzene.

Particular care was taken to exclude air during the reaction. Complex (16) was used as the source of palladium chloride and was freshly washed with petroleum ether, filtered and air-dried before use.

Benzene (400 ml) was saturated with nitrogen by bubbling through the gas for about 15 minutes. Then hydrogen chloride gas was passed through for ca. 1-1/2 minutes. With stirring, 2-butyne (27), (15 ml, 190 mmoles) was added and the solution cooled to 5°. While a strong stream of nitrogen was sweeping upwards out of the reaction flask, dichlorobis(benzonitrile)palladium (16) (12 g, 21 mmoles) was added in small portions over 15 minutes, care being taken that the temperature did not rise above 10°. When the temperature had returned to 5°, the mixture was filtered to remove polymers and palladium metal. The solvent was stripped off as quickly as possible on a rotary vacuum evaporator and to the resulting brown oil was added a solution of light petroleum (200 ml) and 2-butyne (27), (5 ml). The mixture was vigorously shaken for about a minute, and the resulting pale yellow polymeric precipitate filtered off. The clear yellow filtrate was saturated with nitrogen during which time the complex slowly began to crystallise. The flask was stoppered and placed in the freezer for about 4 hours to allow complete crystallisation. A bright yellow powder (32) was isolated (5.2 g, 49%). M.Pt. 100° (dec.).

Anal. Calcd. for $[C_{12}H_{18}Cl_2Pd]_2$: C 42.44 H 5.34
Cl 20.88 Pd 31.33% M.Wt. 679

Found: C 42.20 H 5.55 Cl 20.68 Pd 31.0%
M.Wt. 673, 678 (osmometric, benzene).

Following isolation of the yellow complex, the solvent was removed from the mother liquors on a rotary evaporator. The remaining oil (ca. 13 ml) was stirred with benzene (15 ml) and the solution treated with an excess of anhydrous hydrazine. Black metallic palladium was filtered off, the solvent removed on a rotary evaporator, and the oil chromatographed over alumina using petroleum ether as eluent to give a pale yellow oil (2.0 g). The oil was separated into four components by preparative vpc on a 20% SE-30 column at 185°. Fraction 1 (ca. 10%) was identified by nmr as the vinylpentamethylcyclopentadiene (35).

Fraction 2 (ca. 7%) was a yellow oil. Anal. Calcd. for $C_{16}H_{25}Cl$: C 76.01 H 9.97 Cl 14.02% M.Wt. 252
Found: C 73.53 H 10.50 Cl 13.06% M.Wt. 217 (mass spectroscopic)

The analytical sample probably contained some peroxide. Also, the compound apparently loses chlorine very readily in the mass spectrometer, thereby accounting for the low molecular weight.

Fraction 3 (ca. 25%) was a yellow oil. Anal. Calcd. for $C_{16}H_{22}$: C 89.75 H 10.25 M.Wt. 214
Found: C 89.27 H 10.55 M.Wt. 214 (mass spectroscopic)

Fraction 4 (ca. 55%) was also a yellow oil. Anal. Calcd. for $C_{16}H_{25}Cl$: C 76.01 H 9.97 Cl 14.02 M.Wt. 252

Found: C 75.91 H 9.99 Cl 14.26 M.Wt. 252 (mass spectroscopic), 258 (osmometric, benzene)

The nmr, ir, and uv spectra were recorded.

Reactions of $[(Me_2C_2)_3PdCl_2]_2$, complex (32).

Reaction of complex (32) with triphenylphosphine.

(a) Complex (32), (.340 g, 0.5 mmole) was dissolved in benzene (15 ml) at 25° under nitrogen. To the stirred solution was added triphenylphosphine (1.05 g, 4 mmoles) dissolved in a small quantity of benzene. The colour lightened at once and after 3 minutes a precipitate began to form. Stirring was continued for an additional 30 minutes and the yellow crystalline solid filtered off (.311 g). The infrared spectrum was recorded and was identical to that of an authentic sample of $[(C_6H_5)_3P]_2PdCl_2$ (26).

Anal. Calcd. for $C_{36}H_{30}P_2Cl_2Pd$: C 61.60 H 4.31 Cl 10.10 P 8.83 Pd 15.16%

Found: C 61.02 H 4.46 Cl 10.40 P 9.07 Pd 15.54%

The filtrate was concentrated to about one-fifth of its original volume on a rotary evaporator and the resulting greasy solid stirred with light petroleum (20 ml) for 10 minutes. The pale-yellow solid (.360 g) was filtered and washed with petroleum ether.

The mother liquor was taken to dryness, dissolved in petroleum ether (1 ml) and chromatographed over alumina.

A colourless oil and a white solid were separated; the excess triphenylphosphine was not collected. The white solid was identified by nmr and melting point (164°) as hexamethylbenzene. The oil was separated into two components by preparative vpc on a 15% Carbowax column at a temperature of 140°. Fraction 1 (ca. 25%) was a colourless oil, vinylpentamethylcyclopentadiene (35).

Anal. Calcd. for $C_{12}H_{18}$: C 88.82 H 11.18% M.Wt. 162.140844

Found: C 89.05 H 11.16% M.Wt. 162.139930 (mass spectroscopic)

Fraction 2 (ca. 75%) was a pale yellow oil, chlorovinylpentamethylcyclopentadiene (36). Anal. Calcd. for $C_{12}H_{17}Cl$: C 73.26 H 8.71 Cl 18.02% M.Wt. 196.101872 for $C_{12}H_{17}{}^{35}Cl$ and 198.098922 for $C_{12}H_{17}{}^{37}Cl$

Found: C 72.92 H 8.64 Cl 17.80% M.Wt. 196.103268 and 198.100317 (mass spectroscopic)

The nmr, ir, and uv spectra were recorded.

