THE OLIGOMERIZATION OF ACETYLENES INDUCED BY METALS OF THE NICKEL TRIAD

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ABSTRACT

Acetylenes react with many transition metal complexes to give a wide variety of products, including benzenes and cyclopentadienes, formed by cyclotrimerization of the acetylene. Among the factors which determine the mechanism of cyclotrimerization, an important and hitherto unrecognized one is the formal oxidation state of the metal. This is well illustrated by palladium where two distinct modes of reaction, depending on whether the reactivity entity is Pd^{II} or Pd^0, are observed. The nature of the acetylene and of the other ligands on the metal are also important. Such reactions offer synthetically useful routes to organic compounds as well as metal complexes otherwise difficult to prepare.

Acetylenes are highly reactive compounds which in addition to their normal organic reactions also interact with a wide variety of metal complexes. Their reactions with transition metal compounds in particular have yielded a rich harvest of new types of complexes and novel transformations. This field was first explored by Reppe and his collaborators who found that the then elusive and rare cyclooctatetraene could be synthesized in one step

$$4 \ HC{\equiv}CH \xrightarrow{\ Ni^{II}\ } \ \bigcirc$$
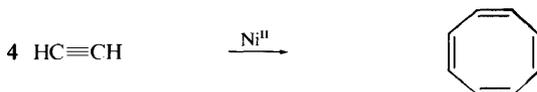
from acetylene with a nickel catalyst[1]. These workers also obtained a variety of novel complexes from the reactions of iron carbonyls with acetylenes[2]. These complexes and others, as well as many derived from cobalt and molybdenum carbonyls, were later characterized, in many cases also by x-ray studies, by Hübel and his collaborators[3]. The general pattern revealed by their studies was that complexes containing one, two, three or even more acetylenes were formed and that very frequently carbon monoxide was incorporated into the organic ligand. The profusion of complexes isolated as well as the formation of organic products makes these reactions interesting but extremely complex.

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In addition to the reactions which occur with metal carbonyls. many other complexes catalyse the oligomerization of acetylenes. These reactions have the advantage, from a mechanistic standpoint, of not involving coordinated carbon monoxide and of often giving single products and hence promise to be simpler to elucidate. Reactions of this type have been investigated by Collman, Hagihara, Whitesides, Wilkinson, Zeiss and many others and some of this work has recently been reviewed[4-6].

In order to understand more fully the processes which occur in these reactions, we have examined in some detail the reactions of acetylenes with complexes of the nickel triad. These elements have a well-understood basic chemistry, and two well-defined and common oxidation states (for organometallic complexes) of 0 and $+ II$, as well as a simple stereochemistry. The elements further react with acetylenes both in their 0 and II oxidation states and a comparison of these reactions is obviously of interest.
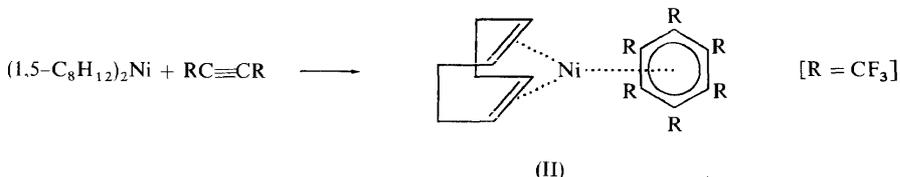
Nickel(II) complexes are apparently the active catalysts in the cyclooctatetraene synthesis[6], but relatively little work has appeared on other such reactions, though Wittig[7] has obtained cyclobutadiene complexes in low yields by dimerization of cyclooctyne with nickel halides. Part of the problem appears to be due to the low solubility of common nickel(II) salts in organic solvents which do not complex strongly and to the high affinity of nickel(II) for oxy-ligands.

Nickel(0) complexes have been reacted with a variety of acetylenes. Meriwether and his co-workers found that monosubstituted acetylenes were oligomerized, largely to linear or to benzenoid trimers, by dicarbonylbis(triphenylphosphine)nickel(0)[8]. Disubstituted acetylenes did not oligomerize and the authors suggested a mechanism for the monosubstituted acetylene reactions which involved the intermediate formation of a nickel(II) acetylide hydride complex (I),
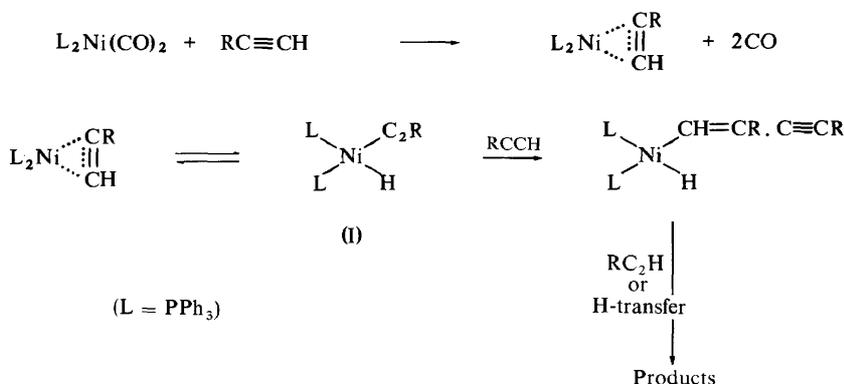

Recently, we have observed that dimethyl acetylenedicarboxylate (DMA) is catalytically trimerized by nickel carbonyl to hexamethyl mellitate[9]. Browning et al.[10] have isolated the complex (II) from the reaction of bis(1.5-cyclooctadiene)nickel with hexafluoro-2-butyne.

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$$Ni(CO)_4 \quad + \quad RC\equiv CR \quad \longrightarrow$$

$[R = COOMe]$

$$(1.5\text{-}C_8H_{12})_2Ni + RC\equiv CR \quad \longrightarrow$$

$[R = CF_3]$

(II)

In addition, a variety of nickel(0) acetylene complexes of the general formula (IIIa) have been prepared[11, 12].
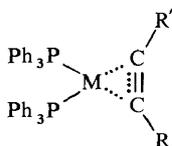
(IIIa) M = Ni; R. R′ = Me. Ph. CF_3
(IIIb) M = Pd; R = R′ = COOMe. CF_3
(IIIc) M = Pt; R. R′. = alkyl. aryl. COOMe. CF_3. etc.

The platinum(0) complexes (IIIc) have been known for many years and were originally prepared by Chatt and his co-workers[13]. We subsequently prepared the palladium(0) complexes and discussed the bonding in some detail[12]. The x-ray structure of the platinum complex (IIIc. R = R′ = Ph) has been reported by Glanville et al[14]. The essential features here are that the two phosphorus atoms. the platinum and one of the acetylenic carbons are coplanar while the other acetylenic carbon is slightly above this plane. In addition. the acetylene is considerably bent into a *cis* configuration (∠ PhCC = 140°) and the coordinated acetylenic bond is lengthened over its normal value.

Preliminary results from a structure determination of the dimethyl acetylenedicarboxylate palladium complex (IIIb. R = R′ = COOMe) by McGinnety[15] show a very similar geometry to this. Furthermore. we have shown by n.m.r. methods that the planar or near-planar structures are retained in solution for (IIIa and IIIb. R = R′ = CF_3 and R = Me. R′ = Ph) and (IIIb. R = R′ = CF_3). Diagrammatically. the bonding in complexes of M^0 of this type can be represented by (IV).
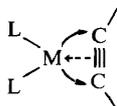

(IV)

which implies that the d–$\pi^\star$ interaction is most important in bonding the metal and the acetylene. In support of this picture, it is found that electron releasing substituents on the ligand (phosphine) and electron-withdrawing substituents on the acetylene stabilize the complexes. In this context the approximate measure of stability is taken to be $\Delta\nu_{C\equiv C}$, defined as[12, 13].

$$\Delta\nu_{C\equiv C} = \nu_{C\equiv C} \text{ (free acetylene)} - \nu_{C\equiv C} \text{ (complexed acetylene)}.$$

A further consequence of this bonding is that the acetylene in suitable M^0 complexes is expected to be rather active as a nucleophile, while the complexes themselves will easily undergo electrophilic attack[12].

