

ORGANO-TRANSITION METAL CHEMISTRY WITHOUT PHOSPHINES: THE PALLADIUM CATALYSED CYCLOTRIMERIZATION OF ACETYLENES

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ABSTRACT

The argument is presented that organo-transition metal complexes also containing phosphines and similar ligands are often too kinetically inert to act as good models for catalytic processes. A new generation of 'lightly stabilized' complexes are needed to probe these reactions more deeply. Some novel palladium complexes of this type, derived from the reactions of acetylenes with either Pd⁰ or Pd^{II}, are described and the mechanisms of acetylene oligomerization are discussed. For Pd⁰ electronic factors seem to be of greatest importance while steric factors play a greater role with Pd^{II}. The structure and properties of a new complex, (Ph₃P)₂Pd(Br)[(CCOOMe)₄H], derived from dimethyl acetylenedicarboxylate, are reported as well as that of [C₅Me₅CHPhCH₂PdCl]₂, derived from but-2-yne, PdCl₂, and diphenylmercury. The latter is a dihapto-cyclopentadiene complex which shows stereochemical non-rigidity in solution. Since this complex also possesses a Pd-alkyl bond it is an ideal 'lightly-stabilized' model and its reactions with acid, base, hydrogen, CO, and triphenylphosphine have been investigated. This work sheds important new light on the chemistry of the Pd—C σ-bond.

I have chosen a deliberately provocative main title to this lecture, 'Organo-transition metal chemistry without phosphines', in order to emphasize a problem which faces many of us working in the field of homogeneously catalysed reactions. The problem is basically that such processes are usually very fast and model compounds are therefore necessary to investigate the properties of the intermediates postulated in the catalytic cycle. Organometallic chemists have for many years made complexes containing, for example, metal-alkyl bonds and these almost invariably also contain strongly bonded co-ligands. The resultant complexes are then 'stable' enough to be isolated and handled but often too kinetically inert to be useful as models.

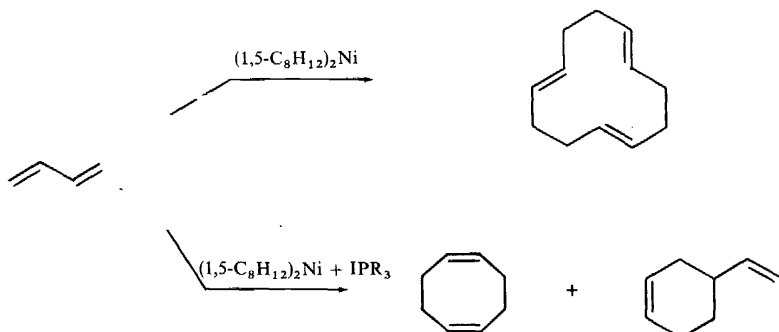
The most typical co-ligands are tertiary phosphines, though many others (e.g. phosphites, π-cyclopentadienyls, Schiffs' bases and even carbonyls) are

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also used. It was originally believed that the main stabilizing effect of the co-ligand was electronic, but more recently it has become clear that the true effect is more often steric. The co-ligands occupy coordination sites on the metal and prevent the coordination of reactants and, in addition, many of the co-ligands bear large substituents (triphenylphosphine is a very good example) which also act to screen the metal from attack. In the absence of a strongly bonded co-ligand metal alkyls are generally highly reactive and also thermally rather unstable.

The present state of knowledge of organo-transition metal chemistry would be much less far advanced if this ruse of using 'strongly stabilized' complexes had not been developed. However, their kinetic inertness makes them rather poor as models and a new generation of 'lightly stabilized' complexes of higher reactivity is now needed.

Of course, there are some reactions, for example, the hydroformylation and hydrogenation reactions catalysed by phosphine-rhodium complexes are investigated by Wilkinson¹ which, in the absence of phosphines or other strongly coordinating ligands, are rapidly deactivated with deposition of metal. In general, if the reacting ligands on the metal have a high enough labilizing influence on the stabilizing co-ligands and if the reaction which occurs is not too demanding sterically, then the disadvantages of the stabilizing co-ligands can be overcome†. However, in a wide variety of processes, particularly oligomerization reactions, the presence of phosphines will often change the course of the reaction and may even stop it entirely. For example, the reaction of nickel(0) with butadiene gives cyclododeca-1,5,9-triene in the absence of phosphines or phosphites but, in the presence of one equivalent of such a ligand, cycloocta-1,5-diene and vinylcyclohexene are formed².



I should like to illustrate these points further with examples from our recent work on organopalladium chemistry. In the first part of the lecture I shall discuss the different modes by which Pd^0 and Pd^{II} oligomerize acetylenes‡ and point out a cross-relation between the two processes and

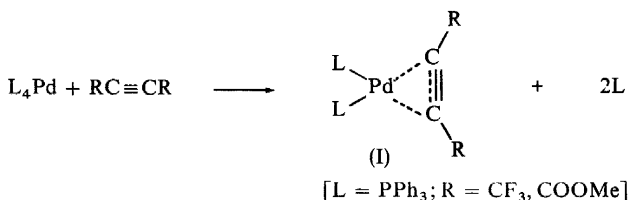
† Another side effect of the use of phosphines as co-ligands is that when these are displaced from the metal in the reaction they too may undergo reaction leading to by-products, and hence further complicate the overall process (see below).

‡ A more detailed account has been given elsewhere³.

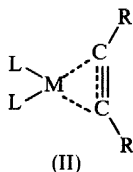
then I shall discuss the chemistry of a novel type of organopalladium complex which serves as a lightly stabilized model for some other catalytic reactions.

REACTIONS WITH PALLADIUM(0)

The normal starting material for investigations of the chemistry of Pd⁰ has, until now, usually been the tris- or tetrakis-triphenylphosphinepalladium (or a similar complex). We showed some years ago that these complexes reacted with certain acetylenes bearing electron-withdrawing substituents, particularly hexafluorobut-2-yne and dimethyl acetylenedicarboxylate (DMA), to give the 1:1 complexes (I)⁴.

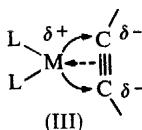


Analogous platinum and nickel complexes had been obtained previously by Chatt⁵ and Wilke⁶ and x-ray structure determinations have been carried out on a number of such complexes (IIa, L = Ph₃P, M = Pt, R = Ph⁷; IIb, L = Bu^tNC, M = Ni, R = Ph⁸; IIc, L = Ph₃P, M = Pd, R = COOMe⁹).



The essential features found are that the two ligand atoms, the metal and both acetylenic carbons are very nearly coplanar; the acetylene is bent into a *cis* configuration[†] ($\angle RCC = 140^\circ$ for IIa, 149° for IIc) and the coordinated triple bond is lengthened to 1.284(16) Å for diphenylacetylene (IIc) compared to its normal value of 1.19(2) Å.

We also showed by n.m.r. that the complexes (II) (L = Ph₃P; M = Ni, Pd, Pt; R = CF₃; and L = Ph₃P; M = Ni, Pt; and acetylene = PhC₂Me) remain planar or near planar in solution and that this structure was therefore very rigid⁴. In our discussion of the bonding in (II), we suggested that it can be represented diagrammatically as (III) where the metal is formally in the 0 oxidation state⁴.