A sample of the chlorovinylpentamethylcyclopentadiene (36) was hydrogenated at 3.2 Atm and 20° over a platinum oxide catalyst in methanol. After removal of the solvent an oil was obtained. The mass spectrum showed this to be a saturated chlorocompound. The molecular ion peaks were observed at m/e 204 ($C_{12}H_{23}{}^{37}Cl$) and 202 ($C_{12}H_{23}{}^{35}Cl$). In addition, peaks corresponding to the cleavage at the quaternary carbon involving (i) loss of methyl (giving $C_{11}H_{20}Cl$, m/e 187, 189) and (ii) loss of

C_2H_4Cl (giving $C_{10}H_{19}$, m/e 139) were found.

Attempts to hydrogenate the vinylpentamethylcyclopentadiene (35) in the presence of a platinum oxide catalyst were unsuccessful, and a white polymer was the only product.

A solution of chlorovinylpentamethylcyclopentadiene (36) (0.04 g) was stirred in benzene at 45° for 18 hours with a solution of tetracyanoethylene (0.03 g). The solvent was removed to leave a violet solid (37). All attempts to purify this adduct from excess TCNE failed. However, the 60MHz ^1H nmr spectrum clearly showed that a 1:1 adduct had been formed. In benzene, resonances were observed at τ 4.87 (doublet, J = 3 Hz, 1H), 5.67 (doublet, J = 3 Hz, 1H), 8.46 (singlet, 6H), 8.56 (singlet, 3H), and 8.66 (singlet, 6H). In $CDCl_3$ the spectrum showed peaks at τ 4.50 (doublet, J = 3 Hz, 1H), 5.15 (doublet, J = 3 Hz, 1H), 8.15 (singlet, 6H), 8.32 (singlet, 6H), and 8.41 (singlet, 3H).

(b) Oxygen was excluded from the reaction of complex (32) with triphenylphosphine by working very carefully under a nitrogen atmosphere in a glove box. Carefully degassed solvents were also used here.

To a solution of triphenylphosphine (1.05 g, 4 mmoles) in benzene (25 ml) at 65° was added the complex (32), (.340 g, 0.5 mmole). The light yellow solution was stirred for 10 minutes, then cooled to room temperature.

A bright yellow precipitate (.141 g) was isolated and washed with light petroleum. The ir spectrum of this material was identical to that of $(Ph_3P)_2PdCl_2$ (<u>26</u>).

Anal. Calcd. for $C_{36}H_{30}P_2Cl_2Pd$: C 61.60 H 4.31 Cl 10.10

Found: C 64.41 H 4.39 Cl 8.02

A second (.109 g) and a third (.062 g) crop of crystals also precipitated from the solution on allowing it to stand; these were collected and washed with light petroleum. Their infrared spectra were identical to the above and their analyses showed them to be $(Ph_3P)_2PdCl_2$ (<u>26</u>).

Found: C 62.34 H 4.45 Cl 9.31; C 62.05 H 4.82 Cl 9.79%

The coprecipitation of some triphenylphosphine probably accounts for differences from theoretical in these three samples.

The orange filtrate was concentrated to about 5 ml. Carbon disulphide (15 ml) was added to the orange-red suspension. (This was done to convert the remaining product, presumed to be largely tetrakis(triphenylphosphine)palladium, into the more stable CS_2 adduct, $(Ph_3P)_2PdCS_2$ (<u>38</u>).[62] After 20 minutes the mixture was concentrated. An orange precipitate formed which was filtered and washed, first with carbon disulphide, then with light petroleum resulting in yellow crystals (.048 g).

Anal. Calcd. for $C_{37}H_{30}P_2S_2Pd$: C 62.82 H 4.27 S 9.07%
Found: C 75.70 H 5.89 S 0.69 Cl 1.76%
This sample was probably a mixture of $(Ph_3P)_2PdCl_2$ (26), Ph_3P, and $(Ph_3P)_2PdCS_2$ (38).

A small amount of petroleum ether was added to the carbon disulphide filtrate and the solution kept under nitrogen overnight. A small quantity of dirty orange crystals (.015 g) were filtered, washed with carbon disulphide and petroleum ether, and dried.

Anal. Calcd. for $C_{37}H_{30}P_2S_2Pd$: C 62.82 H 4.27 S 9.07%
Found: C 59.42 H 3.90 S 11.00%

Further concentration of the mother liquors gave a second crop of brighter orange crystals (.093 g).

Anal. Calcd. for $C_{37}H_{30}P_2S_2Pd$: C 62.82 H 4.27 S 9.07%
Found: C 62.62 H 4.59 S 10.68%

The filtrate was finally taken to dryness, the residue stirred with light petroleum (∿15 ml) and filtered to give the orange-brown complex (.292 g). M.Pt. 120-128° (dec.). This was somewhat lower than the value of 130-133° (dec.) reported by Hagihara *et al.*[62]

Anal. Calcd. for $C_{37}H_{30}P_2S_2Pd$: C 62.82 H 4.27 S 9.07%
Found: C 74.63 H 5.46 S 3.18%
This last sample was probably contaminated with a large excess of triphenylphosphine.

Evaporation of the petroleum ether from the filtrate gave an oily white solid (.354 g) which was shown by nmr to contain in addition to the excess triphenylphosphine, hexamethylbenzene (ca. 15%), vinylpentamethylcyclopentadiene (35) (ca. 5%), and chlorovinylpentamethylcyclopentadiene (36) (ca. 80%).

Reactions of complex (32) with triphenyl-phosphine, -arsine, and -stibine at different temperatures.