Unfortunately, from the point of view of investigating their oligomerization reactions, the complexes (III) are somewhat inert with respect to further reaction with acetylenes*. This appears to be largely an effect due to the presence of the bulky triphenylphosphines as stabilizing ligands. However, Allen and Cook[16] were able to observe replacement reactions of one acetylene by another, probably by the reaction path,

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

$$(Ph_3P)_2Pt + ac' \rightarrow (Ph_3P)_2Pt(ac')$$
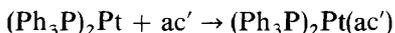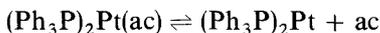
Therefore a study of the mode of reaction of M^0 complexes with acetylenes must use a M^0 complex not containing a phosphine or similar ligand. For nickel, these are well known and the tetracarbonyl or the bis(1.5-cyclo-octadiene) complexes can be utilized[9, 10, 17]. However, since the reactions of M^{II} and acetylenes are much more common for palladium (and to some degree for platinum), it was of greater interest to investigate Pd^0 and Pt^0 complexes.

The key complex for this study, discovered by Takahashi et al. in Japan last year[18], is $(DBA)_2Pd$ (Va, DBA = dibenzylideneacetone). We have recently prepared the platinum analogue $(DBA)_2Pt$ (Vb) and a related complex, $(DBA)_3Pt$, which, however, is only stable in the solid state and which very rapidly dissociates to $(DBA)_2Pt$ and DBA in solution[19]. The complexes (V) are easily prepared from a readily accessible ligand, and are dark red-purple complexes which are relatively stable, both in solution and in the solid state, even in the presence of oxygen.

PhCH=CHCOCH=CHPh + MCl_4^{2-} + ROH + NaOAc $\longrightarrow$
(DBA)

(Va) M = Pd
(Vb) M = Pt

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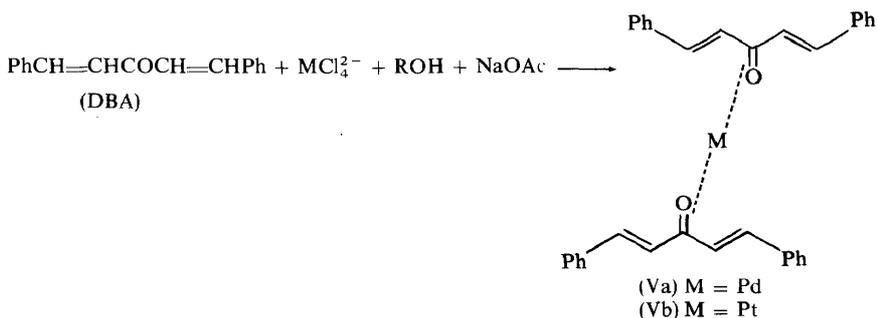
* Recent studies, however, indicate that $(Ph_3P)_2Pt(MeOOCC_2COOMe)$ does catalyse the trimerization of dimethyl acetylenedicarboxylate, but only on heating.

The structures of (V) have been examined spectroscopically[19]. The absence of any shifts or changes in coupling constant in the n.m.r. spectra of (Va) or (Vb) by comparison with free DBA and in particular the absence of any coupling to ^{195}Pt (34 per cent. $I = \frac{1}{2}$) in (Vb) indicates that neither the olefinic bonds nor the phenyl rings are involved in binding the metal. The change in ν_{CO} from DBA to $(DBA)_2M$ of 108 (Va) and 125 cm^{-1} (Vb) respectively indicates that the metal is bonded by the ketonic function of the ligands[19]. The complexes can perhaps best be regarded as stabilized charge transfer complexes and the bonding involved is reminiscent of that in the carbon disulphide complexes, $(Ph_3P)_2MCS_2$ (M = Pd, Pt)[20, 21].
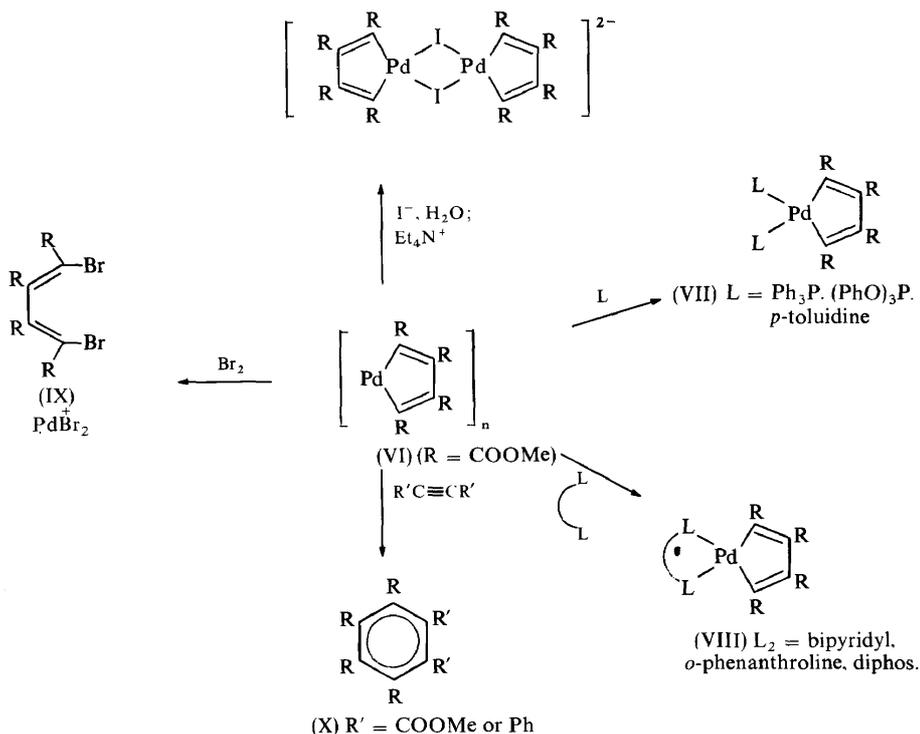

M = Pd. Pt
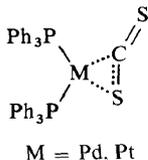
The complexes (V) are very useful starting materials in a number of reactions. Of particular concern here is that they react with acetylenes bearing electron-withdrawing substituents, such as —COOMe. For the palladium complex (Va) the product is the palladiacyclopentadiene. $[Pd(CCOOMe)_4]_n$ (VI) which is rather insoluble in non-complexing solvents[22].

$$(DBA)_2Pd + 2MeOOCC{\equiv}CCOOMe \rightarrow [Pd(CCOOMe)_4]_n$$

$$(VI)$$
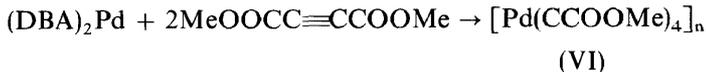
In the presence of various ligands. L. complexes of the type (VII) and (VIII) are formed. The n.m.r. spectra of (VI) in acetone or benzonitrile. and of (VII) and (VIII) in chloroform. show two equally intense singlet resonances due to the carbomethoxy groups. Integration against the protons in the ligands L. as well as analytical and molecular weight determinations. established the structures for (VII) and (VIII). These and other reactions are summarized in *Scheme 1*[22].

Further evidence in favour of the structure (VI) comes from the reaction with bromine to give tetramethyl 1.4-dibromobutadiene-1.2.3.4-tetracarboxylate (IX) and palladium bromide. In addition. various acetylenes reacted with (VI) on heating to give the hexa-substituted benzenes (X); when R′ = COOMe the reaction was catalytic in (VI).