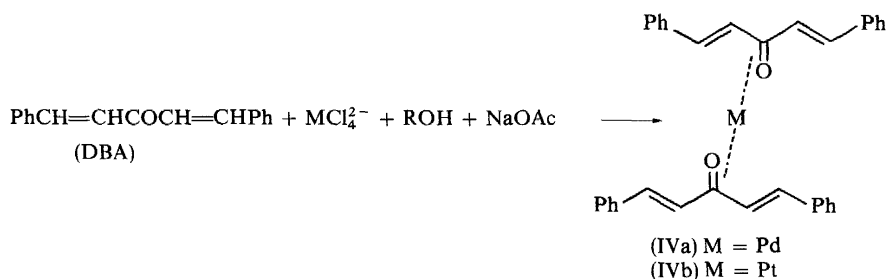


[†] The *cis*-bending also has the interesting consequence that it is possible to stabilize cyclic acetylenes (cyclohexyne, cycloheptyne) which are otherwise very reactive¹⁰.

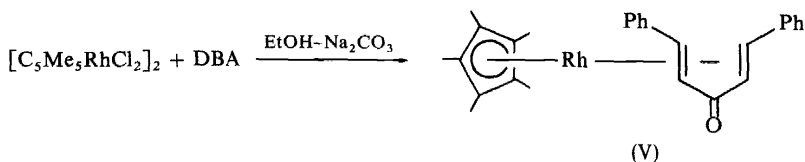
This implies that the $d-\pi^*$ interaction is most important in binding the metal and the acetylene here and that electron-releasing substituents on L (phosphine) and electron-withdrawing substituents on the acetylene (R) will stabilize the complex. Furthermore, these complexes should be active as nucleophiles and should themselves undergo electrophilic attack very easily¹¹.

However, the acetylene complexes (II) are rather inert towards further reaction with acetylenes, an effect that can be ascribed to the presence of the bulky and strongly bonded co-ligands L (usually PPh_3), and in view of this we have carried out reactions using a different type of zerovalent complex as starting material.

The first of these complexes, bis(dibenzylideneacetone)palladium, $(\text{DBA})_2\text{Pd}$, was originally prepared by Takahashi *et al.*¹²; we have shown that the structure of this and the related $(\text{DBA})_2\text{Pt}^\dagger$ is best described by (IV) in which the metal bonds to the DBA by the ketonic rather than the olefinic bonds¹³.



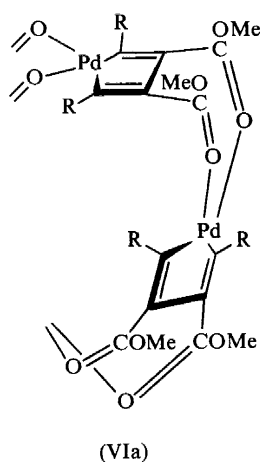
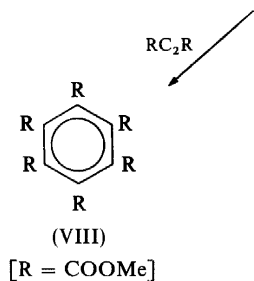
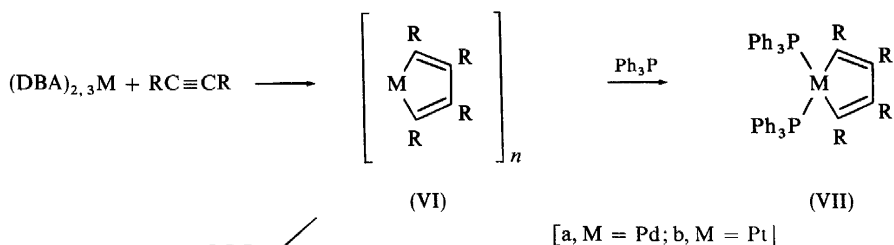
DBA can also sometimes bind to the metal through the olefinic bonds, as in (V)¹⁵ (see also below).



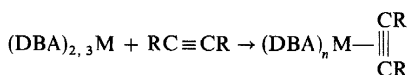
Both the bis and tris DBA complexes react with DMA to give the palladium and platinum-cyclopentadienes, (VI)¹⁶‡. The palladiacyclopentadiene (VIa) was isolated and characterized and a structure involving bonding of the type shown was proposed. The platinacyclopentadiene (VIb) was detected by n.m.r. and isolated as the bistrisphenylphosphine complex (VIIb). Both (VIa) and (VIb) reacted with more DMA to give hexamethyl mellitate (VIII); (VIb) reacted at 20°C while (VIa) needed gentle warming.

† We have also prepared the closely related tris complexes, $(\text{DBA})_3\text{Pd}$ and $(\text{DBA})_3\text{Pt}$ which are yellow (in contrast to the purple and red bis complexes) and easily dissociate in solution^{13,14}. These are often more convenient starting materials and give cleaner products.

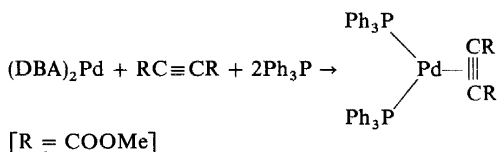
‡ Only acetylenes bearing at least one electron-withdrawing substituent will react with (IV) under normal conditions.



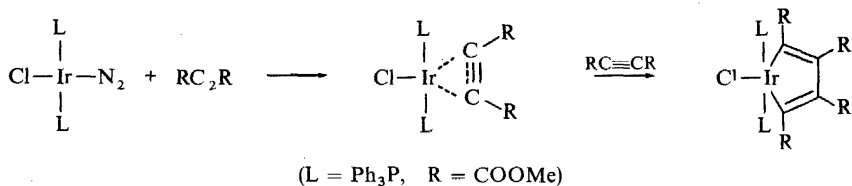
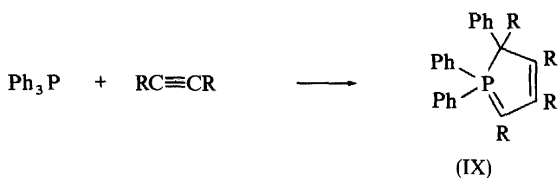
We propose the following mechanisms for these reactions. First, the replacement of DBA in (IV) by DMA to give a monoacetylene complex.



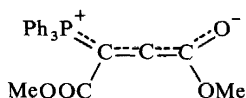
In support of this proposal we have isolated (I) (R = COOMe, L = PPh₃) by reaction of (DBA)₂Pd with two equivalents of PPh₃ followed by DMA:



It is well known that DMA and other acetylenes bearing strongly electron-withdrawing groups are very susceptible to nucleophilic attack. These reactions can give a variety of products but dimerization accompanied by cyclization to give a five-membered ring is very common. A wide variety of nucleophiles will effect this, including for example, triphenylphosphine¹⁷ and also many low-valent transition metal complexes¹⁸, for example:

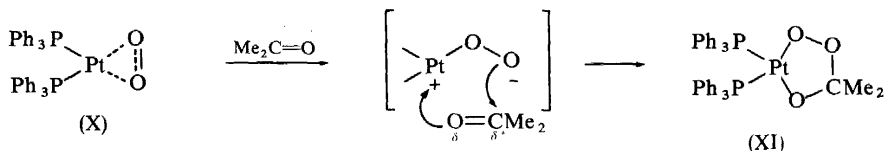


The reaction with triphenylphosphine has been interpreted as proceeding via a dipolar intermediate:

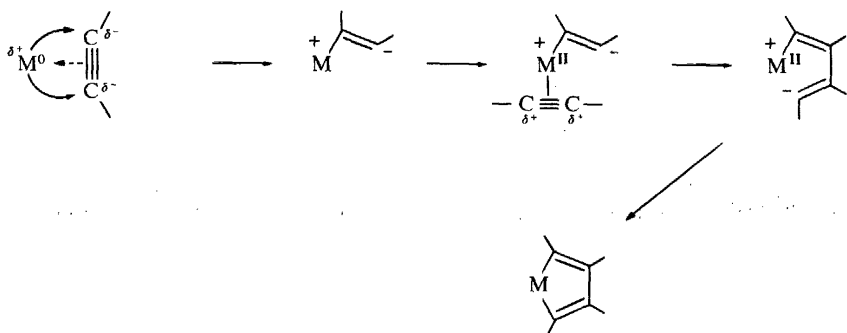


which then reacts as a nucleophile to another DMA with subsequent cyclization and a phenyl shift to give the phosphole (IX)¹⁷.