Complex (32) (.025 g, .037 mmole) and triphenylphosphine (.077 g, .29 mmole) were allowed to react in deuterochloroform solution (total volume ca. 0.5 ml) at 0° for 15 minutes. The solution was decanted from a small amount of precipitated $(Ph_3P)_2PdCl_2$ (26) and analysed for hexamethylbenzene, (35) and (36), quantitatively by ^1H nmr.

Similar experiments were carried out using triphenylarsine (.090 g, .29 mmole) and triphenylstibine (.104 g, .29 mmole), and were also carried out in benzene, at a variety of temperatures. The results are presented in Table I.

Reaction of complex (32) with o-phenanthroline.

To a stirred benzene solution (10 ml) of complex (32), (.340 g, 0.5 mmole) at 25° was added to o-phenanthroline (.360 g, 2 mmoles). A bright yellow precipitate formed at once. Stirring was continued for 30 minutes, the precipitate filtered and washed with benzene. After drying, 0.581 g of a yellow powder containing the complex (40) and o-phenanthrolinehydrochloride was obtained.

Recrystallisation from benzene gave the pure complex 1-(chloro-(o-phenanthroline)palladium)vinylpentamethylcyclopentadiene (40) as small crystals. M.Pt. 200-210° (dec.)

Anal. Calcd. for $C_{24}H_{25}N_2ClPd$: C 59.64 H 5.21 N 5.80 Cl 7.34 Pd 22.02%

Found: C 58.63 H 5.19 N 5.91 Cl 7.48 Pd 21.85%

The ir spectrum showed peaks at 3060(w), 2930(m), 2850(w), 1623 ($\nu_{C=C}$)(w), 1605(w), 1575(m), 1516(m), 1496(m), 1428(s), 1378(m), 1358(w), 1346(m), 1306(w), 1286(w), 1226(m), 1212(w), 1147(m), 1130(w), 1108(m), 1070(m), 1049(m), 908(w), 889(w), 873(s), 852(s), 812(w), 775(m), 734(m), 723(s), 684(w), 646(m), and 316 (ν_{Pd-Cl}) cm^{-1}. The nmr spectrum was recorded.

Reactions of [o-phen $C_{12}H_{17}PdCl$], complex (40).

Reaction of complex (40) with triphenylphosphine.

Complex (40) (0.096 g, .2 mmole) and triphenylphosphine (0.208 g, .8 mmole) were refluxed in benzene (15 ml) under nitrogen for 15 minutes. The reaction mixture was cooled to room temperature and the solvent stripped off under vacuum to give an orange-yellow oil. Light petroleum was added to yield a pale yellow insoluble complex (0.065 g) which was filtered and washed with petroleum ether. The nmr spectrum was recorded.

The reaction also occurred readily at room temperature.

Reaction of complex (40) with acids.

Complex (40) (0.096 g, 0.2 mmole) and trifluoroacetic acid (0.022 g, 0.2 mmole) were stirred in chloroform at -10°. After warming to room temperature the residue was removed by filtration. The solvent was removed under a stream of nitrogen and the nmr spectrum recorded. Hexamethylbenzene was identified (τ 7.77) as the main product while other peaks in the spectrum were not identified.

A solution of the complex (40) in $CDCl_3$ was treated with a stream of anhydrous hydrogen chloride. A precipitate formed at once and was removed by filtration. The nmr spectrum of the filtrate showed a singlet due to hexamethylbenzene and other broad peaks which were not assigned.

Reaction of complex (40) with a 10% aqueous hydrogen chloride solution for two days again showed hexamethylbenzene and other unassigned peaks in the nmr.

Reaction of complex (40) with halogen.

Iodine (0.025 g, 0.1 mmole) and complex (40) (0.048 g, 0.1 mmole) were mixed in chloroform solution. Hexamethylbenzene (ca. 20%) was observed in the nmr spectrum. However, additional low broad peaks could not be identified.

Reaction of complex (40) with cyanide.

The complex (40) (0.096 g, 0.2 mmole) was suspended in a 1:1 mixture of ether-water. Aqueous potassium cyanide (0.065 g, 1 mmole) was added and the solution rapidly stirred for 36 hours. The ether layer was separated, dried over magnesium sulphate, and evaporated on a rotary evaporator to give a colourless oil. The nmr spectrum was recorded but was too complex to make any assignments.

Reaction of complex (40) with hydrazine.

A benzene solution of complex (40) (0.096 g, 0.2 mmole) was treated with anhydrous hydrazine until all the palladium in the complex had been reduced. The mixture was filtered and the solvent removed under vacuum. The nmr in $CDCl_3$ contained a number of peaks in the methyl region and were unassigned.

Reaction of complex (32) with 2,2'-dipyridyl.

This was reacted in a manner analogous to the above but substituting 2,2'-dipyridyl (0.312 g, 2 mmoles) for o-phenanthroline. A yellow powder (0.504 g) containing the complex (41) and dipyridylhydrochloride was obtained. Pure complex (41) was obtained after careful recrystallisation from benzene. M.Pt. 162-165° (dec.)

Anal. Calcd. for $C_{22}H_{25}N_2ClPd$: C 57.53 H 5.49 N 6.10 Cl 7.72 Pd 23.17%

Found: C 56.70 H 5.53 N 6.43 Cl 8.17 Pd 23.71%

The ir and nmr spectra were recorded.

Reaction of complex (32) with lithium aluminum hydride.

To a stirred suspension of lithium aluminum hydride (1.10 g, 30 mmoles) in dry ether (30 ml) at -40° was added complex (32) (2.55 g, 3.8 mmoles). Black metallic palladium separated at once. After 10 minutes the mixture was allowed to warm to room temperature. Filtration and evaporation of the solvent left a pale yellow oil which was contaminated with a little hexamethylbenzene. The oil was separated into three components by preparative vpc on a 20% SE-30 column at a temperature of 120°.