The palladiacyclopentadiene (VI) is very unusual in that in contains two Pd—C σ-bonds and is of good thermal and hydrolytic stability despite the absence of any stabilizing ligands. Comparison of the infrared spectra of (VI). (VII) and (VIII) reveals that the association of individual molecules of (VI) does not arise by π-bonding. but that the carbonyl functions of some of the esters are involved. Thus (VII) and (VIII) show one or two very intense ν_{CO} bands at 1705 ± 20 cm^{-1}; whereas (VI) in Nujol shows an additional very intense band at 1620 cm^{-1} which is absent in (VII) and (VIII) and is only of medium intensity in a KBr disc where (VI) presumably exists largely as $K_2[Br_2Pd(C_4COOMe)_4]$ or a similar species. A similar shift, but in the

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I⁻, H₂O ;
Et₄N⁺

(VII) L = Ph₃P. (PhO)₃P.
p-toluidine

Br₂

(IX)
+
PdBr₂

(VI) (R = COOMe)

R'C≡CR'

(VIII) L₂ = bipyridyl,
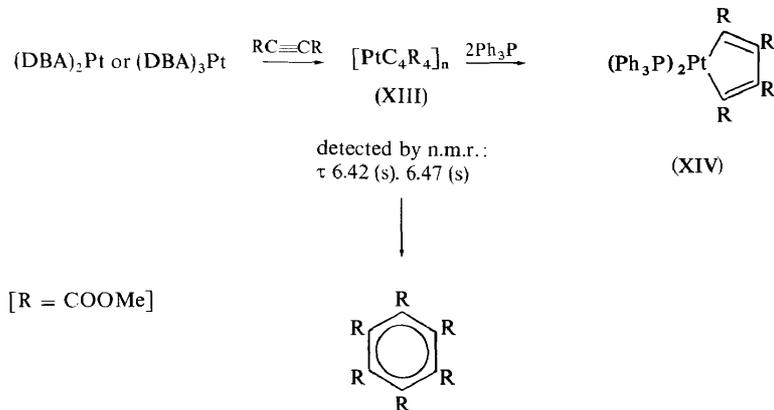o-phenanthroline, diphos.

(X) R' = COOMe or Ph

Scheme 1

opposite direction, is seen in ν_{C-OMe} in the 1200–1300 cm^{-1} region and both these changes are consistent with bonding of the type (XI)[23].

(XI)

[R = COOMe]

(XII) [R = COOMe]
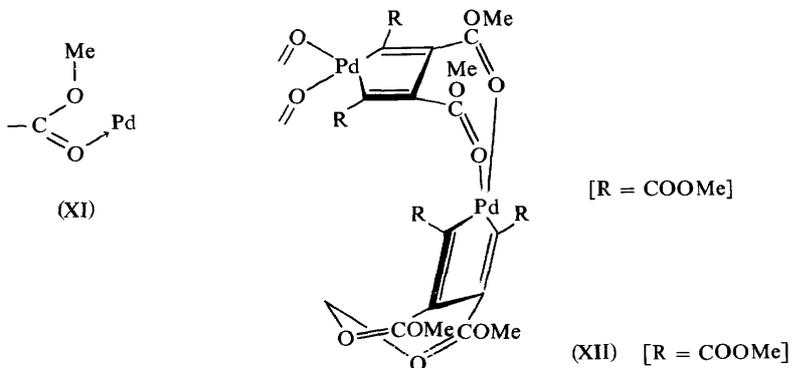
In all the complexes (VI), (VII) and (VIII) $\nu_{C=C}$ remains constant at 1560 ± 10 cm^{-1} and we suggest, therefore, that the bonding between individual units of (VI) is as shown in (XII). A molecular weight determination of (VI) in chloroform gave a value close to that for a trimer and it is possible that (VI) has a cyclic structure.

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The platinum complex (Vb) reacts with the same acetylene at about one-sixtieth of the rate of $(DBA)_2Pd$ (Va). In this case the intermediate (XIII) corresponding to (VI) was detected by n.m.r. and could be isolated and characterized as the triphenylphosphine adduct (XIV)[22]

$(DBA)_2Pt$ or $(DBA)_3Pt$ $\xrightarrow{RC\equiv CR}$ $[PtC_4R_4]_n$ $\xrightarrow{2Ph_3P}$ $(Ph_3P)_2Pt$

(XIII)

detected by n.m.r.:
τ 6.42 (s). 6.47 (s)

(XIV)

[R = COOMe]

The trimer, hexamethyl mellitate. was also formed in this reaction. implying that conversion of the metalacyclopentadiene to the benzene occurs more easily for Pt than Pd.

The reactions of these metals in the + II oxidation state with various acetylenes have also been studied in a number of laboratories. Chatt and his co-workers some years ago found that platinum(II) formed stable 1:1 complexes with a number of heavily substituted acetylenes[24]. and a structure determination of one of these (XV) revealed it to have the structure indicated[25].

(XV)
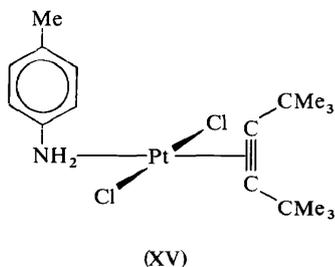
The significant features of this structure are that the acetylene lies perpendicular to the coordination plane of the metal and that the acetylenic substituents are again bent back away from the metal ($\angle$ Bu^{t}CC = 163°). but not to the degree found for the zero-valent complex (IIIc. R = R' = Ph). There is also evidence again for some lengthening of the coordinated triple bond. corroborated by its stretching frequency which is weakly infrared

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active in the complex and is reduced by some $200\ cm^{-1}$ from its value in the free acetylene. This value of $\Delta\nu_{C\equiv C}$ is considerably less than those found for the complexes (III) $(400-500\ cm^{-1})$ and it is to be expected that the bond length of the coordinated triple bond will be found to be appreciably longer in (III) than in complexes of M^{II}. The greater deformation of the acetylene suggests that the bonding between the acetylene and the metal is stronger in (III) and we have proposed that the major contribution to the bonding in complexes of M^{II} [such as (XV)] is of the type (XVI).
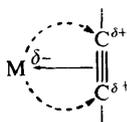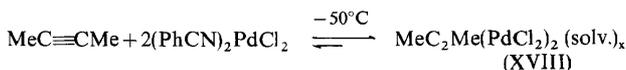

(XVI)

This implies that back-bonding from metal orbitals into the acetylenic $\pi^\star$-orbitals is less important than in (III) and that the major contribution is a dative bonding from the π-orbitals of the acetylene into vacant metal orbitals[12]. This also results in a polarization which should make the co-ordinated acetylene more reactive towards nucleophilic attack, and indeed this property has been amply demonstrated for acetylenes and for olefins (where the same arguments apply) coordinated to Pt^{II} and Pd^{II}.
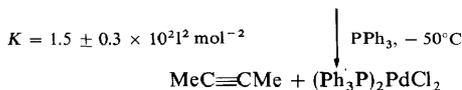
Acetylenes react more easily with Pd^{II} than Pt^{II} and 1:1 complexes are hard to isolate. However, Hosokawa et al.[26] have prepared the di-t-butyl-acetylene complex (XVII) and we have obtained evidence for the formation at low temperatures of a complex of 2-butyne (XVIII) which regenerated the acetylene on reaction with triphenylphosphine at $-50°C$[27].

$$Bu^tC\equiv CBu^t + [C_2H_4PdCl_2]_2 \longrightarrow$$

(XVII)

$$MeC\equiv CMe + 2(PhCN)_2PdCl_2 \underset{-50°C}{\rightleftharpoons} MeC_2Me(PdCl_2)_2\ (solv.)_x$$

(XVIII)

$$K = 1.5 \pm 0.3 \times 10^2 l^2\ mol^{-2} \qquad \downarrow PPh_3,\ -50°C$$

$$MeC\equiv CMe + (Ph_3P)_2PdCl_2$$

The complex (XVIII) is an intermediate in the further reaction with 2-butyne whereas (XVII) is stable and does not show any inclination for further reaction.