The reaction of the dioxygen complex (X) with acetone to give (XI) has also been explained in terms of a similar dipolar intermediate¹⁹,

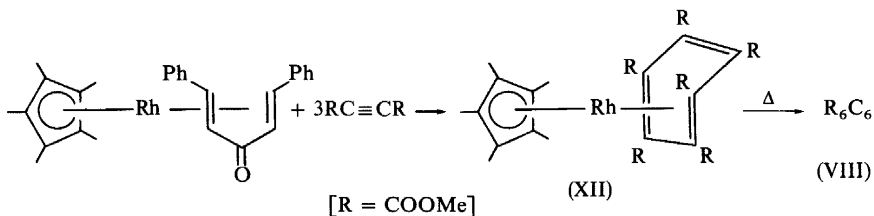


and we invoke an analogous process to account for our reaction³:

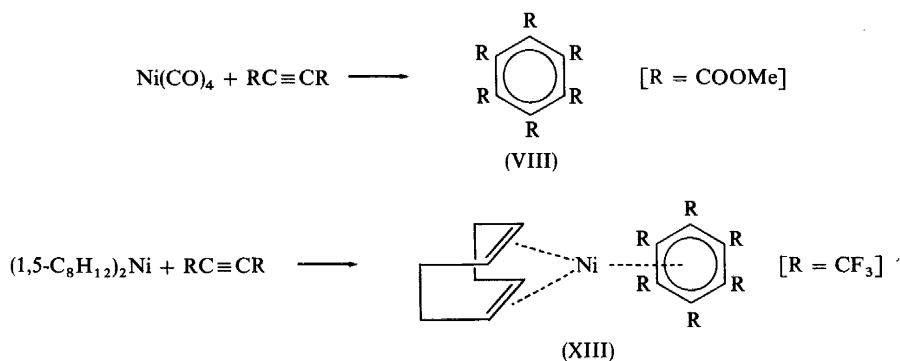


Similar mechanisms have also been proposed for the reactions of Fe⁰, Ru⁰ and Os⁰ complexes with fluoro-olefins and -acetylenes²⁰.

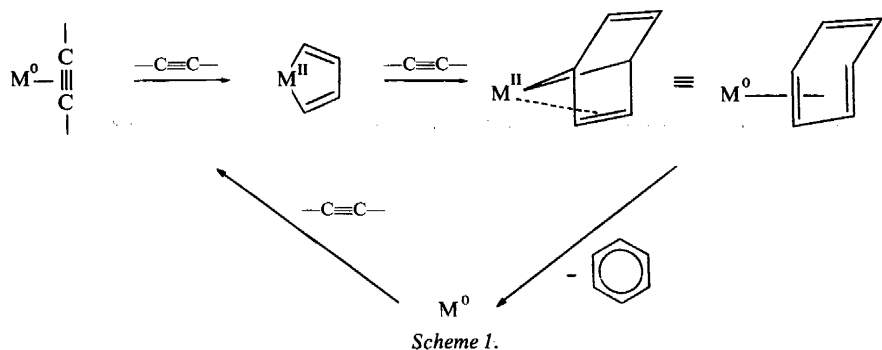
We further propose that reaction of the metallacyclopentadienes (V) with DMA to give hexamethyl mellitate (VIII) goes via a 'bent benzene' (tetrahaptobenzene) complex. We have no direct evidence for this here but we find that the rhodium-DBA complex (V) reacts with DMA on warming to give a quantitative yield of the tetrahaptobenzene complex (XII)^{15, 21}. On heating, this complex exhibits fluxional behaviour in which the metal migrates relative to the ring by a series of 1,2-shifts; this is accompanied by a slow decomposition to (VIII)²¹.



We have also observed that DMA is catalytically trimerized to (VIII) by Ni(CO)₄, Ni(CO)₃PPh₃ or Ni(CO)₂(PPh₃)₂, while Browning *et al.* have isolated the complex (XIII) (probably also a tetrahaptobenzene complex) from bis(cycloocta-1,5-diene)nickel and hexafluorobut-2-yne²².



In this connection it is very pertinent to recall that Bryce-Smith some years ago trimerized DMA catalytically to (VIII) in a heterogeneous reaction



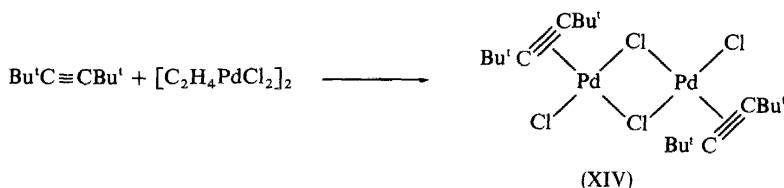
of palladium on carbon²³. We have therefore been able to define more precisely the steps in the cyclotrimerization and to illustrate the similarity between the homogeneous and heterogeneous systems. In summary we can propose the catalytic cycle in *Scheme 1* for the cyclotrimerization, which it will be noted, involves both M^0 (d^{10}) and M^{II} (d^8) complexes.

REACTIONS WITH PALLADIUM(II)

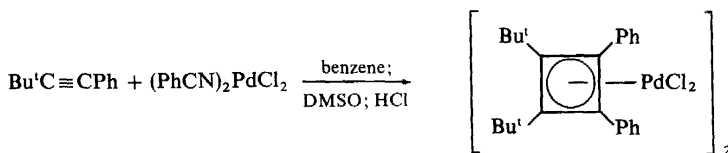
Although, in some cases, the identical end-product is obtained from reactions of acetylenes with Pd^{II} complexes the processes involved are quite different. The starting material here is usually palladium chloride as the bis(benzonitrile) derivative, $(PhCN)_2PdCl_2$; the benzonitrile is very loosely bound and this complex can be thought of simply as a convenient source of soluble $PdCl_2$. Complexes with more strongly bound ligands such as phosphines do not, in general, react under the conditions used here.

Acetylenes of all types react very readily with $PdCl_2$ at ambient temperature and a number of different types of reactions are observed†.

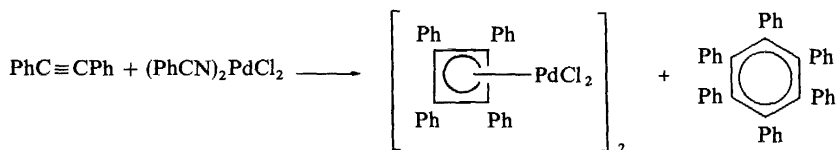
(i) Acetylenes bearing two very bulky substituents (t-butyl) form monoacetylene complexes, e.g. (XIV), and no oligomerization occurs²⁴.