Fraction 1 (ca. 90%) was a colourless oil, ethylpentamethylcyclopentadiene (42). Anal. Calcd. for $C_{12}H_{20}$:
C 87.73 H 12.27 M.Wt. 164
Found: C 87.81 H 12.15 M.Wt. 164 (mass spectroscopic)
The ir and nmr spectra were recorded.

Fraction 2 (ca. 5%) was a colourless oil but was obtained in insufficient amount for an analysis to be done. The ^1H nmr spectrum was recorded but was too complex to assign a structure.

Fraction 3 (ca. 5%) was also a colourless oil and obtained in insufficient quantity for an analysis. From its nmr spectrum the compound was identified as the homofulvene (43); the spectrum was similar to that reported by Criegee and Grüner.[63]

Reaction of complex (32) with hydrazine.

A benzene solution (25 ml) of complex (32) (.680 g, 1 mmole) was cooled to 5°. Hydrazine (.64 ml, 20 mmoles) was added dropwise to the rapidly stirred solution. Black metallic palladium precipitated at once. The temperature was allowed to rise slowly to room temperature. The mixture was filtered and the solvent removed on a rotary evaporator to give a pale yellow oil. This was identified by nmr as the vinylpentamethylcyclopentadiene (35).

Reaction of complex (32) with halogens.

A chloroform solution (ca. .5 ml) of bromine (.016 g, .1 mmole) was cooled to -78° and mixed with complex (32) (.034 g, 0.05 mmole). The solution was quickly transferred to an nmr tube at -78°. Low temperature ^{1}H nmr spectra were recorded on a 100MHz spectrometer. At -51° the initial spectrum was rather broad with peaks appearing at τ 7.94, 8.10, 8.28, 8.36, 8.54, and 8.79. As the temperature was increased the spectrum showed no changes until -15° when a new peak at τ 7.77 (hexamethylbenzene) appeared. At higher temperatures the intensity of this new peak increased and was accompanied by a simultaneous decrease in intensity of the other peaks in the spectrum. At 34° the formation of hexamethylbenzene (τ 7.77) was firmly established. There were no other products and the decomposition had proceeded without the formation of any other detectable intermediates.

Iodine (.025 g, .1 mmole) and complex (32) (0.034 g, 0.05 mmole) were similarly mixed in chloroform at -78°. The solution was allowed to warm slowly to room temperature. The nmr spectrum showed that hexamethylbenzene was the only product.

Reaction of complex (32) with pyridine.

(a) To a stirred chloroform solution (30 ml) of pyridine (1.6 g, 20 mmoles) at -30° was added complex (32) (1.6 g, 2.4 mmoles). A precipitate formed at once. Stirring was continued for 1 hour, after which time a grey solid (.14 g) was isolated. M.Pt. >250°

Anal. Calcd. for $C_{10}H_{10}N_2Cl_2Pd$: C 35.76 H 3.00 N 8.34 Cl 21.12%

Found: C 35.42 H 3.17 N 8.08 Cl 21.11%

The solvent from the filtrate was removed on a rotary evaporator and the greasy orange-yellow solid stirred briefly with petroleum ether. Filtration afforded the orange-yellow complex (2.7 g) (45). M.Pt. 103° (dec.) The complex was not recrystallisable due to decomposition. The ir spectrum showed peaks at 1652(w), 1628(w), 1600(m), 1575(m), 1528(m), 1480(s), 1445(s), 1370(m), 1355(w), 1332(w), 1240(w), 1210(m), 1153(m), 1132(mw), 1075(s), 1060(w), 940(w), 895(s), 767(s), 758(s), 698(s), and

690(s) cm^{-1}. The ^{1}H nmr in $CDCl_3$ showed resonances at τ 4.68 (doublet, 1H), 5.23 (doublet, 1H), 8.24 (singlet, 6H), 9.16 (singlet, 3H), and 9.23 (singlet, 6H) in addition to the pyridine resonances at low field, giving evidence for a complex $(py)_2^*$ $C_{12}H_{17}PdCl$ (45) analogous to the complex (40).

(b) Complex (32) (1.02 g, 1.5 mmoles) was dissolved in benzene (30 ml) at 25°. To the stirred solution was added pyridine (.948 g, 12 mmoles) in benzene. After 5 minutes a precipitate began to separate from the orange solution which was then stirred for 30 hours. The ochre solid was isolated (.309 g), washed with benzene and dried. It was too insoluble to be recrystallised.

The filtrate was evaporated on a rotary evaporator and dried (1 mm H_5) to give orange crystals (0.977 g) (44). M.Pt. 110-113° (dec.). The complex could not be recrystallised due to decomposition. The ir spectrum contained peaks at 2800(m), 1680(m), 1625(w), 1583(w), 1500(w), 1418(m), 1350(s), 1260(mw), 1230(w), 1208(m), 1149(m), 1053(m), 1030(w), 1003(w), 945(m), 873(m), 810(m), 795(w), 748(s), 677(s), 654(m) cm^{-1}. The nmr spectrum was recorded in chloroform and pyridine solutions.

The reaction was repeated using complex (32) (0.340 g, 0.5 mmole) and differing ratios of pyridine (0.158 g, 2 mmoles; 0.079 g, 1 mmole). Both reactions

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*py = pyridine

gave red solutions from which were isolated insoluble red solids (0.310 g and 0.395 g). The compounds were not identified but their infrared spectra were identical. Evaporation of the filtrates gave small quantities of the orange complex (44).