It may be safely stated that virtually all acetylenes react with palladium chloride in a very facile manner to yield products. Our interest in this area was first awakened by the report by Malatesta and his co-workers that a cyclobutadiene complex could be obtained from diphenylacetylene.

However, Phillips[28] had already noted in 1894 that aqueous palladium chloride reacted with acetylene, and Erdmann and Makowka in 1904 used this reaction as a means of estimating palladium in the presence of other platinum metals, since palladium formed a complex which precipitated from water but was soluble in organic solvents[29]. Makowka later studied this reaction in more detail and isolated a complex, C_4H_5ClOPd, which gave butyric acid on treatment with base[30]. More recently, Temkin et al.[31] re-examined this reaction and suggested a π-allylic structure (XIX) for this complex on the basis of its infrared spectrum.
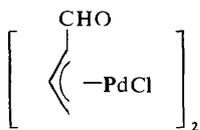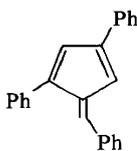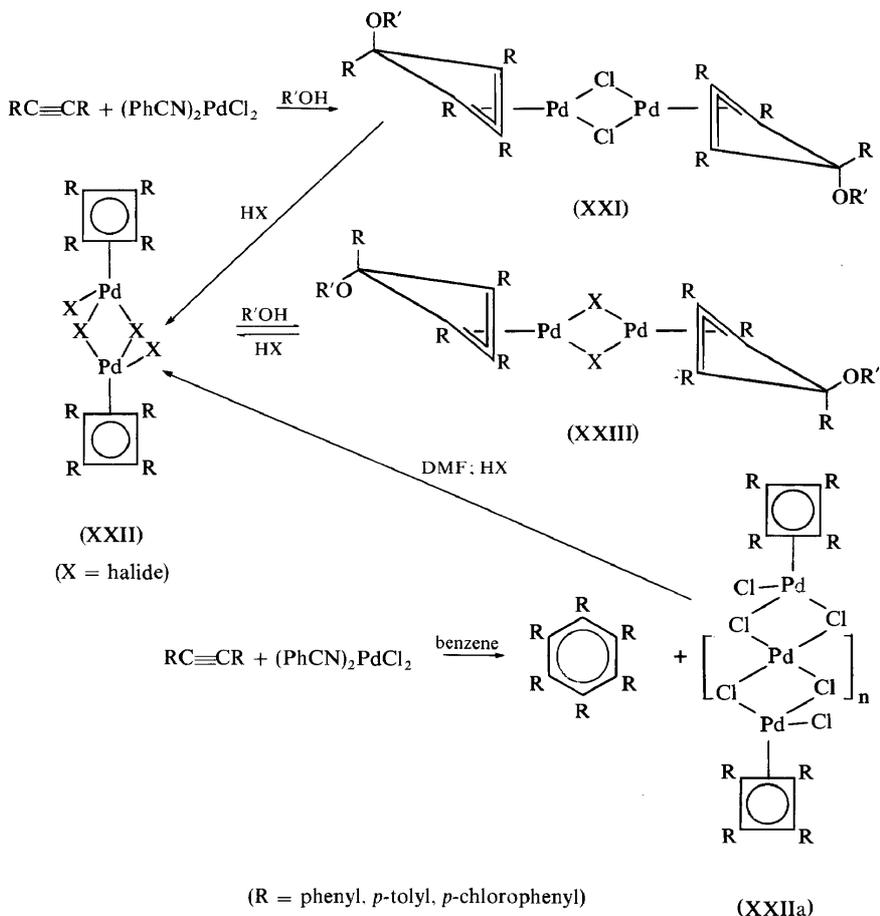

(XIX)   (XX)

In our experience the reactions of acetylene and monosubstituted acetylenes usually give non-stoicheiometric complexes containing acetylenic oligomers. In view of the ease with which autoxidation and hydrolytic processes also occur it would probably be advisable to defer consideration of these reactions until more data are available. However, Avram et al.[32] have obtained a complex, $[Cl(Bu^tC_2H)_3PdCl]$, which we later showed to be a dimer[33], and which gave fulvenes on decomposition[34]. We had previously found that phenylacetylene under suitable conditions was oligomerized to the fulvene (XX) and tetramers of unknown structures which may be dihydropenta-lenes[35]. In the absence of structural data on the complexes from mono-acetylenes one can only conclude at the moment that in addition to the oligomerization processes hydrogen transfer reactions also occur.

The most useful reactions are those undergone by disubstituted acetylenes. These reactions were first noted by Malatesta et al.[36] who obtained tetra-phenylcyclobutadiene palladium chloride from diphenylacetylene and pal-ladium chloride in an easy two-step reaction. Later work by ourselves[37–39] and others[40–42] together with x-ray structure determinations of two cyclo-butenyl complexes[43] showed that the reactions outlined in Scheme 2 occur for diphenyl- and a number of p,p'-disubstituted diphenylacetylenes on reaction with palladium chloride. In general, a convenient starting material is the bis(benzonitrile)-complex which dissociates largely in organic solution and can be regarded simply as a source of soluble $PdCl_2$[27].

Two distinct processes can be differentiated; in alcohols the endo-alkoxy-tetraphenylcyclobutenyl complexes (XXI) are formed which on treatment with acid give the cyclobutadienes (XXII). In aprotic solvents, such as benzene

or acetone, the acetylene is partly trimerized to the hexaphenylbenzene and partly dimerized to a cyclobutadiene complex (XXIIa) closely related to (XXII) but differing from it in having two or more $PdCl_2$ units associated with each organic ligand. This is readily transformed to (XXII).

Interestingly, only the *endo*-alkoxycyclobutenyl complexes are formed from the acetylenes; the isomeric *exo*-alkoxycyclobutenyl complexes (XXIII) arise stereospecifically from the cyclobutadienes (XXII) and alcohols.

$RC{\equiv}CR + (PhCN)_2PdCl_2 \xrightarrow{R'OH}$

(XXI)

(XXIII)

(XXII)

(X = halide)

$RC{\equiv}CR + (PhCN)_2PdCl_2 \xrightarrow{benzene}$
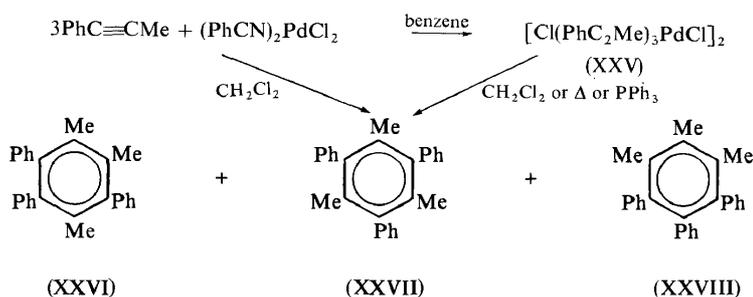
(R = phenyl, *p*-tolyl, *p*-chlorophenyl)

(XXIIa)

Scheme 2

The reaction of t-butyl(phenyl)acetylene also gave a cyclobutadiene, the 1,2-di-t-butyl-3,4-diphenylcyclobutadienepalladium chloride (XXIV)[44, 45]. In this reaction no benzenoid trimers were reported.