(ii) An acetylene with one very bulky and one moderately bulky substituent (e.g. t-butyl(phenyl)acetylene) gives a complex of the acetylene dimer, but no trimer^{25, 26}:



(iii) Acetylenes with two moderately bulky substituents (phenyl) give complexes containing dimers and organic trimers, but no tetramers²⁷⁻³⁴.



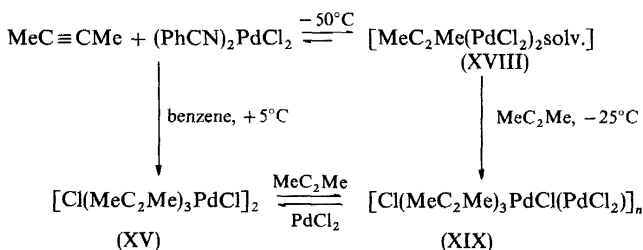
(This reaction is more complex than is apparent from the equation; see **References 3 and 28-34**).

† Only disubstituted acetylenes are considered here; monosubstituted ones also react but the reactions are complicated by hydrogen shifts.

In (XVI) the acetylene lies perpendicular to the coordination plane of the metal, the acetylenic substituents are again *cis*-bent ($\angle \text{Bu}^t\text{CC} = 163^\circ$) but not to the extent found for (II) and the bond-lengthening on coordination [$d(\text{C}\equiv\text{C}) = 1.235(18) \text{ \AA}$] is probably not as great as for (IIc).

The structures and properties of these complexes are consistent with a description of the bonding where the back-bonding ($d-\pi^*$) is less important than the dative bonding from the filled acetylenic π -orbitals to vacant metal orbitals, as shown in (XVII). This should be contrasted to the situation depicted in (III)³. A result of this picture for the Pd^{II} and Pt^{II} complexes is that the coordinated acetylene is now polarized in the opposite sense to that in (III) and that it should be very susceptible to nucleophilic attack. This property has been demonstrated for acetylenes and particularly for olefins (where the same arguments apply) coordinated to Pd^{II} and Pt^{II} .

A careful investigation of the but-2-yne reactions by n.m.r. at low temperatures shows that the first stage of the reaction in CDCl_3 is the formation of a π -acetylene complex (XVIII)^{3,5}.



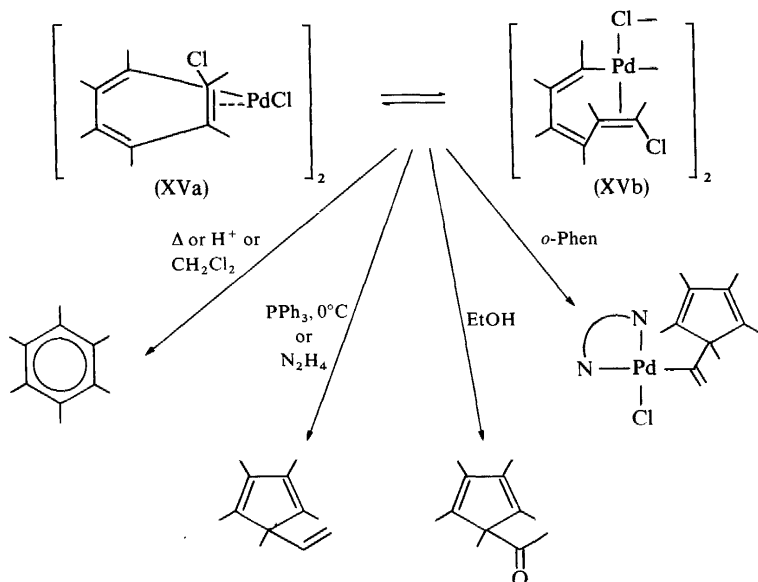
This is transformed in the presence of but-2-yne into a trimer complex (XIX) (which is closely related to the isolated product (XV), and differs from it only in having an extra PdCl_2 attached to each Pd in (XV)³) in a process the rate of which is independent of butyne concentration. This result is consistent with a reorganization of (XVIII) as the rate-determining step and we propose this to be a *cis*-ligand migration of a Pd-bonded chlorine onto the acetylene to give a σ -vinylic intermediate. Such a *cis*-ligand migration is best regarded as an intramolecular nucleophilic attack on the coordinated acetylene. An alternative to this is a *trans* attack by an external nucleophile and this appears to occur in the reaction of diphenylacetylene and PdCl_2 in ethanol³; in both cases, however, a σ -vinylic complex is formed, the only difference being in whether the substituents on the σ -vinyl are *cis* or *trans*.

A generalized scheme for the reactions of acetylenes with $\text{Pd}^{\text{II}}-\text{X}$ ($\text{X} = \text{Cl}$) is presented in Scheme 2, the *cis*-ligand migration being step (b). The further reactions of these σ -vinylic intermediates are by fast stepwise *cis*-ligand migrations onto coordinated acetylenes; the oligomerization proceeds in this way to build up a helical polyene (step c). The extent of this reaction is then governed by the size of the acetylenic substituents. For example, for diphenylacetylene reaction partly ceases after only two acetylenes have reacted and further complexation and *cis*-ligand migrations then compete with other processes, in particular cyclization to a four-membered ring (step

d). For smaller substituents (e.g. methyl) three or even four acetylenes can be incorporated before rearrangement or decomposition reactions (for example, step e) become fast with respect to further oligomerization.

The formation of the benzenes from the trimer complexes is not yet clear, but it seems likely to involve primary ring closure to a cyclopentadiene (for example, step e) which then rearranges with loss of Pd-X.

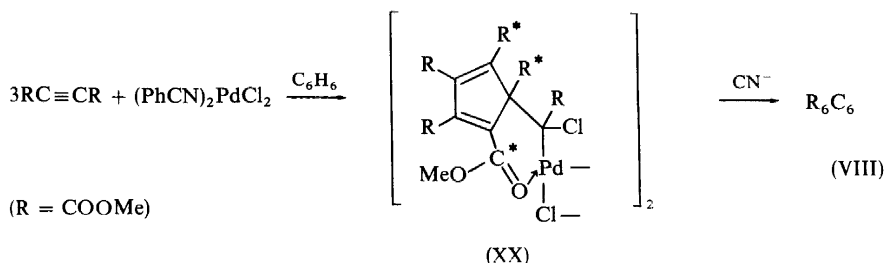
Evidence in favour of this type of cyclization has been presented, particularly in the reactions of (XV), and notably with PPh_3 at low temperatures⁴¹.