(c) Complex (32) (0.034 g, 0.05 mmole) and pyridine (0.032 g, 0.4 mmole) were allowed to react in deuterochloroform solution (total volume ca. 0.5 ml) at 0° for 20 minutes. The solution was transferred to an nmr tube and the 60MHz ^1H nmr spectrum recorded. The spectrum was similar to that of complex (45). After standing at room temperature for 24 hours, further reaction was observed to have occurred by the presence of additional peaks in the nmr spectrum corresponding to vinylpentamethylcyclopentadiene (35).

Similar experiments were carried out using different amounts of pyridine (0.016 g, 0.2 mmole; 0.08 g, 0.1 mmole). When a 1:2 ratio was mixed in $CDCl_3$, the ^1H nmr spectrum showed peaks, among others, corresponding to hexamethylbenzene and vinylpentamethylcyclopentadiene (35). After 24 hours the spectrum had changed and was dominated by broad peaks at τ 8.23 and 9.00. Hexamethylbenzene was the only observed product when a 1:1 ratio of reactants was mixed in $CDCl_3$.

The three reactions described above were also carried out in benzene solution (total volume ca. 0.5 ml). The ^1H nmr spectrum of the reaction using an excess of pyridine (0.032 g, 0.4 mmole) indicated a product identical to the orange complex (44), although the peaks had slightly different chemical shifts, attributable to a solvent effect.

A red solution was obtained when a 1:2 ratio was used. The ^1H nmr spectrum consisted of seven broad peaks at τ 5.37, 6.04, 6.77, 7.29, 7.52, 8.08, and 8.80. The relative intensities were measured with difficulty and were approximately 1:1:1:2:1:4:1. It was not possible to interpret this complicated spectrum.

When a 1:1 ratio of reactants was used, the initial ^1H nmr spectrum contained peaks at τ 7.64, 7.77, 8.00, 8.24, 8.49, and 8.23; additional minor resonances were observed at τ 4.81, 5.50, and 5.94. After 24 hours the spectrum had changed and was characterised by a large broad resonance at τ 8.01 as well as a smaller broad resonance at τ 8.54 in an approximate ratio of 5:1. The peaks were not assigned.

Reaction of complex (32) with aniline.

(a) A benzene solution (1 ml) of aniline (0.372 g, 4 mmoles) was added to a stirred solution of complex (32) (0.340 g, 0.5 mmole) in benzene (10 ml) at 25°. A grey-brown precipitate (0.344 g) (46) formed and was isolated after stirring for 15 hours. M.Pt. >250°

Anal. Calcd. for $C_{33}H_{42}N_3Cl_4Pd_2$: C 47.45 H 5.07 N 5.03 Cl 16.98 Pd 25.48%

Found: C 47.79 H 5.45 N 4.93 Cl 16.80 Pd 24.82%

The ir spectrum showed bands at 3250(m), 3150(m), 3090(w), 2750(s), 2555(m), 2000(m), 1595(w), 1569(m), 1520(w), 1489(m), 1460(m), 1432(w), 1370(m), 1338(w), 1322(w), 1290(w), 1218(m), 1200(w), 1173(w), 1145(s), 1117(s), 1067(m), 1018(s), 901(m), 804(m), 763(s), 755(s), 740(s), 686(s) cm^{-1}.

Evaporation of the filtrate on a rotary evaporator gave an oil which was dissolved in a small quantity of petroleum ether and chromatographed over alumina. The ^1H nmr of this oil in $CDCl_3$ contained resonances due to hexamethylbenzene, vinylpentamethylcyclopentadiene (35), and additional unassigned peaks.

The reaction was repeated but using a different amount of aniline (0.093 g, 1 mmole). An ochre solid (0.36 g) was isolated after two days. The ir spectrum of this material was identical to that described above for complex (46). Evaporation of the filtrate left an oil which was shown to contain some hexamethylbenzene and (35) by its nmr spectrum.

(b) Complex (32) (0.034 g, 0.05 mmole) and aniline (0.037 g, 0.4 mmole) were reacted in deuterochloroform solution (ca. 0.5 ml) at 0° for 20 minutes. The solution was decanted from a small quantity of precipitate and examined for hexamethylbenzene and (35) by nmr. Additional peaks in the spectrum were not identified.

A similar result was obtained when a smaller quantity of aniline (0.019 g, 0.2 mmole) was used.

Similar experiments were carried out in benzene solution (total volume ca. 0.5 ml). Complex (32) (0.034 g, 0.5 mmole) and aniline (0.01 g, 0.1 mmole) reacted to give an nmr spectrum of crowded peaks at τ 7.65, 7.91, 8.03, 8.37, 8.56, 8.72, and 9.03. The two major peaks appeared at τ 8.03 and 8.56, the latter being the largest. The peak at τ 8.03 showed a fine splitting although this may actually have been due to two overlapping singlets. When a larger amount of aniline (0.019 g, 0.2 mmole) was used a similar nmr spectrum was recorded. However, a significant difference was the increased intensity of the peak at τ 8.03 while the peak at 8.56 had decreased. This trend continued when an excess of the aniline (0.037 g, 0.4 mmole) was used to give a spectrum dominated by a broad intense peak at τ 8.03. However, little information can be obtained from these spectra due to a lack of additional information from other parts of the spectrum (i.e. to lower field).

Reaction of complex (32) with p-toluidine.

A benzene solution (10 ml) of complex (32) (0.340 g, 0.5 mmole) was reacted with p-toluidine (0.428 g, 4 mmoles) at 25°. A precipitate soon separated from the brown solution and was isolated after stirring for 2 days. The pale-yellow solid (0.317 g) (47) was washed with a little benzene, then dried. M.Pt. 224-229° (dec.)