$$Bu^tC{\equiv}CPh + (PhCN)_2PdCl_2 \xrightarrow[\text{DMSO; HCl}]{\text{benzene.}} \left[\begin{array}{c} Bu^t \quad\quad Ph \\ \boxed{\ominus}{-}PdCl_2 \\ Bu^t \quad\quad Ph \end{array} \right]_2$$
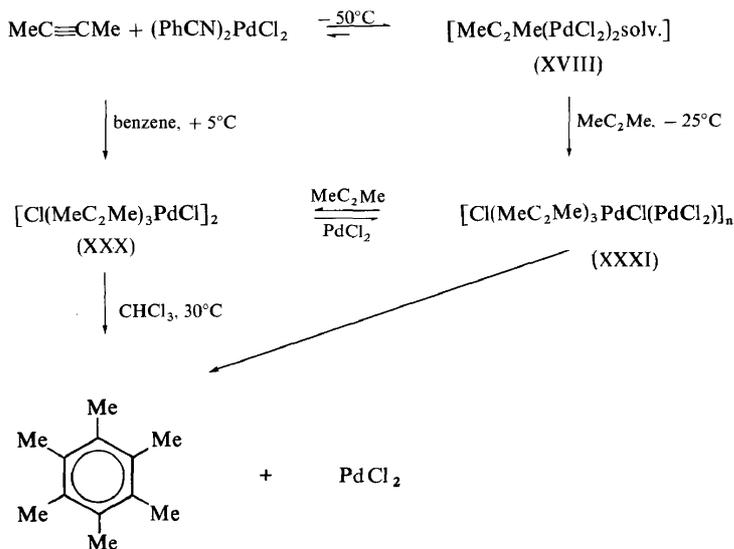
(XXIV)

By contrast, acetylenes with smaller substituents invariably gave at least trimers. In the reaction of methyl(phenyl)acetylene with $(PhCN)_2PdCl_2$ in benzene we were able to isolate a complex (XXV) which decomposed on heating, or in a chlorinated solvent at ambient temperature, or by the action of triphenylphosphine, to give the benzenoid trimers. When the reaction was carried out in chlorinated solvent only the benzenoid trimers were isolated.

$$3PhC{\equiv}CMe + (PhCN)_2PdCl_2 \xrightarrow{\text{benzene}} [Cl(PhC_2Me)_3PdCl]_2$$

(XXV)

$$\xrightarrow[\text{CH}_2\text{Cl}_2]{} \xleftarrow[\text{CH}_2\text{Cl}_2 \text{ or } \Delta \text{ or } PPh_3]{}$$

(XXVI)   +   (XXVII)   +   (XXVIII)

Surprisingly, in addition to the two expected isomers (XXVI) and (XXVII), obtained in 58 and 39 per cent yield, a 3 per cent yield of the isomer (XXVIII) was isolated[27, 46]. A very similar result was obtained by Whitesides and Ehmann[47], who found that trimerization of 1,1,1-trideutero-2-butyne with palladium chloride gave a 10 per cent yield of 1,2,3-tris(trideuteromethyl)-4,5,6-trimethylbenzene (XXIX)

$$3CD_3C{\equiv}CCH_3 \xrightarrow{PdCl_2}$$

(10%)

(XXIX)
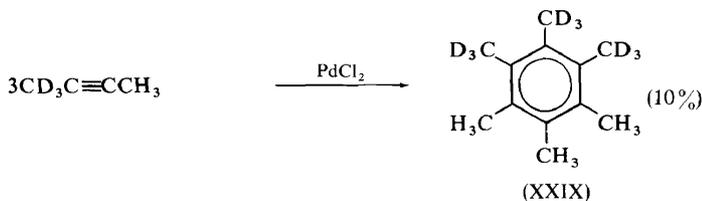
A more complete study of the reaction of 2-butyne with palladium chloride showed that in benzene a complex $[Cl(MeC_2Me)_3PdCl]_2$ (XXX), was formed[27]. This same complex was generated by working under very carefully controlled conditions in chloroform. Two intermediates were detected by n.m.r. in the formation of (XXX) in chloroform; one was shown to be the π-acetylene complex (XVIII) (see above) and the other was a complex (XXXI) closely related to (XXX) but containing one more $PdCl_2$ per organic ligand.

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$$MeC{\equiv}CMe + (PhCN)_2PdCl_2 \xrightarrow[\rightleftharpoons]{-50^\circ C} [MeC_2Me(PdCl_2)_2solv.]$$
$$(XVIII)$$

benzene, + 5°C   MeC₂Me. − 25°C

$$[Cl(MeC_2Me)_3PdCl]_2 \xrightarrow[PdCl_2]{MeC_2Me} [Cl(MeC_2Me)_3PdCl(PdCl_2)]_n$$
$$(XXX) \qquad\qquad (XXXI)$$

CHCl₃, 30°C

+ $PdCl_2$

The complex (XXX) could be crystallized and was moderately stable in the solid state in the cold but it decomposed very rapidly to hexamethyl-benzene on warming, either in solution or in the solid. The n.m.r. spectrum showed the presence of six inequivalent methyl groups, while the infrared spectrum showed the presence of a coordinated and a free double bond. a C—Cl bond and an asymmetric Pd_2Cl_2 bridge[27].

We therefore proposed the structure shown for (XXX) and suggested that (XXXI) only differs from this in having two extra $PdCl_2$ units coordinated to the PdCl groups in (XXX), rather reminiscent of the situation in the cyclo-butadiene complexes (XXIIa). Molecular models indicate that the arrange-ment of the ligand in (XXX) is strain-free and that the ligand can exist in two conformers. One of these, (XXXa), is probably of lower energy and has the coordinated double bond perpendicular to the coordination plane of the metal. The other (XXXb), with the coordinated double bond in the coordina-tion plane. is correctly aligned for a 'cis insertion' reaction[48] to a cyclo-pentadiene. Substituted pentamethylcyclopentadienes are common reaction products from (XXX).

(XXXa)   (XXXb)
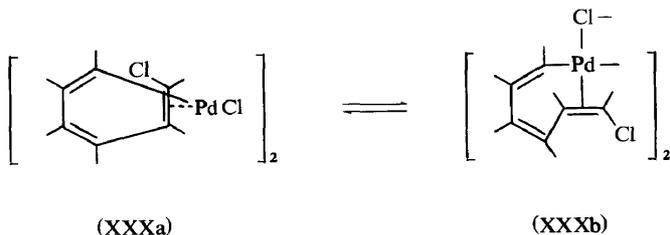
Further evidence for this structure comes from the reaction of (XXX) with triphenylphosphine, -arsine or -stibine[49], which gives as major product

5-vinylpentamethylcyclopentadiene. (XXXIII) (together with 10 per cent of hexamethylbenzene), when it is carried out below 0°C. The mechanism of this reaction has been elucidated in some detail and the essential steps are indicated in *Scheme 3*.