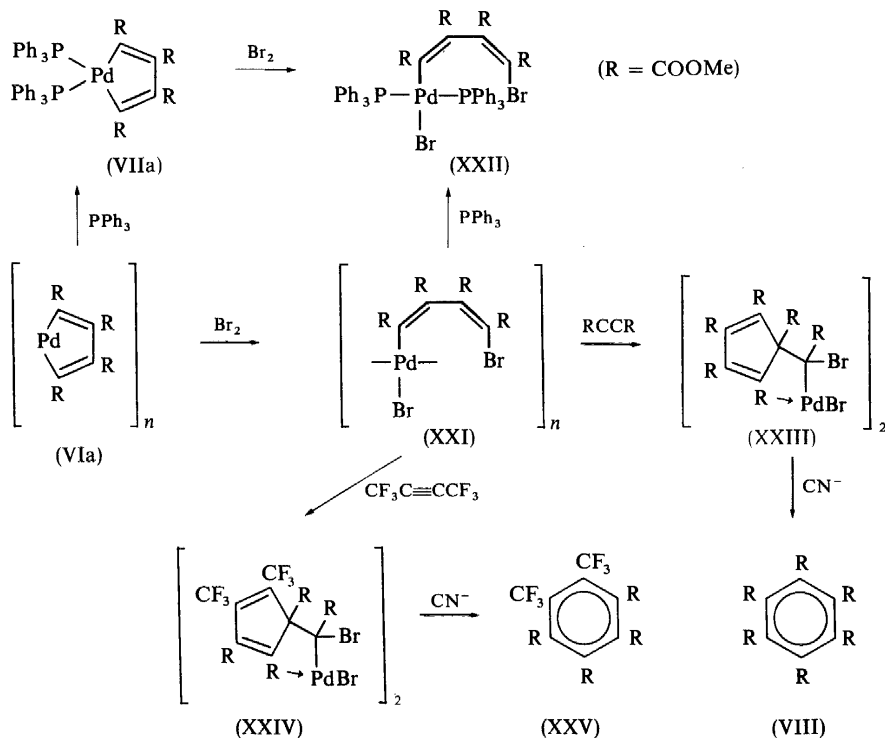
Models show that the complex (XV) can exist in two conformers (XVa and XVb) and the latter is well arranged for an internal cyclization to the cyclopentadiene. This rearrangement provides the key to our understanding of these processes; further evidence for this type of reaction is presented below.

In one case we are also able to define a relation between the Pd^0 and Pd^{II} induced reactions. Avram *et al.*³⁶ and Reinheimer³⁷ showed that DMA reacted readily with $(\text{PhCN})_2\text{PdCl}_2$ in benzene to give a trimer complex, $[\text{Cl}(\text{CCOOMe})_6\text{PdCl}]_2$. The structure originally proposed by the former workers (involving a Dewar benzene ligand) is incompatible with the molecular weight, spectra and other properties of the complex. From a consideration of the n.m.r. and i.r. spectra we tentatively suggest the structure (XX) for the complex in which the fourth coordination site on the metal is occupied by a carbomethoxy carbonyl. This type of internal coordination can explain the i.r. spectrum which shows ν_{CO} bands in the $1600\text{--}1700\text{ cm}^{-1}$ region, well below the range normally associated with esters. Models show there to be three possible sites for attachment to a carbomethoxy group (R^*); one of the possibilities is illustrated[†]³⁸.

[†] An x-ray determination of the acetylacetonate derived from (XX) shows it to have precisely the structure suggested here (C. Calvo, personal communication).

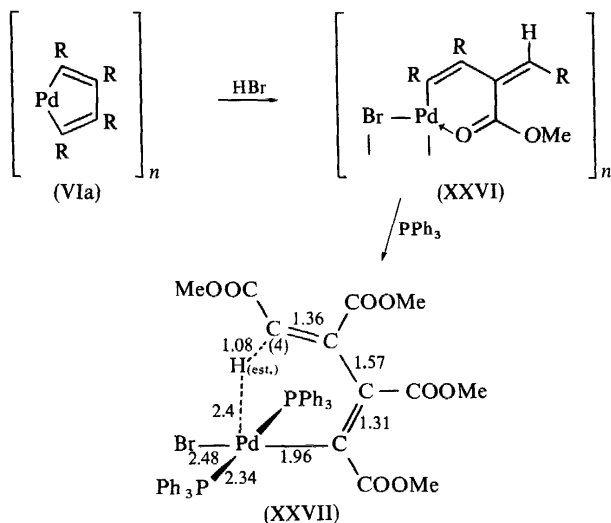


When the palladiacyclopentadiene (VIa) is treated with one equivalent of bromine, a complex (XXI) (n probably equal to 2) is isolated. This, on reaction with PPh_3 gives (XXII), identical to the product obtained on reaction of (VIIa) with one equivalent of bromine. The complex (XXI) reacts with DMA to give $[\text{Br}(\text{CCOOMe})_6\text{PdBr}]_2$, (XXIII), which is completely analogous to (XX) in its properties and of the same structure. On reaction with aqueous cyanide both (XX) and (XXIII) gave hexamethyl mellitate³⁸.



The butadienyl complex (XXI) also reacts with hexafluorobut-2-yne to give a complex which we formulate as (XXIV) by analogy with (XX) and (XXIII) and which, on decomposition with aqueous cyanide gives tetramethyl-1,2-bis(trifluoromethyl)benzene-3,4,5,6-tetracarboxylate (XXV)³⁸.

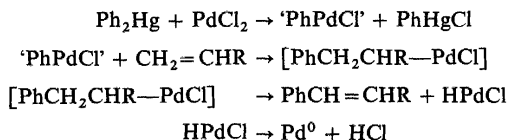
Confirmatory evidence for the σ -butadienyl structure of (XXI) and (XXII) comes from the reaction of the palladiacyclopentadiene with acids. For example, with hydrogen bromide (XXVI) (the analogue of XXI) was formed, which on reaction with triphenylphosphine gave (XXVII)³⁸, an x-ray determination of which shows it to have the structure shown⁴².

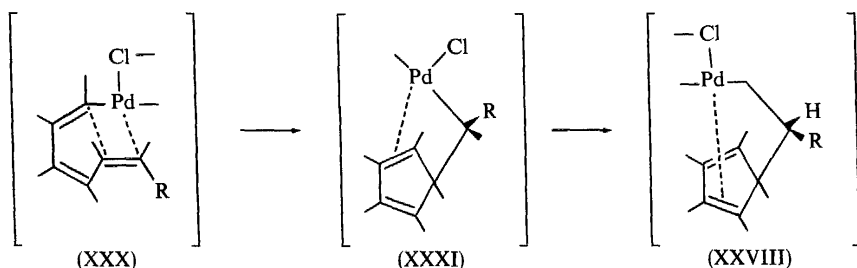


An unusual feature of (XXVII) is that the vinylic H resonates at unusually low field ($\delta = 8.54$) and appears as a triplet ($J_{H-P} = 1.4$ Hz) owing to coupling to the two phosphines. The crystal structure shows that the metal is not coordinated to the double bond of the butadienyl system but the vinylic hydrogen (estimated position, based on the observed geometry at C(4) and an assumed C(4)-H distance of 1.08 Å) occupies the fifth (octahedral) coordination site on the metal, at rather less than the sum of the van der Waals radii. From the observed coupling there appears to be some interaction between the vinylic H and the metal, but this is not accompanied by an increase in hydridic character of this hydrogen; from its chemical shift it in fact appears to be rather more protonic³⁸.

The structure of (XXVII) and, by inference that of (XXI), therefore strengthens our presumption that the basic process in the oligomerization catalysed by Pd^{II} is a stepwise one proceeding through butadienyl intermediates.