Anal. Calcd. for $C_{40}H_{54}N_4Cl_4Pd_2$: C 50.81 H 5.76 N 5.92 Cl 15.00 Pd 22.51%

Found: C 49.48 H 5.83 N 5.86 Cl 14.97 Pd 22.53%

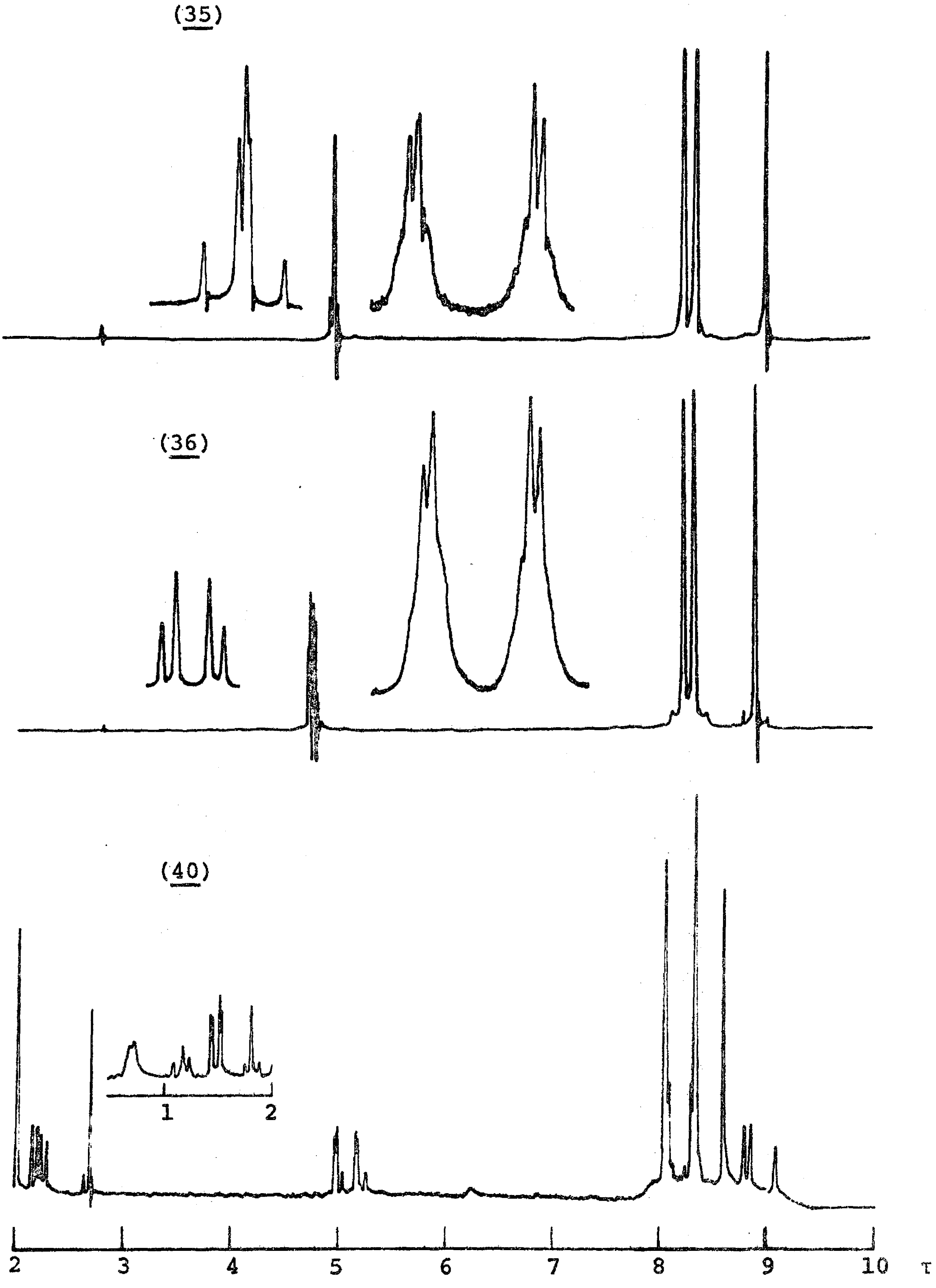
The ir spectrum contained bands at 3250(m), 3150(m), 3090(w), 2750(s), 2555(m), 1890(w), 1611(w), 1575(m), 1500(m), 1445(w), 1390(w), 1370(m), 1320(w), 1290(w), 1218(m), 1205(m), 1180(m), 1150(m), 1120(m), 1100(w), 1070(w), 1043(w), 1022(m), 965(w), 937(w), 834(w), 814(s), 745(m), 728(w), 704(m) cm^{-1}.

The complex was too insoluble for a nmr to be taken.

Evaporation of the filtrate and subsequent chromatography over alumina by elution with light petroleum gave a colourless oil. Analytical vpc analysis on a 5% SE-30 column at 105° separated the oil into four components. The major component, representing about 60% of the mixture was the vinylpentamethylcyclopentadiene (35). The other components represented about 30, 5, and 5% respectively, but were not identified.