Scheme 3
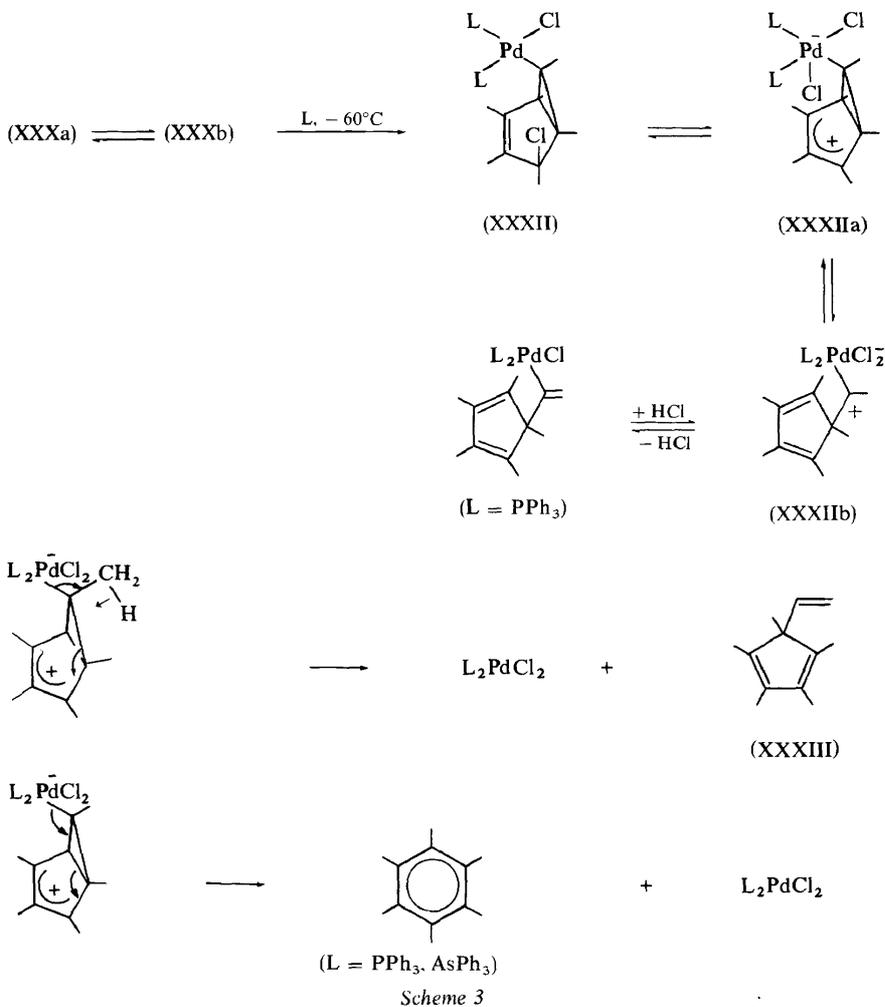
In the course of these reactions the molecule (XXXII) exhibits a fluxional behaviour in which the cyclopropyl ring moves around the five-membered ring in a series of 1,5-suprafacial shifts, probably via (XXXIIa) and (XXXIIb). This type of reaction would result in a scrambling of the methyls and we believe this or a similar process to be responsible for the observed formation of the 'unexpected' benzenoid trimers (XXVIII) and (XXIX).

The oligomerization reactions using Pt^{II} have been relatively little investigated. but Chini *et al.*[50] have shown that a tetraphenylcyclobutadiene complex can be obtained from diphenylacetylene.

$$PhC\equiv CPh + Pt(CO)_2Cl_2 \longrightarrow$$

REACTION MECHANISMS

If we ignore for the present the reactions of monoacetylenes where the presence of acetylenic hydrogen can, and does frequently, obscure the basic paths then we can outline two fundamental mechanisms for complexes of the nickel triad in their reactions with acetylenes. Since these reactions occur most readily and have been investigated most fully for palladium. the discussion will be limited to this element, but there seems no particular reason to expect more than minor variations for the other two elements. The two paths are those which obtain for Pd^0 and Pd^{II} respectively.

The Pd^0 reactions give as the first intermediate that can be isolated the palladiacyclopentadiene (VI) and our work to date suggests strongly that this type of reaction is limited to acetylenes with at least one strongly electron-attracting substituent. From the reaction of $(DBA)_2Pt$ and $(DBA)_3Pt$ with dimethyl acetylenedicarboxylate we can also detect by n.m.r. the presence of an intermediate which may be a 1:1 acetylene π-complex. The speed of the reactions of $(DBA)_2Pd$ precluded the observation of a similar intermediate there but, in the presence of two equivalents of triphenylphosphine. the 1:1 acetylene complex (IIIb, R = R' = COOMe) was isolated.

$$(DBA)_2Pd + 2PPh_3 + MeOOCC\equiv CCOOMe \rightarrow$$
$$(Ph_3P)_2Pd(MeOOCC_2COOMe)$$
$$(IIIb)$$
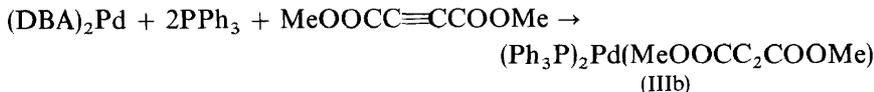
Reactions of other metals with acetylenes to give metalacyclopentadienes are well known. particularly for the cobalt triad[51-55] and the intermediacy of 1:1 π-acetylene complexes has been demonstrated there. The reactions described by Collman *et al.*[52] are typical:


$(R = COOMe, L = PPh_3)$

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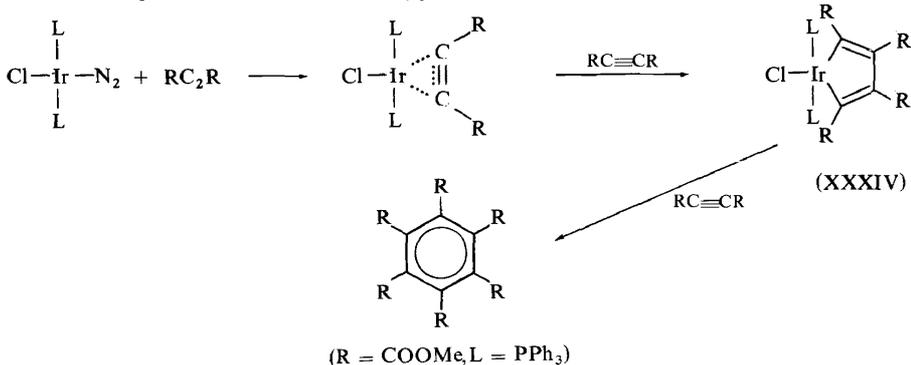
However, these reactions are by no means restricted to transition metals and, given a sufficiently *electrophilic* acetylene such as dimethyl acetylene-dicarboxylate (DMA), they will occur with many nucleophiles. For example, triphenylphosphine itself reacts readily with DMA to give, amongst other products under other conditions. the phosphole (XXXV)[56]. The similarity of this reaction to those in which metalacyclopentadienes such as (VI), (XIII) or (XXXIV) is clear. Analogous reactions also occur with amines and other nucleophiles.

$$Ph_3P \quad + \quad MeOOCC{\equiv}CCOOMe$$

(XXXV)
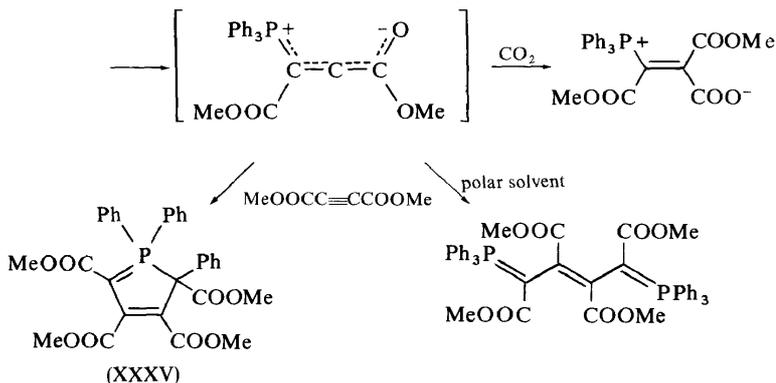
It is obvious therefore that the nucleophilicity of the metal. at least for the palladium(0) and platinum(0) complexes, must be the driving force for the reactions*. We envisage these reactions as proceeding through dipolar intermediates and transition states (*Scheme 4*), an argument which is lent some support by our observation that these reactions are considerably accelerated in polar solvents. In this case the second acetylene, now coordinated to a metal formally in the (+ II) oxidation state, is activated towards nucleophilic attack and undergoes an internal attack by the vinylic anion.

(VI)
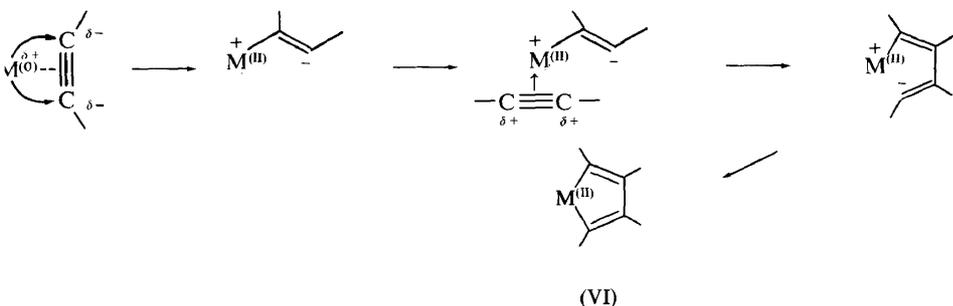
Scheme 4

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* This is not. apparently. the case for Rh[1]. for example. where acetylenes which are poor electrophiles can still give metalacyclopentadienes[54]. The nature of the metal exerts an additional subtle effect.