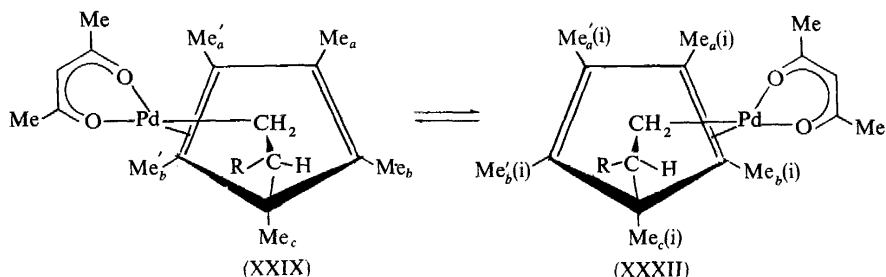
Heck⁴³ has shown that a phenylpalladium species (here designated as 'PhPdCl') formed *in situ* from diphenylmercury and palladium chloride, will effect the phenylation of olefins to styrenes by the route shown.





In this case, however, the acyclic trienyl complex (XXX) readily undergoes cyclization to (XXXI), which is itself not stable with respect to a 1,2-hydride shift giving (XXVIII). The reason for this is probably that the stabilization of the complex (XXXI) by π -bonding of the fourth coordination site of the metal to a double bond of the cyclopentadiene is very low, since models indicate (XXXI) to represent an extremely strained system. In contrast, the stabilization of (XXVIII) is very good and the x-ray structure (of XXIXb) and models of (XXVIII) show that all angles and bond lengths are normal.

The n.m.r. spectrum (XXIXa) shows variation with temperature above 0°C ; below this temperature the spectrum remains invariant and it can be analysed in terms of the presence of two isomers in the ratio of 4:1¹⁵. Since there is little change on further cooling we assign the major isomer to the form present in the crystal, that is, with the phenyl and the coordinated double bond on the same side. The minor isomer is then identified as (XXXIIa), with the metal coordinated to the other double bond.

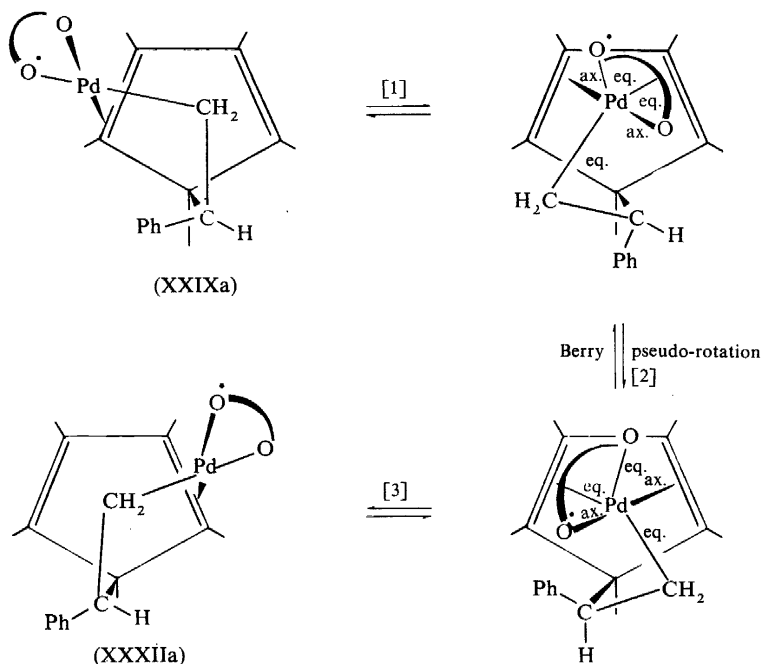


(a, R = phenyl, b, R = *p*-tolyl)

Above 0°C coalescence is observed between the resonances of Me_{b'} and Me_{b'(i)}, Me_b and Me_{b(i)}, and Me_c and Me_{c(i)}, and the metal oscillates from one double bond to the other ('molecular windshield wiper'). The coalescence temperature is $+27^\circ\text{C}$ with $k = 36\text{ s}^{-1}$ and $E_a = 24\text{ kcal mol}^{-1}$ ¹⁵.

Below 0°C the two different acetylacetonate methyls in (XXIXa) are observed as two sharp singlets and these too coalesce on warming at the same temperature as the cyclopentadiene methyls. We therefore conclude that the two processes are related¹⁵.

The simplest and most reasonable explanation for the mechanism of this oscillation is in terms of a Berry pseudo-rotation⁴⁵ of a trigonal bipyramidal intermediate†. In this process the five-coordinate intermediate is formed by a movement of the metal towards the ring centre accompanied by coordination (axially) to the other double bond (*Scheme 3*, step [1]). If the σ -bond to carbon (equatorial) is regarded as the pivot then the pseudo-rotation (step [2]) exchanges (i) the original π -bond (equatorial) with the new one, and (ii) the two ends of the acetylacetonate (one equatorial, one axial). The isomer (XXXIIa) is then produced by a movement of the metal atom towards the other double bond coincident with breaking of the now axial π -bond (step [3]). This process has the overall effect of causing one exchange of the acetylacetonate methyls for every switch from one double bond to the other.

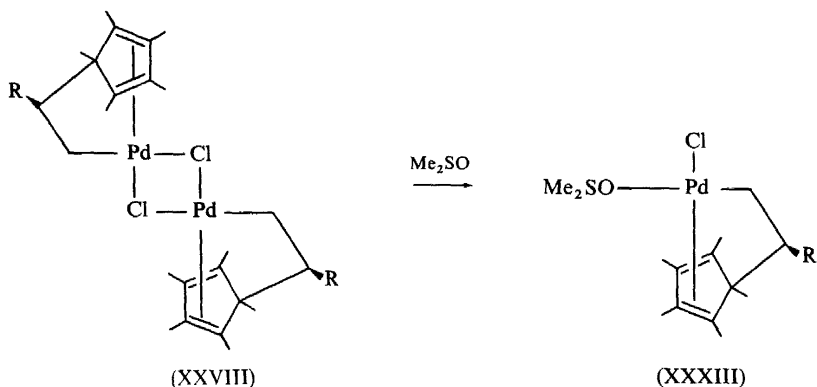


Scheme 3.

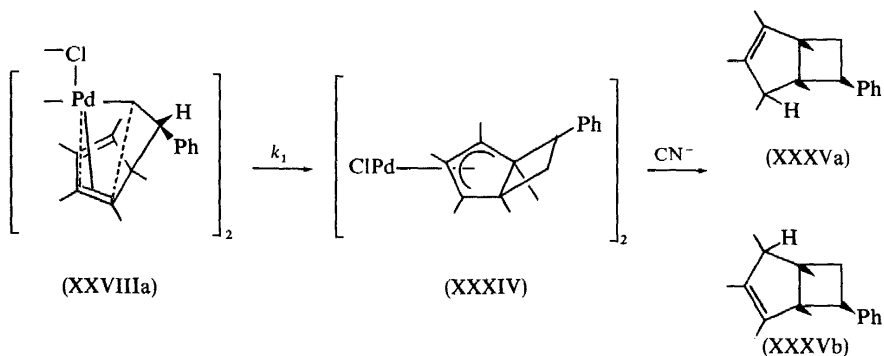
Although the spectra are poorer the chloride-bridged dimer (XXVIIIa) undergoes a similar process with approximately the same coalescence temperature. However, in this case, the addition of small amounts of dimethyl sulphoxide (DMSO) progressively lowers the coalescence temperature and the rate of oscillation increases sharply. This effect of DMSO can be attributed to its ability to break Pd—Cl bridges to form the monomer (XXXIII).