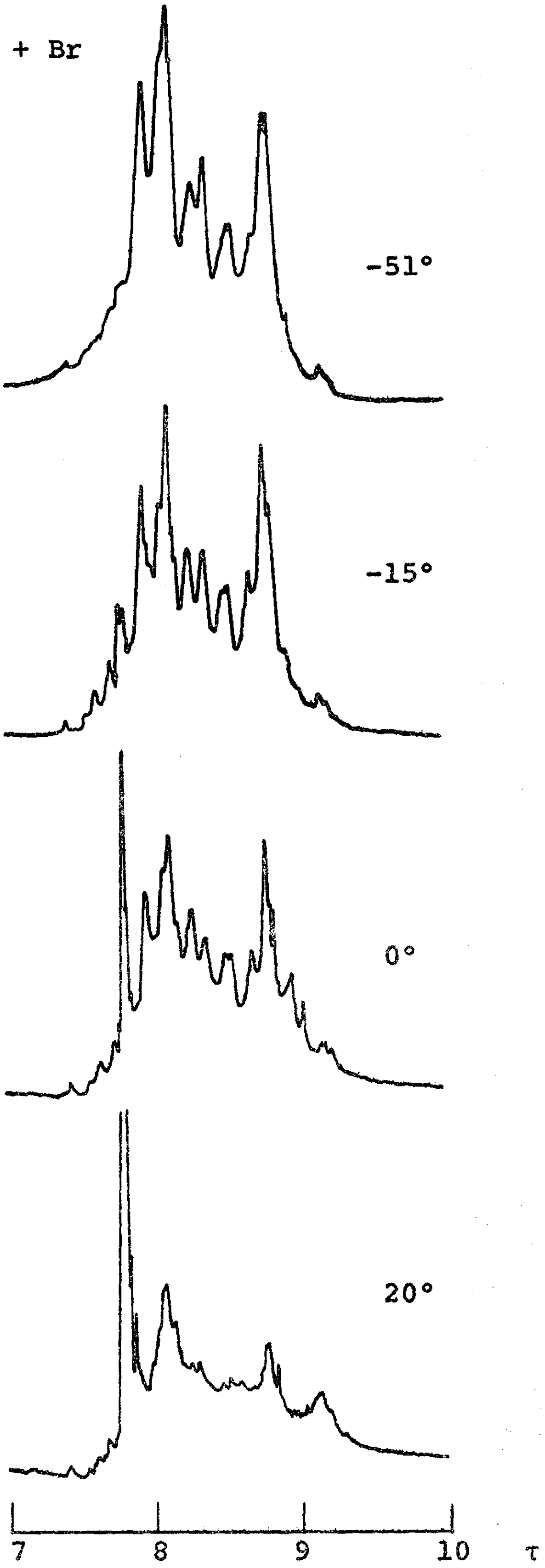
APPENDIX

APPENDIX I



APPENDIX II

$[(Me_2C_2)_3PdCl_2]_2$ + Br



BIBLIOGRAPHY

BIBLIOGRAPHY

1. G. N. Schrauzer, Angew. Chem., Internat. Ed. Engl. 3, 185 (1964).
2. G. N. Schrauzer, "Advances in Organometallic Chemistry Vol. 2", edited by F. G. A. Stone and R. West, Academic Press, New York, 1964, pp. 27-31.
3. L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, J. Org. Chem. 27, 3930 (1962).
4. L. Vaska and J. W. Siluzio, J. Am. Chem. Soc. 83, 2784 (1961).
5. J. P. Collman and J. W. Kang, ibid. 89, 844 (1967).
6. E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, Can. J. Chem. 46, 3879 (1968).
7. J. Chatt, L. A. Duncanson, and R. G. Guy, J. Chem. Soc. 827 (1961).
8. J. Chatt, R. G. Guy, L. A. Duncanson, and D. T. Thompson, ibid., 5170 (1963).
9. J. L. Boston, S. W. Grim, and G. Wilkinson, ibid., 3468 (1963).
10. J. Chatt, B. L. Shaw, and A. A. Williams, ibid., 3269 (1962).

11. J. Chatt, L. A. Duncanson, and R. G. Guy, Chemistry and Industry, 430 (1959).

12. J. O. Glanville, J. M. Stewart, and S. O. Grim, J. Organometal. Chem. (Amsterdam) 7, 9 (1967).

13. G. R. Davies, W. Hewertson, R. H. B. Mais, and P. G. Owston, Chem. Commun., 423 (1967).

14. W. Hübel, in "Organic Syntheses via Metal Carbonyls", I. Wender and P. Pine, Ed., Interscience Publishers, New York, N.Y., 1968, p. 273 and references therein.

15. H. Greenfield, H. W. Sternberg, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, J. Am. Chem. Soc. 78, 120 (1956).

16. W. G. Sly, ibid. 81, 18 (1959).

17. W. Hübel and E. H. Braye, J. Inorg. Nucl. Chem. 10, 250 (1959).

18. R. P. Dodge and V. Schomaker, J. Organometal. Chem. (Amsterdam) 3, 274 (1965).

19. O. S. Mills and G. Robinson, Proc. Chem. Soc., p. 187 (1964).

20. U. Kruerke, C. Hoogzand, and W. Hübel, Chem. Ber. 94, 2817 (1961).

21. V. O. Reikhsfeld and K. L. Makovetskii, Russ. Chem. Rev. 35, 510 (1966).

22. C. Hoogzand and W. Hübel, in "Organic Syntheses via Metal Carbonyls", I. Wender and P. Pino, Ed.,

Interscience Publishers, New York, N.Y., 1968, p. 343.

23. J. P. Collman and W. R. Roper in "Advances in Organometallic Chemistry Vol. 7", edited by F. G. A. Stone and R. West, Academic Press, New York, 1968, pp. 65-67.

24. W. Reppe, O. Schlichting, K. Klager, and T. Toepel, Annalen 560, 1 (1948).

25. (a) L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, J. Org. Chem. 26, 5155 (1961).
    (b) L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, ibid. 26, 5163 (1961).
    (c) E. C. Colthup and L. S. Meriwether, ibid. 26, 5169 (1961).

26. W. Hübel and C. Hoogzand, Chem. Ber. 93, 103 (1960).

27. W. Hübel and R. Merényi, ibid. 96, 930 (1963).

28. C. Hoogzand and W. Hübel, Tetrahedron Letters, 637 (1961).

29. E. M. Arnett and J. M. Bollinger, J. Am. Chem. Soc. 86, 4729 (1964).

30. R. Criegee and G. Schroeder, Ann. 623, 1 (1959).

31. W. Hübel, E. H. Braye, A. Clauss, E. Weiss, U. Krüerke, D. A. Brown, G. S. D. King, and C. Hoogzand, J. Inorg. Nucl. Chem. 9, 204 (1959).