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Such processes are analogous to the reaction of the platinum oxygen complex (XXXVI) with acetone to give (XXXVII)[57], and which can be represented as:

(XXXVI)   (XXXVII)
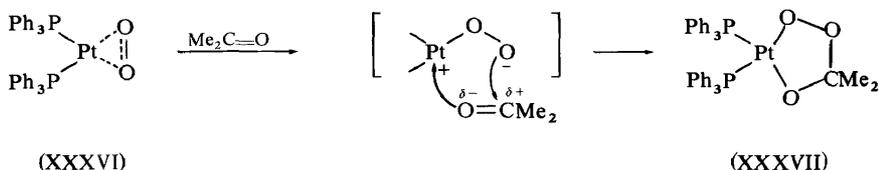
Similar mechanisms have been proposed by Burt *et al.* for the reactions of iron(0), ruthenium(0) and osmium(0) complexes with fluoro-olefins and -acetylenes[58].

The further reactions of the metalacyclopentadienes with acetylenes are still under investigation, but it appears likely that reaction occurs to give a π-tetrahaptobenzene ('bent-benzene') complex. We have, in a rather different context, shown that dimethyl acetylenedicarboxylate reacts with the pentamethylcyclopentadienylrhodium and -iridium acetates to give (XXXVIII)[59]. in which the benzene exhibits fluxional behaviour on heating accompanied by a slow decomposition to hexamethyl mellitate.

(XXXVIII)

(M = Rh, Ir; R = COOMe) Δ; slow
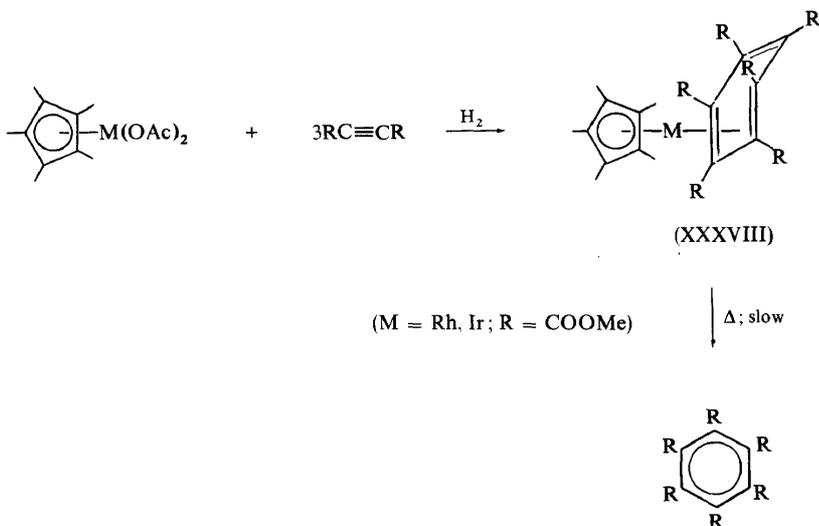
The likelihood of such an intermediate in the palladium and platinum reactions is increased by the observation that the complex formulated as (II), but more likely also to be a 'bent-benzene' complex, arises from the reaction of hexafluoro-2-butyne and a nickel(0) complex[10].

We have not, so far, been able to detect analogous intermediates in the palladium and platinum reactions and we presume them to be of low stability. It is of considerable interest that Bryce-Smith[60], some years ago, found that

DMA was trimerized to hexamethyl mellitate in a heterogeneous catalytic reaction by palladium on carbon. We have therefore been able to define this reaction a little more precisely by working under homogeneous conditions, and a catalytic cycle can be postulated:
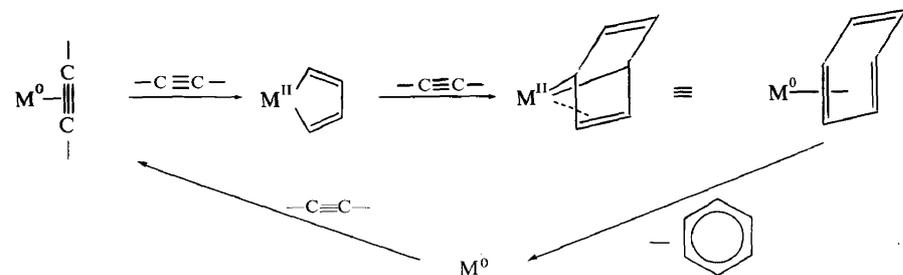

The situation is quite different for the reactions of palladium(II). In the first place, steric factors are much more important than electronic ones; thus, di-t-butylacetylene only gives a 1:1 π-complex while t-butyl(phenyl)-acetylene gives a cyclobutadiene complex, as does diphenylacetylene. In the latter case, however, the benzenoid trimers are also produced. With smaller substituents no cyclobutadienes are formed, instead (for example, with methyl(phenyl)acetylene) only benzenoid trimers, arising from complexes of the type $[Cl(ac)_3PdCl]_2$, are obtained. When the substituents are still smaller, for example dimethylacetylene, tetrameric species are produced in addition to the trimers.

A series of experiments with diphenylacetylene showed that the tetraphenylcyclobutadiene complex (XXII) was *not* an intermediate in the formation of hexaphenylbenzene and therefore both must arise from a common intermediate[37, 61, 62]. Although we have not been able to test this hypothesis further as yet, it appears likely that this is also true for other acetylenes.

The other point of difference to the metal(0) catalysed reactions is that the 1:1 π-acetylene metal(II) complexes which can be safely presumed to be the initially formed active species are now strongly activated towards nucleophilic attack. They also very easily undergo 'cis insertion' reactions, which can in some ways be regarded as intramolecular variants of the above reaction, particularly as it is probably the σ-bonded group which 'migrates' rather than the olefin or acetylene which 'inserts'.

In the formation of the 2-butyne derived complex (XXXI) from the π-acetylene complex (XVIII) at $-27°C$ we have observed no change in rate with change in the 2-butyne concentration. This is consistent with a reorganization of (XVIII) as the rate-determining step and we propose this to be a *cis*-ligand migration of the palladium bonded chlorine onto the coordinated acetylene to give a σ-vinylic intermediate (step [1], *Scheme 5a*). Further reaction of this, by fast stepwise *cis*-ligand migrations onto coordinated acetylenes causes the oligomerization to build up a helical polyene (steps [2], *Scheme 5*, and *Scheme 6*).