In the Berry pseudo-rotation of both (XXVIIIa) and (XXIXa) the originally (approximately) trigonal bipyramidal geometry must change to (approximately) square pyramidal. During this change the angle subtended by the chelating

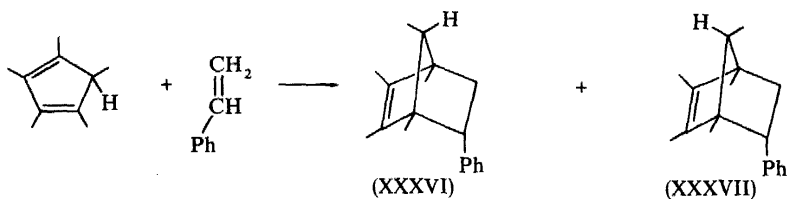
† A 'turnstile rotation' would appear to explain the results equally well⁴⁶.



ligand (acac or Cl₂Pd—) is then constrained to less than 90°, a constraint which the chelate will resist. Accordingly, part of the energy barrier to this exchange process must be ascribed to a deformation of the chelate ring; in its absence, when the chelate is broken, this constraint is removed and the rate of oscillation increases. Addition of DMSO to the acetylacetonate (XXIX) has no effect; presumably the chelate ring is not cleaved by this reagent.



In addition to this oscillation the complex (XXVIIIa) also undergoes a slower internal cyclization to the bicyclic allylic complex (XXXIV). This complex has been characterized by n.m.r., i.r. and by degradation to a bicyclo[3.2.0]heptene, either (XXXVa) or (XXXVb)⁴⁷. Alternative structures for the hydrocarbon (and hence for the complex XXXIV) were eliminated by synthesizing authentic samples of the bicyclo[2.2.1]heptenes (XXXVI) and (XXXVII).



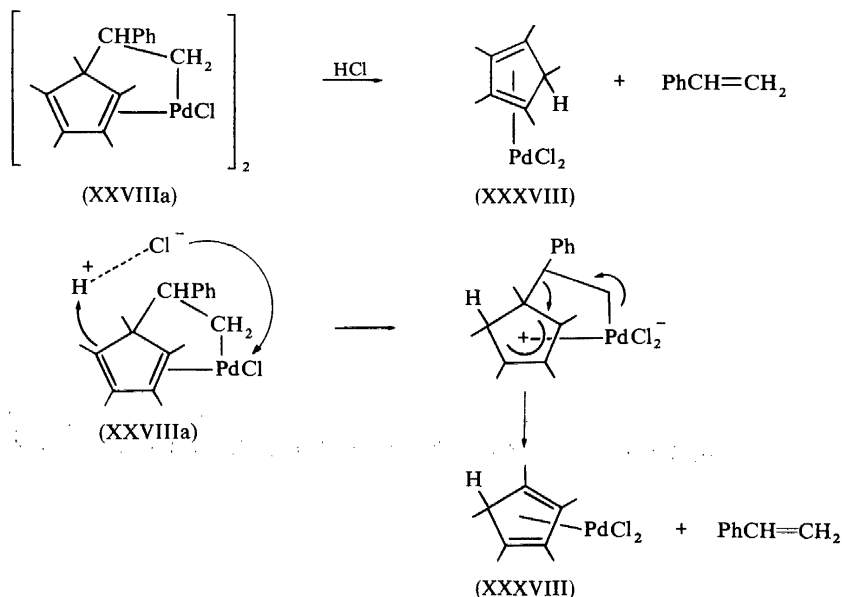
The n.m.r. and mass spectra of (XXXVI) and (XXXVII) were similar and quite different to those of (XXXV).

The rate of isomerization (XXVIIIa) \rightarrow (XXXIV) was found to be first order and somewhat solvent dependent ($k_1 = 6.2 \times 10^{-3} \text{ min}^{-1}$ in CDCl_3 ; 7.1×10^{-3} in C_6H_6 ; and 1.7×10^{-2} in $\text{CDCl}_3\text{-DMSO-d}_6$ (1:1); all at 36°C). The increase in rate in the presence of DMSO parallels the increase in the rate of flipping of (XXVIIIa), and it appears probable that the two processes are related. This is particularly likely since the geometry of the complex when it proceeds along the reaction coordinate to the five-coordinate intermediate in the oscillation (*Scheme 3*, step [1]) is the one which is necessary for the *cis*-ligand migration to occur, that is, the Pd—C σ -bond and the coordinated double bond become parallel. It therefore appears that one cyclization to (XXXIV) occurs for approximately every 10^6 oscillations^{15,47}.

A 'LIGHTLY STABILIZED' PALLADIUM(II) MODEL COMPLEX

The complex (XXVIII) can also act as a very useful model to investigate the properties of Pd—C σ -bonded intermediates, particularly those which are present in catalytic reactions and which are much less amenable to study in the more highly stabilized phosphine-containing complexes.

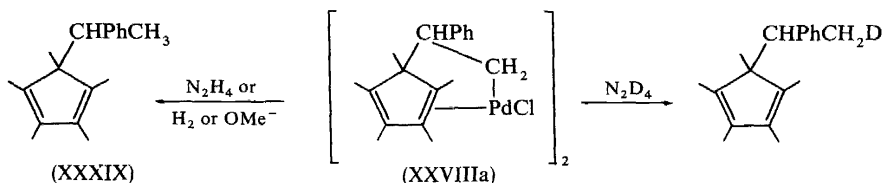
For example, we find the Pd—C σ -bond to be relatively inert to acid (HCl) and direct cleavage does not occur. The slow reaction which is observed, namely, the formation of styrene and dichloro(pentamethylcyclopentadiene)palladium, (XXXVIII), can only reasonably be understood in terms of initial protonation at the cyclopentadiene ring⁴⁸.



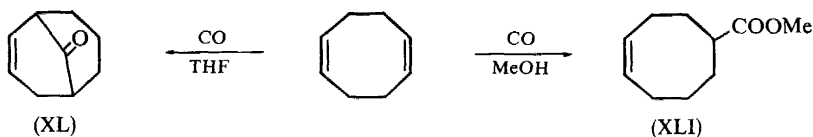
This result is not entirely unexpected since the polarity of the Pd—C bond is low and hence a displacement reaction is unlikely. Acid cleavage

of methyl-Pt^{II} bonds has been shown to proceed via oxidative addition of HCl to give a Pt^{IV} intermediate⁴⁹; again, since Pd^{IV} is much less easily accessible this route would be less favoured here.

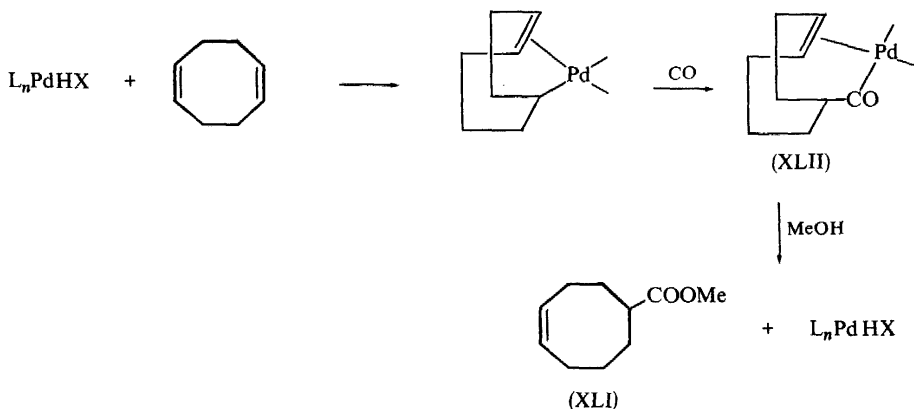
By contrast, base (sodium methoxide in methanol) or hydrazine or hydrogen (1 atm, 20°C) all cleaved the Pd—C bond to give 1-phenyl-1-(penta-methylcyclopentadienyl)ethane, (XXXIX). Presumably all these reactions involve a hydridic intermediate.