32. A. Nakamura and N. Hagihara, Bull. Chem. Soc. Japan 34, 452 (1961).

33. J. L. Boston, D. W. A. Sharp, and G. Wilkinson, J. Chem. Soc., 3488 (1962).

34. P. M. Maitlis and A. Efraty, J. Organometal. Chem. (Amsterdam) 4, 172 (1965).

35. W. Hübel and R. Merényi, ibid. 2, 213 (1964).

36. P. M. Maitlis, D. F. Pollock, M. L. Games, and W. J. Pryde, Can. J. Chem. 43, 470 (1965).

37. R. C. Cookson and D. W. Jones, J. Chem. Soc. (London), 1881 (1965).

38. R. Hübel and H. J. Neugebauer, Tetrahedron Letters, 3541 (1964).

39. L. Malatesta, G. Santarella, L. Vallerino, and F. Zingales, Angew. Chem. 72, 34 (1960); Atti. Accad. Naz. Lin. Rend. Cl. Sci. Fis. Mat. Nat. 27, 230 (1959).

40. A. T. Blomquist and P. M. Maitlis, J. Am. Chem. Soc. 84, 2329 (1962).

41. L. F. Dahl and W. E. Oberhausli, Inorg. Chem. 4, 629 (1965).

42. G. N. Schrauzer, J. Am. Chem. Soc. 81, 5310 (1959); Chem. Ber. 94, 1403 (1961).

43. M. E. Volpin, V. A. Dubovitskii, O. V. Nogina, and D. N. Kursanov, Dokl. Akad. Nauk. SSSR 151, 1100 (1963).

44. K. Sonogashira and N. Hagihara, Bull. Chem. Soc. Japan 39, 1178 (1966).

45. E. H. Braye, W. Hübel, and I. Caplier, J. Am. Chem. Soc. 83, 4406 (1961).

46. A. A. Hock and O. S. Mills, Acta. Cryst. 14, 139 (1961).

47. E. Bayer, H. Brune, and K. L. Hock, Angew. Chem. 74, 872 (1962).

48. E. O. Fischer, K. Bittler, and H. P. Fritz, Z. Naturforsch. 18b, 83 (1962).

49. R. P. Slodge, O. S. Mills, and V. Schomaker, Proc. Chem. Soc., 380 (1963).

50. H. Yamazaki and N. Hagihara, J. Organometal. Chem. (Amsterdam) 7, P22 (1967).

51. J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, Inorg. Chem. 7, 1298 (1968).

52. J. T. Mague and G. Wilkinson, ibid. 7, 542 (1968).

53. W. Kein, J. Organometal. Chem. (Amsterdam) 16, 191 (1969).

54. M. R. Churchill and R. Mason, "Advances in Organometallic Chemistry, Vol. 5", edited by F. G. A. Stone and R. West, Academic Press, New York, 1967, p. 120.

55. H. Dietl and P. M. Maitlis, Chem. Commun., 481 (1968).

56. H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, J. Am. Chem. Soc. 90, 5321 (1968).

57. E. D. Bergmann, "The Chemistry of Acetylenes and Related Compounds", Interscience, New York, 1948, p. 93.

58. H. C. Longuett-Higgins and L. E. Orgel, J. Chem. Soc. (London), p. 1969 (1956).

59. P. M. Maitlis, "Advances in Organometallic Chemistry, Vol. 4", edited by F. G. A. Stone and R. West, Academic Press, New York, 1966, pp. 95-141.

60. C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, Proc. Chem. Soc., 312 (1961).

61. G. M. Whitesides and W. J. Ehmann, J. Am. Chem. Soc. 90, 804 (1968); ibid. 91, 3800 (1969).

62. T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, Bull. Chem. Soc. Japan 41, 296 (1968).

63. R. Criegee and H. Grüner, Angew. Chem. internat. Ed. 7, 467 (1968).

64. W. Schäfer and H. Hellman, ibid. 5, 518 (1967).

65. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 2", Permagon Press, New York, 1966, p. 710.

66. S. D. Robinson and B. L. Shaw, J. Chem. Soc., 4806 (1963); ibid., 5003 (1964); S. F. A. Kettle and R. Mason, J. Organometal. Chem. 5, 573 (1966).

67. B. L. Shaw and G. Shaw, J. Chem. Soc. (A) 602 (1969).

68. P. Cossee, Rec. Trav. Chim. 85, 1151 (1966).

69. B. L. Shaw, Chem. Commun., 464 (1968).

70. R. F. Heck, Accts. Chem. Res. 2, 10 (1969).

71. H. Reinheimer, unpublished results.

72. R. F. Childs and S. Winstein, J. Am. Chem. Soc. 90, 7144 (1968); ibid., 7146 (1968).

73. V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, Chem. Commun., 389 (1969).

74. L. A. Paquette and G. R. Krow, Tetrahedron Letters, 2139 (1968); H. Hogeveen and H. C. Volger, Rec. Trav. Chim. 87, 1042 (1968); ibid. 88, 353 (1969).

75. A. Aguilo, "Advances in Organometallic Chemistry, Vol. 5", edited by F. G. A. Stone and R. West, Academic Press, New York, 1967, p.321; P. M. Henry, J. Am. Chem. Soc. 86, 3246 (1964); ibid. 88, 1595 (1966).

76. U. Belluco, M. Giustiniani, and M. Graziani, ibid. 89, 6494 (1967); U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaolo, Inorg. Chem. 6, 718 (1967).