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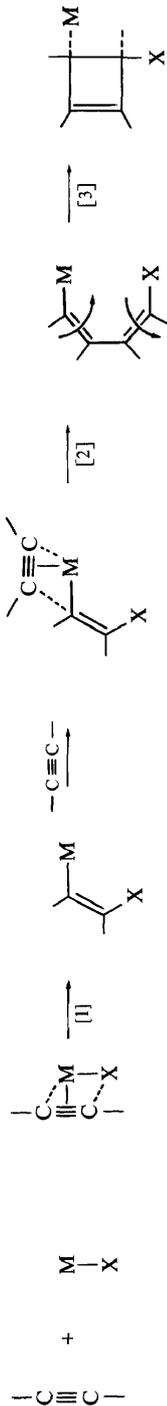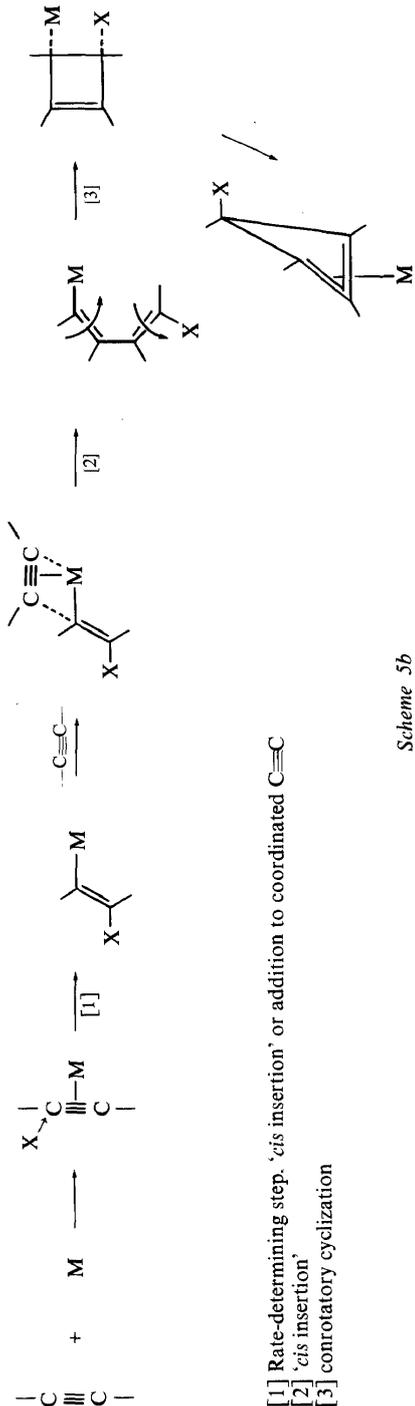
Scheme 5a

Scheme 5b

[1] Rate-determining step. '*cis* insertion' or addition to coordinated C≡C
[2] '*cis* insertion'
[3] conrotatory cyclization

In the most general case we believe the extent of this reaction to be governed largely by the sizes of the substituents on the acetylenes. Thus for bulkier groups (e.g. phenyl) the reaction effectively ceases after two acetylenes have reacted. In other words, further *cis*-ligand migration reactions compete unfavourably with other processes, in particular cyclization to a four-membered ring (steps [3], *Scheme 5*). Alternatively, for smaller groups. reaction continues until three or even four acetylenes are incorporated into the product, when rearrangement or decomposition reactions become fast with respect to further oligomerization.

One case is of particular interest, that of the diphenylacetylenes with palladium chloride in the presence of alcohols. In this case. only the *endo*-alkoxycyclobutenyl complexes are formed (XXI). If, as seems most reasonable, the initial π-acetylene complex undergoes nucleophilic attack by alkoxide (or alcohol), a *trans*-σ-vinylic complex is formed (step [1], *Scheme 5b*) which then, in a further fast reaction with another acetylene gives a butadienyl complex (step [2], *Scheme 5b*). This complex has the correct stereochemistry for a thermally allowed conrotatory electrocyclic cyclization to the cyclobutene (step [3], *Scheme 5b*) which is simply the σ-allylic form of the *endo*-alkoxy-π-cyclobutenyl complex (XXI).

Similar arguments can be used to account for the direct formation of the cyclobutadiene complexes by elimination of a cyclobutenyl chlorine. e.g..


The mechanism of formation of the benzenes from the trimer complexes [Cl(ac)$_3$PdCl]$_2$, (step [4], *Scheme 6*) is not yet clear, but it seems very likely that this is complex and involves a fluxional intermediate at one stage (see above).
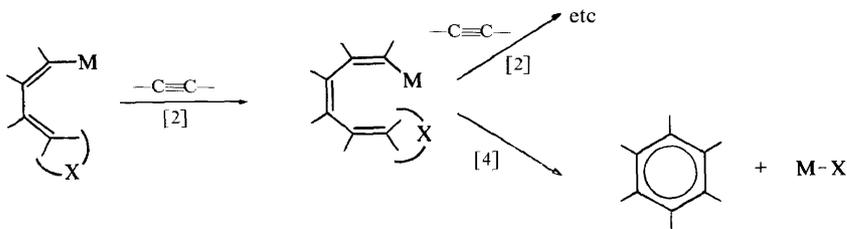

Scheme 6

Analogies for the various processes involved in the cyclodi- and cyclo-trimerization reactions are well known. For example. Yukawa and Tsutsumi[63] showed that the acetylene (XXXIX) reacted with chloropalladate in methanol to give (XL), where *trans* addition of Pd–Cl to the triple bond had effectively occurred.

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$PhC{\equiv}CCH_2NMe_2 + Li_2PdCl_4 \xrightarrow{\quad MeOH \quad}$

(XXXIX)

(XL)
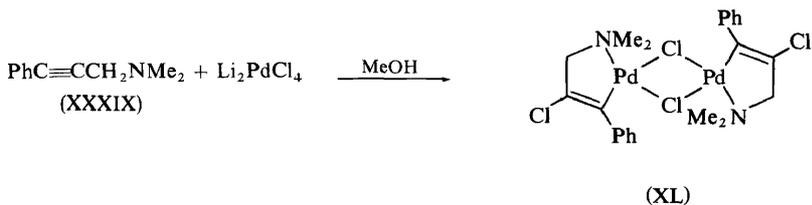
Models for the subsequent processes which we invoke are also plentiful; for example Clark *et al.* have elegantly demonstrated the high reactivity of π-acetylene platinum(II) complexes towards nucleophiles[64] and also have shown that hexafluoro-2-butyne undergoes a '*cis* insertion' reaction into a Pt—Me bond via a π-acetylene complex (XLI) to give (XLII)[65].

$+ \quad CF_3C{\equiv}CCF_3 \quad \longrightarrow$

(XLI)

3 weeks at 25°C
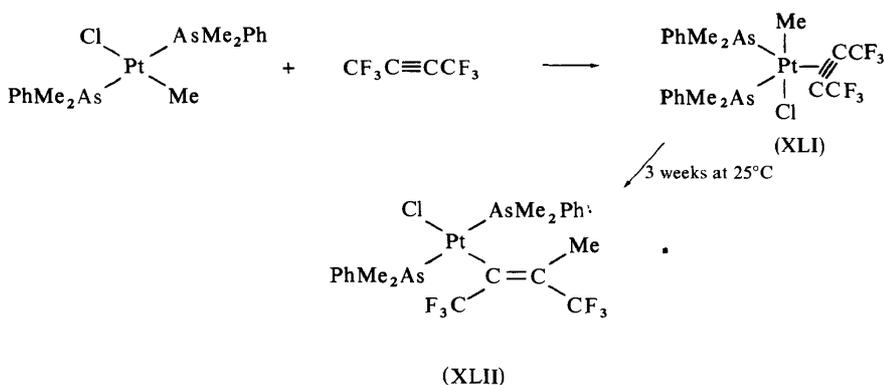
(XLII)

The recently determined structure of the iridium complex (XLIII)[66] also represents a good model for an intermediate in these acetylene oligomerization reactions.

$(Ph_3P)_3Ir(H)CO + CF_3C{\equiv}CCF_3 \quad \longrightarrow$

(XLIII)
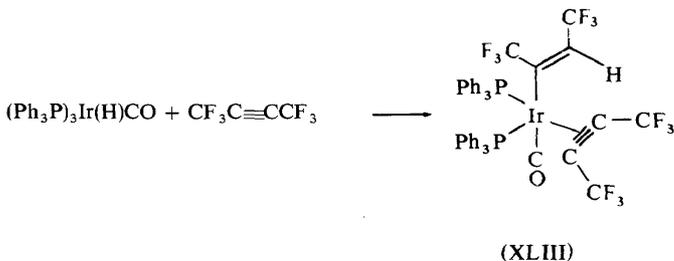
Finally, it should be mentioned that oligomerization reactions of this type do not appear to be restricted to acetylenes; Yamamoto and Yamazaki have recently proposed a similar type of oligomerization involving isonitriles[67].

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