The carbonylation of palladium complexes is a well-known reaction and has been widely used catalytically. However, a number of aspects of this reaction are obscure. For example, Brewis and Hughes⁵⁰ showed that, using (Bu₃P)₂PdI₂ as a catalyst, cycloocta-1,5-diene was carbonylated (at 150°C and 1000 atm!) to bicyclo[3.3.1]non-2-en-9-one (XL), in THF, and to methyl cyclooct-4-ene-1-carboxylate (XLI), in methanol.

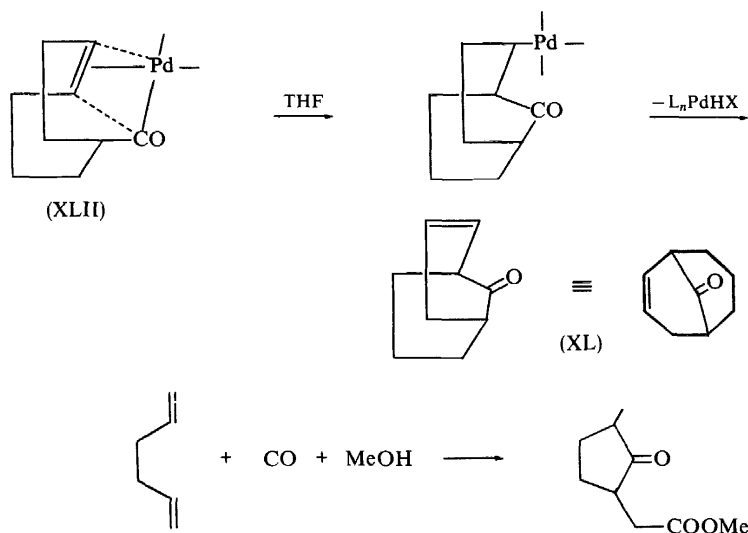


They suggested that in both solvents the reactive species was a hydride, L_nPdHX, and that the reaction occurred via an acyl-Pd intermediate (XLII), which was either solvolysed or underwent a *cis*-migration cyclization reaction.

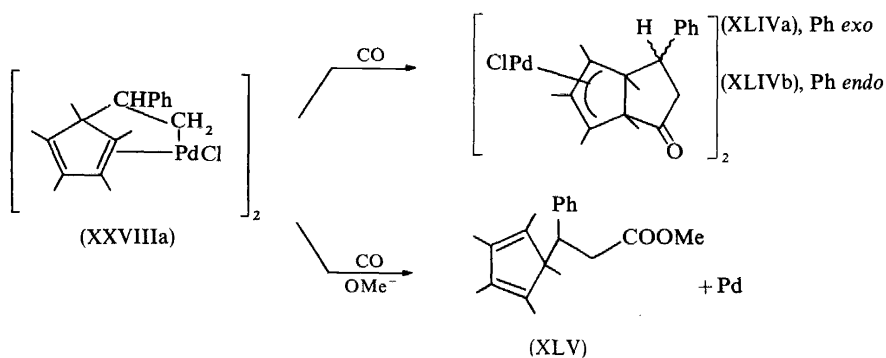


However, carbonylation of hexa-1,5-diene in methanol gave the cyclic γ -keto ester (XLIII). This suggests that the rates of cyclization and solvo-

lysis (of intermediates such as (XLII)) must be comparable and it is therefore surprising that no bicyclic ketone (XL) is formed in the methanol carbonylation of cycloocta-1,5-diene.

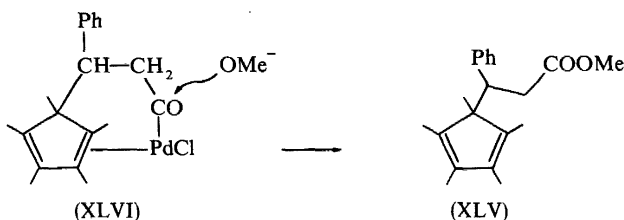
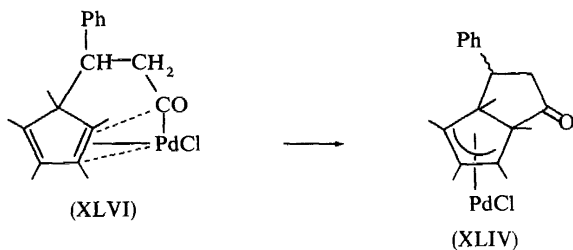


The carbonylation of the cyclopentadiene complex⁴³ (XXVIIIa) (or XXIXa) can lead to two different types of product. In neutral or acid solution, even in methanol, carbonylation (1 atm, 20°C) is accompanied by cyclization to give the bicyclic keto-allylic complexes (XLIV), whereas in methanol in the presence of base the product is only the ester (XLV).

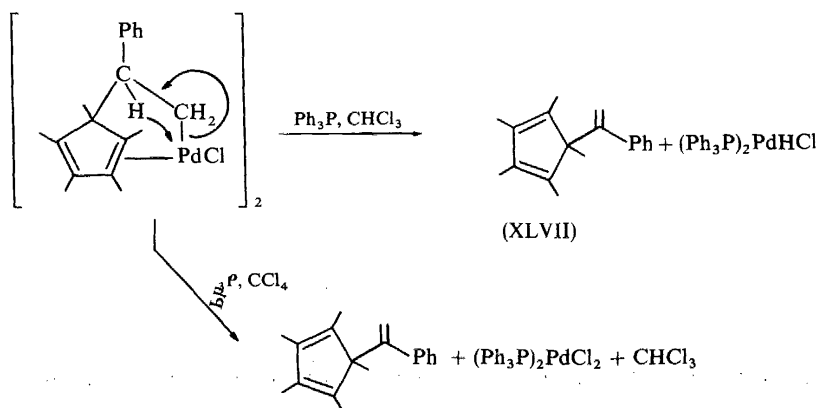


We envisage the reaction in either case to proceed via the acyl complex (XLVI), which in the absence of base cyclizes readily to (XLIV). In the presence of methoxide, however, nucleophilic attack occurs, presumably at the acyl carbon⁵¹, to give (XLV).

We may therefore generalize that, where two pathways can exist, one leading to cyclization and the other to solvolysis, the mode of reaction will be determined by the basicity of the medium.



The β -elimination of Pd-H from organopalladium intermediates is a reaction which has often been postulated to occur, particularly in catalytic reactions⁵². Owing to the high reactivity of palladium hydrides it has not yet been demonstrated in a stoichiometric reaction. We find that reaction of the complex (XXVIIIa) with triphenylphosphine leads to a smooth reaction in which the hydride, $(\text{Ph}_3\text{P})_2\text{PdHCl}$, and the α -(pentamethylcyclopentadienyl)styrene (XLVII) are formed. The hydride is surprisingly stable in deacidified chloroform under argon, but reacts immediately with carbon tetrachloride to give chloroform and $(\text{Ph}_3\text{P})_2\text{PdCl}_2$ ⁴⁸.



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